Shining light on plasmonic silver nanoparticles for catalysis

by

Alexandra Marie Flora Gellé



Centre for Green Chemistry and Catalysis, Department of Chemistry McGill University, Montréal, QC, Canada April, 2021

Thesis submitted to McGill University in partial fulfilment of the requirements for the degree of Doctor of Philosophy

©Alexandra Gellé, 2021

To anyone who was once told that they didn't belong,

If you see the wonder of a fairy tale You can take the future, even if you fail

ABBA - I have a dream

1 Preface

Abstract

Plasmonic nanoparticles (PNPs) are currently actively researched for their application towards enhancing photocatalytic transformations, owing to a unique physical phenomenon called localized surface plasmon resonance (LSPR). This appealing interaction with light featured by coinage metal nanoparticles under visible light irradiation translates into thermal and electromagnetic properties, which can subsequently be used to drive chemical transformations. Different examples of how LSPR allows to perform catalytic reactions under mild conditions are discussed in this thesis.

The importance of nano-photocatalysts, especially plasmon-driven ones, for the development of more sustainable alternatives is first introduced, along with reviews focusing on organic transformations mediated by plasmonic nanoparticles and plasmon-enhanced water splitting.

The catalytic properties of silver nanocubes towards the oxidation and hydrogenation of carbonyls using hot electrons are then presented. The synthesis, characterization and usage in continuous flow chemistry of these plasmonic nanocatalysts are detailed in this thesis. The use of plasmonic silver nanoparticles in antenna-reactor heterometallic is also discussed. The field enhancement in the vicinity of Ag PNPs was exploited for the projects presented in the last chapters. The plasmon-induced field enhancement allowed to boost the activity of a well-known photocatalyst, Tris(bipyridine)ruthenium(II), towards selective oxidation with singlet oxygen. Finally, the use of two other photocatalysts, Rose Bengal and Methylene Blue, in such antenna-reactor systems is reported. This work sheds light onto the importance of the careful design of these decorated plasmonic nanoantenna to maximize their photocatalytic activity.

Résumé

Les nanoparticules plasmoniques (PNP) font actuellement l'objet de nombreuses recherches ayant pour but d'améliorer les transformations photocatalytiques, en exploitant un phénomène physique unique appelé résonance plasmonique de surface localisée (LSPR). Cette interaction attrayante avec la lumière que présentent les nanoparticules de métaux du groupe 11 se traduit par des propriétés thermiques et électromagnétiques, qui peuvent ensuite être utilisées pour réaliser des transformations chimiques. Différents exemples de la façon dont la LSPR permet de réaliser des réactions catalytiques dans des conditions douces sont discutés dans cette thèse.

L'importance des nano-photocatalyseurs, en particulier ceux exploitant les plasmons de surface, pour le développement d'alternatives plus durables est d'abord présentée, ainsi que des revues axées sur les transformations organiques médiées par des nanoparticules plasmoniques, et le craquage de l'eau éxalté par les plasmons de surface.

Les propriétés catalytiques des nanocubes d'argent pour l'oxydation et l'hydrogénation des carbonyles à l'aide d'électrons chauds sont ensuite présentées. La synthèse, la caractérisation et l'utilisation en chimie à flux continu de ces nanocatalyseurs sont détaillées dans cette thèse. L'utilisation de nanoparticules d'argent plasmoniques dans des antennes-réacteurs hétérométalliques est également discutée. L'augmentation du champ à proximité des PNP d'Ag a été exploitée pour les projets présentés dans les derniers chapitres. Le renforcement du champ induit par les plasmons a permis d'augmenter l'activité d'un photocatalyseur bien connu, le Tris(bipyridine)ruthénium(II), pour l'oxydation sélective avec l'oxygène singulet. Enfin, l'utilisation de deux autres photocatalyseurs, Rose Bengale et Bleu de Méthylène, dans de tels systèmes antenne-réacteur est rapportée. Cette étude met en lumière l'importance d'une conception méticuleuse de ces nanoantennes plasmoniques décorées pour maximiser leur activité photocatalytique.

Acknowledgements

I was fortunate to join a bright (get ready, this is only the first photochemistry-related pun) science community, and call Montréal home for eight years. I would have never believed I would be staying here today, with a few hundred pages about silver. In light of my initials, maybe I should have seen it coming. This wouldn't have been possible without the help of many, and I am extremely thankful to you all. While writing this thesis has been a solitary endeavour, I have never felt alone.

I would like to start by acknowledging that my PhD research was carried out on the traditional land of the Huron, Abenaki, and Anishinaabeg peoples. I am grateful for the opportunity I had to live and work on Turtle Island, and for being given the chance to immigrate to Canada. Over the years, I have enjoyed the beauty and the resources this country has to offer, and my meetings with other immigrants, settlers and Indigenous peoples has shaped my experience and nurtured me.

Thank-you to my supervisor, Dr. Audrey Moores, for giving me the chance to join her lab. She didn't know what she had put herself into when taking me on board, and I am grateful for her patience and her scientific guidance. She helped an overly excited and curious young woman with big dreams grow into the older, and hopefully a bit wiser, overly excited and curious woman with bigger dreams that I am today. Merci for being the lighthouse to my PhD, shining light to help me find my way.

I would like to thank all of my collaborators for making this research possible and their valuable insights. We cast light on the importance of interdisciplinary work, and your work was crucial to make these projects happen. Thank you Dr. Stamplecoskie, Dr. Landry, Dr. Gauvin, Dr. Besteiro, Dr. Barrett, Dr. Amara, Nicolas Brodusch, Graham Beaton and Frédéric Voisard.

I would like to express sincere gratitude to my committee members, Dr. Li and Dr. Cosa, for their helpful feedback.

Then, I would like to thank the technical staff at McGill University and Université de Montréal for their help and advice, and in particular, Dr. Stein, Vanessa Kairouz and Mohini Ramkaran.

Merci dear Chantal Marotte, for keeping the department float and being a life raft in storms. You will probably get my thesis one minute before the deadline, so my apologies in advance, but anyways I am sure you gave me a deadline earlier than the real one because this is how great you are.

I also owe a thank-you to the various funding agencies that helped make our big ideas a reality, and to the Faculty of Science for the scholarship to attend the mini-MBA program.

To my labmates who had to endure my (sometimes questionable) music choices, my extremely bad singing and my overfilling energy: sorry, not sorry. I know you secretly enjoyed the French Céline Dion songs, catching *the dancing queen who is only seventeen* dancing while clearing glassware. Thank you for all your help around the lab, and the much needed chocolate and ice cream breaks. There will always be chocolate in the top drawer of my desk in case you come visit, for celebration or issues, as I will carry on my tradition wherever I end up. Hopefully with me stepping out of the lab, the curse of Friday afternoon instrument breaks and weekend floods tradition will stop though. Thanks for the good laughs and fruitful discussions, but please don't make me drive you to Boston ever again! Four chemists – all belonging to different nationalities, French, Chinese, Mexican and Canadian – driving across the border, isn't a joke I'd like to repeat. But I'll repeat this story to my friends forever, be reassured of that.

For the students out there, who read this thesis in hope of finding answers to their PhD existential crises, induced by an endless list of failed experiments: don't lose hope. Here is a

quote by a wise intern I had the chance to supervise: Nanoscience and astrology sometimes have a lot in common, the stars need to be aligned - © Gareth Price.

Most of this thesis is centered around (a few) experiments that led to positive results, but it doesn't shed light on all the failed experiments, frustration and questioning, nor the laughter, brainstorming sessions and parties, that are the equally important reagents in the PhD process. I will be forever thankful to my friends who reminded me there was light at the end of the tunnel, and outside of our lab in the Otto Maass basement.

We often hear it takes a village to get a PhD. I would argue it takes an army of inspiring people, who are ready to do what it takes to see you succeed. I hope I will be able to bring to light with only a few words all the gratitude I have for them sticking by my side, for the best and the worst, over the last years. These human experiences provided the most valuable results that I'll take with me wherever I go next.

A special shout out to my basement lab co-pensioners who have lit up my PhD. Alain, Júlio and Aude, for their unwavering support and friendship inside and outside of the lab, YouAreUnbearableButILoveYou, and we'll need a Tomsone Ouz reunion. Since my first day in the lab, Alain has found numerous ways to laugh with me, and at me, sometimes. *Shake it off* Your impersonations, (h)air flip, and dance moves are unforgettable. Like a headlight, you brought comfort during the darkest nights of my PhD. Júlio, the Brazilian singer and guitar player who is always ready — yet late — for a party. You have been the rock(star) and the rainbow of my PhD. Saúde to many more years of laughing all night and not remembering what the topic was the next day. *Now soooooo tell//// meeeeeee, what is your extraction protocol?* Ma chère Aude, it has been *AWESOME!* to share a fumehood with someone as messy, yet organized, as me. You have brought much needed oxygen into the group, and you are such a delight on ski trails, bike paths, and beyond.

A special shout out to my habibi deskmate Hatem, mon amiiiiiiii, the gem of the basement (yes I am also doing crystallography puns), for being the plants savior; to Gareth, the best

intern the Moores group has ever had and will ever have, and to mama Madhu who brightened the room with her wisdom and happiness.

To complement the Montpellier and lab 400 team, I'd like to thank Aurélie. No matter the time of the day, your voice messages novels are the spark I need. You helped me to stay grounded, and also brought me - or followed me - on crazy adventures. Our friendship started in Montréal and has already brought us across Europe. A pandemic hasn't stopped us so what could? I am still waiting for a pint (of science) in London!

And the last Montpellier musketeer: Sosthène! You are the worst at keeping secrets, but you have many other qualities which make you an excellent friend. Kevin, you have also been one of the cool kids, even if you belong to Pulp and Paper. I will never get enough of your fine TOC and culinary critics.

My chemistry family wouldn't be complete without the chemists "from the other side of the mountain", and in France.

Mes chères Chtimistes Margaux et Léa, il me semble bien loin le temps des dosages et circuits électriques dans cet amphi de Lille pourtant rien ne semble avoir changé une fois réunies. Parsemées mais avec des liens incassables, toujours réactives et des retrouvailles explosives!

Un énorme merci à la gang de chimiste de l'Université de Montréal qui m'a accueilli à bras ouverts. Aucun d'entre nous n'aurait parié que la Alexe Française perdue que j'étais à l'époque et qui ne comprend pas quand on lui dit de se tirer une bûche en serait là aujourd'hui. Leur encouragement et leur camaraderie y sont pour beaucoup.

Marie-Pier, ma partenaire de lab, et de nombreuses aventures jusqu'en Australie. J'attends toujours que tu déclares au Canada que je suis ta partenaire de vie et que j'ai ma citoyenneté... Stephanie, meuf t'es au top! Cricri, mon boloss préféré sans qui je n'aurais pas

passé le cours de chimie quantique, et qui aurait oublier de se pointer aux examens ou de graduer si je lui avait pas rappelé, on est dû pour une séance de magasinage ensemble Mr. Christophe. Aux étudiants et profs de l'UdeM, qui m'ont fait sentir à la maison à Roger Gaudry, au Café-In, pendant une game d'ultimate en pleine tempête de neige et à la Maiz, je vous suis infiniment reconnaissante. Mes années à l'UdeM ont forgé ma passion pour la chimie et ma soif d'apprendre. Un merci tout particulier à Vaness pour m'avoir appris à me servir de mes deux mains - et de mon cerveau - dans un lab, et à Dr. Dollé pour m'avoir ouvert la porte de son bureau et toujours avoir trouvé les mots justes.

Mon passage à l'UdeM m'a mené jusqu'en Australie pour un semestre qui a fait une grande différence dans ma carrière scientifique et en Grèce avec ma (bio)chimiste préférée Moana, princesse des îles égarée dans les couloirs glacés de Roger Gaudry en septembre 2013. Ce cours de chimie organique a créé un lien si bord que notre amitié résonne encore de part et d'autre de l'océan (oui oui je fais aussi des blagues de NRM).

The Canadian science communication community welcomed me with open arms, and I owe so much to these passionate and dedicated scientists. It has been an honor and privilege to be involved in various science communication initiatives throughout the country, and to meet some of the most inspiring people I know. Thanks to my SciComm buddies for being constant reminders of how cool science is, and shining examples of how fun and diverse scientists can be.

Listing all of them would require adding an annex, but I want to put under the spotlight a few key people who had a huge influence on me during my PhD years.

You have supported, inspired and invigorated me for my studies. Thanks for all the non PhDrelated projects that I enjoyed working on with you, and the time spent together nerding out. I truly believe you all made me a better scientist. Little did I know that speaking about science in bars would lead me to such transformative encounters and experiences. As I am

writing this today, a science communication job awaits me, and it will likely not be the only one of my career. None of that would have been possible without you all.

Cylita, Rackeb, Farah, Diane, Alexia, Emily, Chantal, Julia, Alice — and Virginia on the other side of the border — you are my SciComm sheroes. So far physically, but always a message away: you made me love science even more, and have paved the way for many other science enthusiasts to speak up. Your trust, empowerment, and advice are invaluable.

Cylita and Rackeb, meeting you in Boston at ComSciCon in 2018 was life changing. I looked up to you, and I am so humbled to call you my friends. Farah, like many others of my SciComm friends, you started as a vague connaissance on Twitter, and a person I admire. You also became my pandemic penpal, English proofreader, French inquisitor, future coauthor, and so much more. I have learned so much by your side and I cannot wait to be physically by your side again, because I NEED to know what these Ottawa's shawarmas are about and I owe you a ski lesson. Diane, you have opened so many doors for me to walk through. You have been the mentor I didn't know I needed. Alexia, je suis tellement reconnaissante que tu sois incapable de dire non aux projets un peu fous que je te propose parce que la team #SciCommAlexes est allumée et éclatante.

For once, women outnumbered men, but Pramodh the Quantum Fluid Mechanic, and Cristian, the wise and silly papa bear, have never failed to put a smile on my face and to impress me.

Thank you to all the volunteers of Pint of Science and ComSciCon who believed in me, and worked hard to make science shine coast to coast. I have learned tremendously by your side.

While I can't highlight all of the wonderful friends I have made over the last few years, I'd like to cast light on two Québécoises rays of sunshine: Alexandrine and Eva. Je ne pensais pas revenir d'Australie avec une amie pour la vie à Montréal, et pourtant la ptite et la grande Alexe ont encore des belles soirées à chanter du Céline Dion et se conter des histoires de

fougères géantes devant elles. Je suis tellement reconnaissante d'avoir été adoptée par Eva, une personne au grand cœur qui m'a fait une petite place entre son chien et les trois chats.

A ma famille, qui m'a vu parcourir le monde dans tous les sens et ne se demande toujours où je suis, merci pour m'avoir soutenue dans mes rêves.

Mes chers parents, Rosina et Thierry, je vous en ai fait voir de toutes les couleurs mais vous avez toujours cru en moi et m'avez aidé à accomplir mes projets les plus fous. Peu importe sur quel continent j'étais et à quel point vous étiez loin, j'ai toujours su que vous étiez là pour moi et me souhaitait tout le meilleur – même si ce n'était pas vraiment ce qui vous arrangeait! Merci de m'avoir emmené maintes fois au musée des sciences de Paris et la Géode. Et de m'avoir montré que les frontières ne devraient pas être une limite.

Sensei Nathan et Solenne la stagiaire de compèt, vous n'êtes pas toujours calés sur le bon fuseau horaire mais toujours prêts pour déconner. Je sais qu'un de vous deux est plus pinte et l'autre plus science, mais vous faites un excellent cocktail.

A mon grand-père qui m'a transmis son amour pour la science, le chocolat extra noir et les avions dès mon plus jeune âge.

A ma mamy, qui a fait mille et une fois les visites des parfumeries de Grasse avec moi dans mon enfance et qui a maintenant dois écouter mes cours de chimie organique sur la distillation et l'extraction quand on retourne à la capitale mondiale des parfums. A ma mamie, qui est la plus belle preuve de résilience et de courage que je connaisse, et qui m'a transmis son amour pour la cuisine, et l'art de la pifométrie replicable.

Finally, I am extremely grateful to the one who could make me laugh in any circumstances, who broadened my horizons, and taught me I could dream bigger than I am. Erin, tu es un vrai rigolo, and you brightened up my PhD days. From Jay Peak to Garibaldi Park, from McGill Pizza to Desolation Sound, you were a constant source of inspiration, positivity and knowledge. You made me discover the beautiful British Columbia and beautiful people, for

which I will be forever thankful. This thesis wouldn't exist without you, and not only because you introduced me to the Piano Guys who saved me from losing my mind writing this thesis.

I thought this day would never come, and that March 2020 would never end but *see that girl, what that scene*. Nothing happened as planned, but here I am writing this, amid a pandemic. I haven't developed a COVID-19 vaccine nor flown a drone on Mars, but here is my humble contribution to the field of science. Who knows what scientists will need one day. I may hang up the pipettes for ever, but will hopefully continue working among brilliant scientists.

My PhD years will probably turn out to be the best and worst years of my life. I am grateful for the opportunity I had to learn, to experiment, and to learn what I didn't know. Most of you will probably never realize how important you were for me over the last few years. Thanks to everyone who have been my best cheerleaders and critics from around the globe. I don't know what's up next, but I'll keep surprising you I'm sure.

Thank you.

Merci.

A la prochaine !

Table of content

<u>1</u>	<u>Pref</u>	ace	<u>3</u>
	Abst	ract	3
	Résu	mé	4
	Ackr	owledgements	5
	Table	e of content	13
	List o	of figures	19
	List o	of schemes	27
	List o	of tables	28
	List o	of equations	29
	Abbr	eviations	30
	Cont	ribution of Authors	33
<u>1</u>	<u>Cha</u>	pter 1 – Introduction	<u> 34</u>
	1.1	Photochemistry : harvesting energy from light	34
		1.1.1 A brilliant idea inspired by Nature	34
		1.1.2 Bringing photocatalysts under the spotlight	35
	1.2	Shining light on coinage-metal	40
	1.3	Green chemistry principles: Call for change	44
		1.3.1 The light bulb idea	44
		1.3.2 Contribution of nano-catalysis	47
	1.4	Scope and contribution to original knowledge of the presented research	49
	1.5	References	53
<u>2</u>	<u>Cha</u>	<u>pter 2 – Applications of Plasmon-Enhanced Nanocatalysis to Org</u>	<u>;anic</u>
<u>Tra</u>	nsfor	rmations	<u> 60</u>

2.1	Introduction	61
2.2	Mechanisms of plasmon-enhanced nanocatalysis	63
	2.2.1 Principles of localized surface plasmon resonance	63
	2.2.2 LSPR theories and properties	63
	2.2.3 LSPR and catalysis	69
	2.2.4 LSPR characterization	72
2.3	Design of plasmon-enhanced nanocatalysts	73
	2.3.1 Design of free-standing plasmonic NPs	74
	2.3.1.1 Polyol synthesis of Ag and Au PNPs	75
2.4	Application of LSPR to organic transformations	78
	2.4.1 Oxidation reactions	78
	2.4.1.1 Oxidation of alcohols	80
	2.4.1.2 Oxidation of alkenes and aromatics	85
	2.4.1.3 Oxidation of amines	
	2.4.1.4 Oxidation of carbon monoxide	
	2.4.2 Reduction reactions	
	2.4.2.1 Reduction of alkenes and alkynes	
	2.4.2.2 Reduction of aldehydes and ketones	92
	2.4.2.3 Reduction of nitro compounds	93
	2.4.3 C-C and C-N Bond-Forming Coupling Reactions	96
	2.4.3.1 Suzuki-Miyaura coupling reactions	
	2.4.3.2 Other C-C coupling reactions	102
	2.4.3.3 C-N Coupling reactions	103
	2.4.3.4 A ³ Coupling reactions	
2.5	Conclusion	105
2.6	References	107

3.1	Introduction	127
-----	--------------	-----

	3.2	Semiconductor-catalyzed photoelectrochemical water-splitting	129
	3.3	Surface plasmon resonance in group XI metal nanoparticles	132
	3.4	Plasmonic nanoparticle supported on titanium dioxide as photocatal	yst for
	wate	r splitting	133
		3.4.1 Gold nanostructures on titanium dioxide	135
		3.4.2 Silver nanostructures on titanium dioxide	140
		3.4.3 Copper nanoparticles on titanium dioxide	142
	3.5	Conclusion	143
	3.6	References	145
<u>4</u>	<u>Cha</u>	oter 4 – Unveiling the potential of Ag NCs for plasmon-o	<u>lriven</u>
phc	otoch	emistry	<u> 151</u>
	4.1	Introduction	152
	4.2	Synthesis of the nanocatalysts	153
	4.3	Characterization of nanocatalysts	159
		4.3.1 Morphology and nature of the Ag NCs	159
		4.3.2 Optical properties of the Ag NCs	162
	4.4	Photo-nanocatalysis in batch	164
		4.4.1 Oxydation of aldehydes (work done by Michael Landry)	164
		4.4.2 Hydrogenation of carbonyls (work done by Michael Landry)	165
	4.5	Going with the flow	167
		4.5.1 Introduction to continuous flow chemistry	167
		4.5.2 How to access greener reaction conditions with flow processes	168
		4.5.3 From batch to flow conditions	171
	4.6	Conclusion	174
	4.7	References	176
E	Char	ator 5 Enhancing cinglat average photocotalysis with place	monic

<u>5</u>	Chapter 5	5 -	Enhancing	singlet	oxygen	photocatal	<u>ysis</u>	with	plasmonic
<u>nan</u>	oparticles .		<u></u>			••••••	•••••	•••••	

	5.1	Introduction	182
	5.2	Synthesis and characterization of plasmon-active supports for photocata 184	lysis
		5.2.1 Synthesis of Ag@SiO $_2$ and Ag@SiO $_2$ -[Ru] NPs	185
		5.2.2 Characterization of Ag@SiO $_2$ and Ag@SiO $_2$ -[Ru] NPs	186
	5.3	Photocatalytic studies	189
	5.4	Electron Energy Loss Spectroscopy	193
		5.4.1 Experimental data from scanning transmission electron microscopy.	193
		5.4.2 Simulations using boundary element method	195
	5.5	Conclusion	197
	5.6	References	198
<u>6</u> pho	<u>Cha</u> otocat	pter 6 - Rational for antenna-reactor design using Ag PNPs to bo	<u>bost</u> 206
			007
	6.1	Introduction	207
	6.1 6.2	Introduction Synthesis of plasmon-active supports for photocatalysis	207 209
	6.1 6.2 6.3	Introduction Synthesis of plasmon-active supports for photocatalysis Characterization of Ag@SiO ₂ and Ag@SiO ₂ -[photocatalyst] NPs	207 209 210 211
	 6.1 6.2 6.3 6.4 6.5 	Introduction Synthesis of plasmon-active supports for photocatalysis Characterization of Ag@SiO ₂ and Ag@SiO ₂ -[photocatalyst] NPs Evaluation of the bosting of the emission and catalytic activity of	207 209 210 211 the
	 6.1 6.2 6.3 6.4 6.5 photo 	Introduction Synthesis of plasmon-active supports for photocatalysis Characterization of Ag@SiO ₂ and Ag@SiO ₂ -[photocatalyst] NPs Evaluation of the bosting of the emission and catalytic activity of pocatalysts	207 209 210 211 the 211
	 6.1 6.2 6.3 6.4 6.5 photo 	Introduction Synthesis of plasmon-active supports for photocatalysis Characterization of Ag@SiO ₂ and Ag@SiO ₂ -[photocatalyst] NPs Evaluation of the bosting of the emission and catalytic activity of ocatalysts	207 209 210 211 the 211 211
	 6.1 6.2 6.3 6.4 6.5 photo 	Introduction Synthesis of plasmon-active supports for photocatalysis Characterization of Ag@SiO ₂ and Ag@SiO ₂ -[photocatalyst] NPs Evaluation of the bosting of the emission and catalytic activity of ocatalysts 6.5.1 Influence of the plasmonic core on the luminescence properties 6.5.2 Photocatalytic studies	207 209 210 211 the 211 211 213
	 6.1 6.2 6.3 6.4 6.5 photo 6.6 	Introduction Synthesis of plasmon-active supports for photocatalysis Characterization of Ag@SiO ₂ and Ag@SiO ₂ -[photocatalyst] NPs Evaluation of the bosting of the emission and catalytic activity of ocatalysts 6.5.1 Influence of the plasmonic core on the luminescence properties 6.5.2 Photocatalytic studies Time-resolved spectroscopy study	207 209 210 211 the 211 211 213 218
	 6.1 6.2 6.3 6.4 6.5 photo 6.6 6.7 	Introduction Synthesis of plasmon-active supports for photocatalysis Characterization of Ag@SiO ₂ and Ag@SiO ₂ -[photocatalyst] NPs Evaluation of the bosting of the emission and catalytic activity of ocatalysts 6.5.1 Influence of the plasmonic core on the luminescence properties 6.5.2 Photocatalytic studies Time-resolved spectroscopy study Conclusion	207 209 210 211 the 211 211 213 218 221
	 6.1 6.2 6.3 6.4 6.5 photo 6.6 6.7 6.8 	Introduction Synthesis of plasmon-active supports for photocatalysis Characterization of Ag@SiO ₂ and Ag@SiO ₂ -[photocatalyst] NPs Evaluation of the bosting of the emission and catalytic activity of ocatalysts 6.5.1 Influence of the plasmonic core on the luminescence properties 6.5.2 Photocatalytic studies Time-resolved spectroscopy study References	207 209 210 211 the 211 213 218 221 222
7	6.1 6.2 6.3 6.4 6.5 photo 6.6 6.7 6.8 Cha	Introduction Synthesis of plasmon-active supports for photocatalysis Characterization of Ag@SiO ₂ and Ag@SiO ₂ -[photocatalyst] NPs Evaluation of the bosting of the emission and catalytic activity of ocatalysts	207 209 210 211 the 211 213 213 221 222 225

	7.2	Outlo	oks		227
	7.3	Refer	ence	S	
<u>8</u>	<u>Ann</u>	iex			<u> 232</u>
	8.1	Supple	emei	ntary information - Unveiling the potential of Ag NCs 1	for plasmon-
	drive	en phot	oche	mistry	
		8.1.1	Ag	NCs synthesis	
		8.1.2	Hyd	drogenation catalytic tests reactions	
		8.1.3	Oxi	dation catalytic tests	
		8.1.4	Cor	ntinuous flow	
		8.1.5	Cha	aracterization	
	8.2	Supple	emei	ntary information - Enhancing singlet oxygen photoca	atalysis with
	plası	monic n	anop	particles	
		8.2.1	Syn	thesis of Ag NPs	
		8.2.2	Syn	thesis of Ag@SiO2 NPs	
		8.2.3	Imr	nobilization of $[Ru(bpy)_3]^{2+}$ to form Ag@SiO ₂ -Ru NPs	
		8.2.4	Sur	face loading and surface coverage	
		8.2.5	Ma	thlab	241
		8.2.6	Dis	cussion synthesis and optimization of materials	
		8.2	.6.1	Plasmonic core: metal and size NPs	
		8.2	.6.2	Surface loading: determination optimal surface coverage	
		8.2.7	Nar	noparticle Characterization	
		8.2	.7.1	BET surface area	
		8.2	.7.2	ζ-potential	
		8.2	.7.3	UV Vis absorption	
		8.2	.7.4	Luminescence	
		8.2	.7.5	EELS	
		8.2.8	Pho	otocatalytic tests	251
		8.2	.8.1	Mechanism	
		8.2	.8.2	Experimental conditions	

		8.2.8.3 Effect of surface loading	
		8.2.9 Comparison with previous s	tudies
	8.3	Supplementary information - Ratio	nal for the antenna-reactor design using Ag
	PNP	s to boost photocatalysis	
		8.3.1 Experimental section	
		8.3.1.1 Synthesis of SiO ₂ NPs	
		8.3.1.2 Synthesis of SiO ₂ @Ag-[Ru] NPs and SiO ₂ @Ag-MB NPs258
		8.3.2 Synthesis of SiO ₂ @Ag-RB N	Ps
		8.3.2.1 Nanoparticle Characteriza	ation
		8.3.2.2 Catalytic tests	
		8.3.2.3 Time-resolved spectrosco	py261
		8.3.3 BET surface area	
		8.3.4 ζ-potential	
		8.3.5 Real-Time Spectroscopy	
	8.4	References	
<u>9</u>	<u>Bibl</u>	iographie	

List of figures

when expanded or contracted. Friction with the supporting surface will also cause damping (purple). Reproduced from ref ⁶⁹. Copyright 2020 American Chemical Society.

- Figure 2-4 Description of PNPs growth via a polyol process, light-mediated synthesis, and nanosphere lithography with the variety of morphologies obtained. (A, C–I) Reproduced with permission from ref¹⁵⁰. Copyright 2007 American Chemical Society.
 (B) Reproduced with permission from ref¹⁸⁰. Copyright 2009 American Chemical Society.
 (J) Reproduced with permission from ref¹⁸⁰. Copyright 2011 American Chemical Society. (K, L) Reproduced from ref¹⁸¹. Copyright 2003 Nature. (M) Reproduced from ref¹⁸². Copyright 2010 American Chemical Society.

igure 2-6: Proposed mechanism for the hydrogenation of carbonyl compounds with H_2
catalyzed by Ag NCs. From reference ²⁰⁹ . Copyright 2017 American Chemical Society.

- Figure 3-6 Schematics of the Au-NP fabrication procedure via chemical reduction. Reproduced from Ref. ³⁷⁶with permission from The Royal Society of Chemistry...... 138
 Figure 3-7 - (left) Energy level diagram superimposed on a schematic of an individual unit of the plasmonic solar water splitter, showing the proposed processes occurring in its various parts and in energy space. CB, conduction band; VB, valence band; EF, Fermi energy. Reprinted by permission from Macmillan Publishers Ltd: NATURE NANOTECHNOLOGY (reference ³⁸⁸), copyright 2013. (right) Schematic diagram of excitation and separation of electrons and holes on TiO₂-1 wt% Au@TiO₂/Al₂O₃/Cu₂O

permission of The Royal Society of Chemistry	
Figure 3-8 - Synthetic procedure for accessing TiO2 nanotube vertical arrays, f	followed by
the deposition of Ag NPs. Reproduced from Ref ³⁹⁴ with permission of	The Royal
Society of Chemistry	142
Figure 4-1 - Mechanism for the formation of Ag NCs via AgCl NCs proposed by	y Rioux and
coworkers. Schematic of 28 h growth process of Ag nanocubes with fou	r identified
stages: (i) initial formation of AgCl nanocubes; (ii) reduction of AgNO $_3$ to A	g seeds and
their subsequent etching by in situ formed HNO3; (iii) dissolution of AgCi	along with
AgNO ₃ reduction; and (iv) the continued growth of Ag nanocubes along	, with AgCl
disappearance. From ref ¹⁷⁹	155
Figure 4-2 – SEM images of NPs samples when using 1,5-pentanediol as a reduc	ing agent at
different time points (19, 21, 24, 27 et 30 h) after being centrifuged in etha	nol 157
Figure 4-3 - SEM images of NPs sampled at different time point (19, 21, 24, 27 ef	t 30 h) after
being centrifuged in ethanol when using ethylene glycol as a reducing agen	t 159
Figure 4-4 – Images of the Ag NCs by TEM (A), SEM (B) and BFSTEM (C)	160
Figure 4-5 - BFSTEM image of the Ag NCs (A) with the corresponding EDS lines	an (B), XPR:
spectrum (C) and XRD diffractogram (D)	
Figure 4-6 - UV-Vis spectrum of the Ag NCs in ethanol	
Figure 4-7 - Localized surface plasmon (LSP) energy-filtered STEM images of a	a 50 nm NC
extracted from a spectrum image acquired with spectrometer disp	ersion was
0.055 eV/channel with an energy width of ΔE = 0.21 eV. (a) Edge LSP with E	$E_f = 3.53 \mathrm{eV},$
(b) corner LSP with E_f = 2.95 eV, (c) overlapped spectra extracted from the	corner and
edge LSPs. LSP energies determined by Gaussian fit are 3.32 and 3.53 eV fo	the corner
and edges spectra respectively. Reproduced with permission from ref	erence ¹⁴⁶ .
Copyrights 2020 Elsevier	
Figure 4-8 - Scope of products obtained from SPR-enhanced oxidation of aldehy	des with Ag
NCs using the conditions detailed in Scheme 4-1. Reproduced with perm	ission from
reference ⁴²⁵ . Copyright 2007 American Chemical Society	

heterostructure photoelectrodes in PEC system. Reproduced from Ref $^{\mathbf{384}}$ with

Figure 4-9 - Scope of products obtained from SPR-enhanced hydrogenation of ketones with
Ag NCs using the conditions detailed in Scheme 4-2. Reproduced with permission from
reference ⁴²⁵ . Copyright 2007 American Chemical Society
Figure 4-10 - Set up featuring the injection sites, the pumps, the tube-in-tube, the irradiated
coil and the product collection171
Figure 4-11 - Close up tube-in-tube. Reproduced with permission from Ref ⁴²⁹ . Copyright
2017 American Chemical Society 172
Figure 4-12- Continuous-flow reactor set-up used for the purple light-mediated oxidation
of 4-bromobenzaldehyde catalyzed by Ag NCs (5 mol%) including a VapourTec module
connected to a tube-in-tube module and a PFA coil (1mm I.D.) around a LED tower.
Figure 5-1 - A) Synthesis of the silver plasmonic nanoparticles core with a silica shell and

Figure 5-5 - Simulations of the intensity of the LSPR peaks at energies ranging between 2.25
and 3.75 eV for Ag@SiO ₂ with shell ranging from 0 to 45 nm obtained with Matlab
MNPBEM toolbox in vacuum (A) and in CH_3CN (B)
Figure 5-6– Intensity of the LSPR peak calculated with Matlab MNPBEM toolbox in CH ₃ CN
as a function of the distance from the Ag surface for naked Ag NPs and Ag@SiO $_2$ with
7, 19 and 28 nm shells
Figure 6-1- A) Uv-Vis spectra of $Ag@SiO_2$ NPs and the three photocatalysts used,
$[Ru(bpy)_3]^{2+}$, MB and RB, and B) B) synthesis of the silver plasmonic nanoparticles core
with a silica shell and immobilization of the photocatalysts
Figure 6-2- Emission and catalytic enhancement factors measured for the three
photocatalvst
Figure 6-3 - Lifetimes Tay for SiO ₂ -[Ru ⁺] (brown curve), Tay (vellow curve), T ₁ (blue curve), T ₂
(green curve) determined for [Ru(bpv) ₃] ²⁺ immobilized on Ag@SiO ₂ NPs with different
thicknesses, and phosphorescence enhancement factor (grev curve) measured for the
same samples 220
Figure 6-4 - Decay rates ($K_{\text{non-rad}}$ et K_{rad}) determined for $[Ru(bpy)_3]^{2+}$ immobilized on
commercial SiO ₂ NPs and Ag@SiO ₂ NPs with different thicknesses and emission
enhancement factor measured for the same samples 221
Figure 8-1 - SEM images of Ag NCs
Figure 8-2 - BESTEM images of Ag NCs on Cu/Jacev carbon grid 237
Figure 8-3 - STEM image (ton left) and EDS spectra (ton right and bottom) of Ag NCs. The
bottom view focuses on the silver region where the silver contribution is provided in
orange over the total count in vollow.
Figure 9.4. VDS full scen (A) and closeum on Cl2n scen (D). Ag2d scen (C) and C1s (D) of Ag
Figure 6-4 - APS full scall (A) and closeup on Ci2p scall (B), Agod scall (C) and CIS (D) of Ag
NCS
Figure 8-5 - Structure and measurement of Ru(bpy) ₃ ²¹ radius for determination of the
surface coverage
Figure 8-6 - Simulations, Laurentzian multi linear least squared fit and residuals of the
plasmonic excitations of a 80 nm silver sphere with varying thickness of silica shell, in
water and acetonitrile

Figure 8-7 - Energy (color) and intensity of the fitted peaks for vacuum and CH_3CN at
varying shell thickness. A red shift is present on all the peaks but is much more
significant in the vacuum environment then in the acetonitrile
Figure 8-8 - Extinction spectra of naked Ag NPs and with SiO_2 shell upon 6 TEOS additions
Figure 8-9 - A) Shift of the SPR band observed upon 6 TEOS additions and B) corresponding
thickness of the SiO $_2$ shell measured by TEM
Figure 8-10- Emission of $Ru(bpy)_3$ ²⁺ for similar surface loadings (6.5E-5 mmol of
$[Ru(bpy)_3]^{2+}/m^2)$ with various thickness of silica. The quantity of Ru(bpy) ₃] ²⁺ in solution
was kept constant
Figure 8-11 – Emission of Ru(bpy) $_3$] ²⁺ for similar silica layers (Ag@SiO ₂ _28nm NPs) with
various surface loadings of photosensitizer. The quantity of NPs in solution was kept
constant
Figure 8-12 - EELS spectra of a single naked Ag NP and Ag@SiO_2_28nm NP with different
plasmon modes between 5, 8 and 25 eV. LSP was measured at 3.4 eV (365 nm) 250
Figure 8-13 - Detailed mechanism of the citronellol photooxidation reaction. ⁵¹⁸
Figure 8-14 - Photograph of the photoreactor used
Figure 8-15 -Sample gas chromatogram for a crude reaction product showing the internal
standard, remaining reagent, the two product peaks and also the quenching agent and
its oxidized form
Figure 8-16 - Conversion of citronellol as determined by GC-MS (green) and NMR (blue)
after 3h of reaction in comparison with the intensity of the fluorescence measured for
Ag@SiO ₂ -Ru NPs (orange), plotted as a function of SiO ₂ shell thickness. Conversion by
NMR for $[Ru(bpy)_3]Cl_2$ homogeneous (*) and $[Ru(bpy)_3]Cl_2$ immobilized on commercial
SiO ₂ NPs (\blacklozenge). The molecular catalyst loading of photosensitizers was identical for each
reaction (0.0034 mol%) independently of the nanomaterial used
Figure 8-17 – Conversation by GC-MS over time or $[Ru(bpy)_3]^{2+}$ homogeneous or
immobilized on various nanomaterial255
Figure 8-18 - Conversion determined by NMR for various thickness of silica and surface
loadings of $[Ru(bpy)_3]^{2+}$ immobilized on Ag@SiO ₂ _28 nm NPs 256

Figure 8-19 - Time resolved emission for $[Ru(bpy)_3]^{2+}$ @SiO ₂ standard with 5 microsecone
pulse rate and acquisition window
Figure 8-20 - Experimental data for the emission of $[Ru(bpy)_3]^{2+}$ immobilized on commercial
SiO $_2$ NPs and Ag@SiO $_2$ NPs with different thicknesses, and fitting of the lifetime. Inser
on 2B shows the lifetime short component

List of schemes

Scheme 2-1 - Oxidation of alcohols, alkenes and aromatics, amines, and carbon monoxide
Scheme 2-2: Reduction of organic compounds by PNPs95
Scheme 2-3 - Coupling reactions catalyzed by PNPs
Scheme 4-1 – Reaction conditions for the oxidation of aldehydes using the Ag NCs 165
Scheme 4-2 - Reaction conditions for the hydrogenation of carbonyls using Ag NCs 166
Scheme 4-3 - Conversion of 4-bromobenzaldehyde aldehyde into 4-bromobenzoic acid in
presence of Ag NCs in the continuous flow photoreactor
Scheme 5-1- Reaction scheme for the oxidation of citronellol using Ag@SiO ₂ -[Ru] NPs.
Standard reaction conditions: 0.33 mmol citronellol, CH_3CN , 3 h, O_2 balloon, 3.4
mmol% in $[Ru(bpy)_3]^{2+}$ for Ag@SiO ₂ -[Ru], white LED illumination189
Scheme 6-1 - Reaction scheme for the oxidation of citronellol using Ag@SiO_2- $% \left[{{\left[{{\left[{{\left[{\left[{\left[{\left[{\left[{\left[{$
[photocatalyst] NPs. Standard reaction conditions: 3 h and O_2 balloon. For Ag@SiO ₂ -
[Ru] : 0.33 mmol of citronellol and 0.0034 mol% in $[Ru(bpy)_3]^{2+}$ in acetonitrile. For
$Ag@SiO_2-MB 0.42 mmol of citronellol and 0.0011 mol\% in MB in isopropanol. For$
Ag@SiO ₂ -RB, 0.42 mmol of citronellol and 0.0009 mol% in RB in isopropanol

List of tables

Table 2-1 - PNP properties and relevance to catalysis 69
Table 4-1 - Comparison of the yields obtained for the oxidation of 4-bromobenzaldehyde
aldehyde to 4-bromobenzoic acid under flow and batch conditions, and with and
without catalysts
Table 6-1 – Summary of the emission and photoactivity enhancement factors observed for
Ag@SiO2-(photocatalyst) with 33 and 28 nm shells respectively, the spectral overlap
for the free photocatalyst and their QY
Table 8-1 -Results for the hydrogenation of camphor with Ag NCs as catalyst as a function
of temperature, H_2 pressure, and light exposure
Table 8-2 - Table comparing optimization conditions for the standard photo-oxidation
reaction. Control experiments showed no reactivity when the catalyst was not present,
or when the reagent gas was not air
Table 8-3 - Elemental identification and quantification of Ag NCs by XPS
Table 8-4 -BET surface area of Ag@SiO $_2$ NPs with various silica thickness shell
Table 8-5 – ζ -potential of Ag@SiO2 NPs with 28 and 33 nm shell before and after
immobilization of [Ru(bpy) ₃] ²⁺ 247
Table 8-6 - Conversions for the oxidation of citronellol under various reaction conditions
Table 8-7- Comparison of the different separation distances used for various core-shell and
photosensitizer systems studied
Table 8-8 - BET surface area of Ag@SiO $_2$ NPs with various silica thickness shell
Table 8-9 – ζ -potential of Ag@SiO2 NPs with 28 and 33 nm shell before and after
immobilization of [Ru(bpy) ₃] ²⁺
Table 8-10 - Measured lifetimes, amplitudes, and residuals for each sample as well as the
calculated average lifetime, radiative and non-radiative decay rates

List of equations

Equation 2-1 -Extinction cross section for a small spherical NP, where ϵm is the dielectric
function of the medium, ϵ_1 and ϵ_2 the real and imaginary part of the metal's permittivity,
and λ the wavelength of incident light
Equation 2-2 - Position of an electron in a PNP, where m is the mass of the electron, τ is a
phenomenological relaxation time or mean free time between electronic collisions with
the background, ω_0 is a frequency, and E_{ext} is the external magnetic field driving the
charge movement
Equation 8-1 - Area of one $Ru(bpy)_3^{2+}$
Equation 8-2 - Area of occupied by one mol of $Ru(bpy)_3^{2+}$ ions
Equation 8-3 - Surface coverage
Equation 8-4 - Relationship between the lifetime (T avg) and the fitting functions, with t_1
and t_2 emission lifetimes with respective β_1 and β_2 contribution amplitude values 265
Equation 8-5A-D- relationships between the emission enhancement, the quantum yield Φ ,
the radiative (Kr) and non-radiative (Knr) decay rates and th lifetime (t average) 265

Abbreviations

- acac acetylacetone
- AIBN 2,2'-azo-bis-isobutyronitrile
- APTES 3-Aminopropyl)triethoxysilane
- BET Brunauer-Emmett-Teller
- BINAP 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
- BINOL 1,1'-Bi-2-naphthol
- BSPP bis(p-sulphonato-phenyl)phenylphosphine dihydrate dipotassium
- CB conduction band
- CID chemical interface damping
- CTAB cetrimonium bromide,
- DCP dicumyl peroxide
- DFT density functional theory
- DMAB dimercaptoazobenzene
- DOS density of states
- EBL electron beam lithography
- EDC 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide
- EDX energy dispersive X-ray
- EELS electron energy loss spectroscopy
- EGOR ethylene glycol oxidation reaction
- EM electromagnetic
- EO ethylene oxide
- fcc face-centered cubic
- FDTD finite difference time domain
- GO graphene oxide
- HAADF high annular dark field
- HOMO highest unoccupied molecular orbital
- HPS hyper cross-linked polystyrene
- HT hydrotalcite

- KIE kinetic isotope effect
- LDOS local density of states
- LED Light-emitting diode
- LSPR localized surface plasmon resonance
- LUMO lowest unoccupied molecular orbital
- MB methylene blue
- MEF metal enhanced fluorescence
- MOF metal-organic framework
- NB nanoblock
- NC nanocube
- ND nanodisk
- NIR near-infrared
- NP nanoparticle
- NR nanorod
- NSL nanosphere lithography
- OER oxygen evolution reaction
- PATP p-aminothiophenol
- PFA perfluoroalkoxy alkane
- PDMS polydimethylsiloxane
- PDOS projected density of state
- PET polyethylene teraphthalate
- PMET plasmon-mediated electron transfer
- PMMA poly(methyl methacrylate)
- PNP plasmonic nanoparticle
- PNTP p-nitrothiophenol
- PPF photopolyermizable formulation
- PVP polyvinylpyrrolidone
- QY quantum yield
- RS Rose Bengal
- RWGS reverse water-gas shift

- SEF surface enhanced fluorescence
- SERS surface enhanced Raman spectroscopy
- SET Single electron transfer
- SS superstructure
- STEM scanning transmission electron microscopy
- TA transient absorption
- TERS tip-enhanced Raman scattering
- TMPTA trimethylolpropane triacrylate
- TNI transient negative ion
- TPA (2-pyridylmethyl)amine
- UV ultraviolet
- VB valence band

Contribution of Authors

Prof. Audrey Moores (AM) provided funding, research objectives, experimental design and intellectual guidance for all the projects described in this thesis.

Chapter 1 was written by Alexandra Gellé (AG) and edited by AM.

Chapter 2 was adapted from the published review written and edited by AG, Tony Jin, Luis de la Garza, Gareth Price (GP), Lucas Besteiro and AM.

Chapter 3 was adapted from a published review written by AG and by AM.

For Chapter 4, AM and Michael Landry (ML) initiated the project. MJ focused on the catalysis test. AG developed the synthesis and characterized the materials. Beryl Meng helped with the characterization. AM, ML, AG and Christopher Barrett co-authored the published article. The EELS data were acquired by Nicolas Brodusch (NB) using samples made by AG. Hendrix Demers performed experiments that are not presented in this thesis. NB, AG, AM and Raynald Gauvin (RG) co-authored the published article.

For Chapter 5, AG, AM and Zacharias Amara (ZA) initiated the project. AG designed and performed all the experiments, beside EELS. GP assisted in data collection and AG trained him for all laboratory techniques involved in the paper. The EELS data were acquired by NB using samples made by AG. Frédéric Voisard performed the EELS calculations. AG, AM, RG and ZA co-authored the submitted article, which was adapted for this chapter.

For Chapter 6, AG and AM initiated the project. ZA helped with experimental design. AG performed all the experiments, except real time spectroscopy. Graham Beaton (GB) and Kevin Stamplecoskie (KS) designed and performed the real time spectroscopy experiment. AG, GB, KS and AM co-authored the manuscript in preparation, which was adapted for this chapter.

1 Chapter 1 – Introduction

1.1 Photochemistry : harvesting energy from light

1.1.1 A brilliant idea inspired by Nature

Life on Earth relies on photosynthesis so it is no surprise that Nature and its use of photochemistry have inspired chemists to harvest energy from photons. While scientists cannot be credited for inventing photochemistry, extensive studies have been done over the last century to develop this field, by exploiting light to drive a large variety of chemical transformations. As early as 1912, Giacomo Ciamician envisioned a future society powered by sunlight rather than fossil fuels.¹ Several other seminal studies laid the foundation stones of photo-responsive materials for catalysis.²⁻⁴ In the 21st century photocatalysis has spurred renewed interest and started to develop a wide variety of photo-active materials which can be used as catalysts for numerous transformations.⁵⁻⁹ Nowadays, scientists are still captivated by using light to drive chemical transformations. As solar panels bloom on the roof of buildings and in fields, many scientists are working on developing more photocatalysts for various applications such as hydrogen generation *via* water splitting, depollution of wastewater,¹⁰⁻¹² redox transformations^{13, 14} and singlet oxygen excitation¹⁵ for reduction, oxidation^{16, 17} and coupling reactions.¹⁸⁻²³ More specifically, the development of visible light-driven photocatalysts is of particular interest as it accounts for a large portion of the wavelengths emitted by the sun.²⁴

Many photocatalysts require UV light excitation due to their larger band gap. Such a high source of energy could hinder chemical transformations due to absorption of the solvents and potential degradation of organic substrates. Fortunately, some organic molecules such as fluorescein, chlorophyll, and rhodamine (Figure 1-1) have an inherent small enough energy gap, allowing their excited states to be populated using visible light or near UV irradiations. Some semiconductors,²⁵ including titania (TiO₂), CdS and ZnO, and organometallic complexes²⁰ such as tris(2,2'-bipyridine) ruthenium (II), [Ru(bpy)₃]²⁺, and tris[2-phenylpyridinato-C2,N] iridium (III), [Ir(ppy)₃], (Figure 1-1) also feature an appealing

energy gap, and have been used for visible light-triggered excitation or using near-UV excitation.



Figure 1-1 - Common organic and organometallic compounds activated by light

A wide range of photo-responsive materials and molecules with catalytic properties have been reported since the process of photosynthesis was revealed. Different kinds of homogeneous and heterogeneous photocatalysts, and their advantage as sustainable alternatives are described in this chapter.

1.1.2 Bringing photocatalysts under the spotlight

Organic compounds, organometallic complexes and nanoparticles with appealing light properties have been used for a wide range of catalytic applications.¹³ While the excitation mechanism varies from one structure to another, they all offer a venue to excite electrons, which can be subsequently used for chemical transformations.

Chapter 1 – Introduction

First, some organic compounds have been employed to perform homogeneous photocatalytic reactions. Rose Bengal,²⁶ Eosin Y,²⁷ acridinium salts²⁸ and porphyrin derivatives²⁹ (Figure 1-2) are only but a few examples of photocatalysts³⁰ used for singlet oxygen production³¹⁻³³ and redox^{8,34} reactions, for example. Yet many catalytic reactions employ organometallic complexes which feature long excited state lifetimes and higher photostability. Ru- and Irbased organometallic complexes were for instance reported for homogeneous photoredox and light-induced singlet oxygen production.^{9, 19, 20, 23}



Figure 1-2 - Common organic compounds used in photooxidations and photoredox reactions

Transition metal complexes started to receive great attention in the early 2000s following pioneer studies by the MacMillan and Yoon groups revealing the potential of ruthenium complexes for photocatalysis, and new pathways and molecules were accessed for the first time.³⁵ Several Ru, Ir and Os-based organometallic complexes have been since employed as catalysts for a large variety of organic transformations including couplings, oxidations, polymerizations and cyclizations.³⁵⁻³⁷

Out of the organometallic complexes, Ru and Ir-based structures stand out owing to their excited states which can be efficiently accessed through both UV and visible radiations, and their long-lived triplet states.³⁸⁻⁴⁰ [Ru(bpy)₃]²⁺ was one of the first reported visible light-driven photocatalysts. Promotion of an electron to the excited state happens *via* metalligand charge transfer (MLCT),³⁵ and can be followed by energy transfer to form singlet oxygen (¹O₂), a strong oxidant, which can subsequently mediate organic transformations.
In addition to synthesis, ${}^{1}O_{2}$ is crucial to human life and has also been used in for cancer therapy. The ground state of O_{2} is ${}^{3}\Sigma_{\bar{g}}$ and the lowest excited state of O_{2} , ${}^{1}\Delta_{g}$, features an empty low lying Π orbital which makes it a highly reactive species⁴¹ commonly used for organic and biological transformations. Transition from ${}^{1}\Delta_{g}$ to the ground state ${}^{3}\Sigma_{\bar{g}}$, is spin forbidden, which makes ${}^{1}\Delta_{g}$ O_{2} a long-lived species. The second excited state ${}^{1}\Sigma_{g}^{+}$, is short lived as the transition to ${}^{1}\Delta_{g}$ state is spin-allowed.³¹



Figure 1-3 - Representations of molecular oxygen ground state and excited states³¹

Photosensitization of O_2 into 1O_2 can be triggered by many organic and organometallic compounds, including dyes (Rose Bengal, Methylene Blue, BODIPY, etc), porphyrins and other macrocycles, semiconductors, and Ru-, Pt-, Re- and Ir-based complexes.³¹ Excitation by a sensitizer is achieved *via* a one-photo transition between the ground state and a singlet excited state (Figure 1-4A). The triplet state can be accessed by excitation by a sensitizer *via* a one-photo transition from the ground state to the singlet excited followed by an intersystem crossing (ISC) transition as described in Figure 1-4A. The equations describing the formation of a photosensitizer in the triplet state and 1O_2 are the following:

$$P(S_0) \rightarrow h\nu P(S_1) \rightarrow k_{ISC} P(T_1)$$
$$P(T_1) + {}^3O_2 \rightarrow k_{EF} P(S_0) + {}^1O_2$$

where P is the photosensitizer; S_0 the singlet ground state; S_1 the first excited singlet state; T_1 , the first excited triplet state; k_{ISC} , the rate constant of intersystem crossing; k_{EF} , the

rate constant of energy transfer; ${}^{3}O_{2}$, the ground state triplet oxygen, and ${}^{1}O_{2}$, the singlet oxygen.

Quenching of ${}^{1}O_{2}$ can happen by interaction with other species, leading in some cases to oxidations. Studies reported that ${}^{1}O_{2}$ is more oxidizing than O_{2} , thus making it a better electrophile and enabling reaction with C-C bonds, sulfides, amines and anions. ${}^{1}O_{2}$ can undergo several oxidation pathways such as [4+3] or [2+2] cycloadditions and Schenck Ene reactions, depending on the substrate of interest.⁴²⁻⁴⁴ Allylic hydroperoxides formed from unactivated olefins with allylic hydrogen ^{45, 46} can lead to the formation of alcohols upon quenching.(Figure 1-4B)



Figure 1-4- Excitation of $[Ru(bpy)_3]^{2+}$ followed by the formation of 1O_2 (A) and the Schenck Ene reaction mechanism using 1O_2 (B)

This reaction is of particular interest for the synthesis of high value terpenes such as Rose oxide which is used in perfume industry and artemisinin, an anti-malarial drug.¹⁶ The synthesis of these two commercially important terpenes can be achieved from citronellol (Figure 1-5) and dihydroartemisinic acid respectively. The commercial synthesis of these common industrial products relies on ¹O₂-mediated photooxidation.⁴⁷



Figure 1-5 - Synthesis of Rose oxide from citronellol

Nanoparticles (NPs) can also be interesting photocatalysts, and have the intrinsic advantage of easy separation from the reaction and recyclability, also they are often more robust. The photocatalytic properties of metal oxides for the photodegradation *via* oxidation of organic compounds under UV light were reported as early as 1955. ⁴⁸TiO₂ owes its popularity to its heterogeneous photocatalysis abilities following observations made by Fujishima and Honda in 1972,⁴⁹ when they brought to light the photocatalytic properties of TiO₂ for the formation of H₂ from water. Since then, TiO₂ which features appealing band gap and energy levels to trigger transformations,⁵⁰ have been exploited beyond water splitting. TiO₂ is of great interest in the field of light-triggered nanophotocatalysis as it is cheap, abundant and highly stable.⁵¹ A wide range of photo-responsive oxide semiconductors NPs, including ZnO, CdS and Sb₂O₃, have been exploited for various reactions such as oxidations and reductions⁵², couplings,⁵³ water decontamination,⁵⁴⁻⁵⁶ and water splitting.^{57,58}

The main drawbacks of semiconductor-catalyzed reactions are the fast recombination of charges following excitation of an electron from the valence to the conduction band of the material.⁵⁹ Strategies such as bimetallic materials, doping and couplings with organic compounds have been extensively studied in an effort to address the issues related to UV light excitation, and to extend the lifetime of the excited electrons.⁶⁰

Despite the fast growing interest for photocatalysis, major limitations remain. Several organometallic complexes are highly efficient and can be excited by visible light, but require rare toxic transition metals which are hard to recover and often have low quantum yield. On the other hand, most heterogeneous photocatalysts feature high stability, can be recycled and require UV activation. However, many strategies such as dopping and addition of cocatalysts permit to drive transformations using visible light even though the band gap of the photoactive materials correspond to UV irradiation.

Photo-responsive nanomaterials have recently attracted a lot of enthusiasm for catalytic applications due to their ability to harvest energy from light and because they can be used as heterogeneous catalysts, therefore being of particular interest from sustainability and green chemistry perspectives.⁶¹

1.2 Shining light on coinage-metal

Nanoparticles of group XI metals, also refered to as coinage metals (Cu, Ag, Au), exhibit a different behaviour when irradiated from the one of other photo-active nanomaterials. The unique interaction with light of these materials, called plasmonic nanoparticles (PNPs), make them of particular interest for light-driven heterogeneous catalysis, and embrace several green chemistry principles. Their attractive response to light irradiation has been known for centuries, but only received a great deal of attention over the last 20 years, in physics, medecine, engineering and chemistry. Yet many questions still persist about their behaviour upon irradiation and their use in catalytic applications.

Their appealing optical properties manifested in vivid colors have been observed very early on. The dichromic Lycurgus cup (Figure 1-6A), made in the 4th century by Romans, turns from green to red when illuminated, and is a texbook example of how Au NPs were used in ancient times to craft art pieces.⁶² The windows of Notre-Dame de Paris cathedral (Figure 1-6B) are another famous example of tinted glass with both esthetic and scientific appeal.

The unexpected red color of nano-size Au peaked the interest of many scientists but remained mysterious, until Faraday created what he called "activated gold" by reducing a yellow solution of gold chloride with phosphorus. Faraday finally elucidated the enigma of his "ruby gold" solution (Figure 1-6C) when he realized that the solution was made of suspended colloidal gold, and not only dissolved salt as originally thought, with unique scattering properties.



Figure 1-6 - Photographs of the Lycurgus cup (A), Au NPs solution produced by Faraday (B) and Notre-Dame cathedral rose window (C). Credits: The British Museum, Paul Wilkinson and Patrick Kovarik.

Beyond a wide palette of colors, plasmonic materials offer unique interactions with light, which opened the door to many other applications.⁶¹ PNPs have been employed in a large variety of fields, including but not limited to, biosensors,⁶³ nanotherapy,⁶⁴ nanophotonics,⁶⁵ photovoltaics,⁶⁶ nanorobotics,⁶⁷ spectroscopy⁶⁸ and catalysis⁶⁹ (Figure 1-7). The latter is a rapidly emerging field since major breakthroughs which paved the way in the early 2000s.



Figure 1-7 - Main applications of plasmonic nanoparticles in various fields

PNPs can play a pivoting role in mediating chemical transformations triggered by light. The reactivity of the PNPs is often due to the presence of highly energetic charge carriers, so-called hot electrons or hot holes These are formed upon irradiation at the resonance frequency of the material, which induces surface plasmon resonance (SPR).⁷⁰ Excitation at the SPR wavelength results in coherent oscillation of the free electrons centered on the PNP. The energy distribution of the band structure is impacted to generate hot electrons and holes.⁷¹ Subsequent injection of these so-called hot electrons into nearby substrate molecular orbitals can trigger chemical transformations.

This contrasts with semiconductor bandgaps and complexes HOMO-LUMO gaps for which electrons have to be promoted individually by irradiation at a specific wavelength. On the contrary, PNP SPR bands cover a large range of wavelengths and SPR leads to a collective excitation of electrons over a range of energies. Along with the formation of these light-induced hot electrons, an increase in temperature, and enhancement of the electric field at the vicinity of NPs are observed.⁷¹ Hence the mechanisms by which PNP can mediate

organic transformations are due to 1) a local thermal effect resulting from the relaxation of the hot electrons, 2) a field enhancement in the NP surroundings arising from the alteration of the field distribution, 3) energetic charge carriers at the surface of the plasmonic metal, and 4) any combination of the previously mentioned. ^{69,72,73}

PNPs unique response to light irradiation provides appealing catalytic properties to materials that are usually considered to have weak catalytic potential. Hot electrons can even "do the impossible" as Halas and coworkers wrote when reporting plasmon-induced dissociation of H₂ catalyzed by Au PNPs (Figure 1-8A).⁷⁴ Several transformation pathways thought to be impracticable, because not feasible under traditional thermal conditions, are now accessible using such photo-active materials.

Additionally, bimetallic systems gave a vibrant new direction to the field of plasmonmediated catalysis. PNPs are employed in such systems as light harvesters, combined with highly active catalytic materials commonly used under thermal conditions. These bimetallic nanostructures have offered new perspectives to photo-nanocatalyst designs using PNPs with semiconductors, weakly absorbing metals with catalytic capacity or organometallic complexes. The combination of visible light responsive PNPs with species featuring high catalytic activity have been used by Swearer *et al.* to selectively form ethylene by hydrogenation of acetylene catalyzed by Pd@Al antenna-reactor systems (Figure 1-8B). PNPs have also been exploited to harvest visible light and trigger reactions using catalytic semiconductors which would otherwise require UV activation.⁷⁵ Such bimetallic system, combining UV active semiconductors with plasmonic material able to mediate transformations using visible light, have also been reported to drive water splitting under visible illumination using TiO₂ coupled with coinage metals for example.⁷⁶

Another strategy, inspired from surface-enhanced Raman spectroscopy (SERS), explored by the Yamashita group showed that the photoactivity of a Ru-based organometallic complexes can be boosted when in proximity of PNPs. In such systems, the activity of photoreponsive compounds can be increased by PNPs as previously showed by Heyne and

coworkers.⁷⁷ They used PNPs to boost the production of ${}^{1}O_{2}$ and thus enhance the antibacterial performance of Rose Bengal (Figure 1-8C). Increasing the photoactivity of organic compounds located in the surrounding of the PNP has also been used extensively in spectroscopy techniques such as surface enhance fluorescence.



Figure 1-8 - Photoactive materials developed and their application, by Mukherjee et al. (A) ⁷⁴, Swearer and al. (B)⁷⁵, and Planas et al. (C)⁷⁷

1.3 Green chemistry principles: Call for change

1.3.1 The light bulb idea

Chemical innovation has undoubtely shaped society and greatly influenced how we live today. From the invention of plastic to high performance drugs, our quality of life is greatly correlated with scientific advancement. As chemical processes became more performant, larger quantities were produced more rapidly, for better and for worst. Most of those

innovations came at high cost for the environment, and processes implemented in the industry are often safety hazards. It is now time to rethink how we do chemistry and consider all the inputs and outputs of our processes, rather than focussing only on the formation of the desired products.⁷⁸

The twelve principles of Green Chemistry, first published in 1998 by Anastas and Warner,⁷⁹ provide guidelines for chemists to design experiments and products with sustainability criteria in mind (Figure 1-9). Green Chemistry was described by Taylor in 2010 as "a revolutionary change in preventing pollution and health problems starting at the chemical design stage".⁸⁰ Green chemistry is therefore neither a new branch of science nor a synonym of environmental chemistry, but instead revisits how we approach chemistry. It could however be considered as a new way of thinking and methodology, which takes into account the production, use and disposal of chemicals to design sustainable and safer chemical processes. The twelve principles mainly adress toxicity, feedstock, biodegradability, waste generation and energy consumption.⁸¹ These principles overlap with sustainability goals and propose a modern version of how chemical transformations could be performed. They aim to lead scientists to carefully design their protocols by encouraging a decreasing dependence on limited non-renewable resources and an increasing focus on preventing pollution byproducts of the chemical industry.⁸⁰ It also requires a shift from a product perspective to a global vision, which takes into account the origin of resources, energy consumption and life cycle. The objective is to raise awareness among chemists of the hazard and environmental impacts of their field, and thus reduce toxicity, hazard and pollution in the chemical industry, while conserving high efficiency.



Figure 1-9 - The twelve principles of Green Chemistry

Tremendous experimental and computational studies have been conducted to make progress towards the design of environmentally benign chemical processes following the guidelines descriped by Anastas and Warner. Widespread use of Green Chemistry concepts has led to the reduction of hazardous reagents and solvents usage, energy efficiency improvement, and enhanced the design of products for end of life.⁸¹ Even though Green Chemistry has made its way in the teaching, research and industry⁸² laboratories, stakeholders^{83, 84} show reluctance due to the implementation cost, and lack of clear guidelines and metrics for comparison.^{82, 85, 86}

Moreover, there is always a greener alternative to be found, and also it takes substantial amount of time to implement.⁷⁸ Hence there is still a long road to go but there is light at the end of the tunnel. Hopefully, the future will prove Crabtree right, and confirm that "in a few decades it won't be special anymore... Everyone will be doing green chemistry" as written in 2009. Ideally, all chemists will contribute to the green revolution, as green chemistry is not a field of study but another perception of chemical processes that every chemist can relate to and adopt.

1.3.2 Contribution of nano-catalysis

Catalysis is one of the fundamental pillar, and one of the 12 principles, of green chemistry as it allows to reduce waste and energy consumption by preventing the use of stoichometric reagents and lowering the energy barrier.^{81,87} Heterogeneous catalysis permits to recover and recycle the catalytic species readily, and threfore reduces waste by limiting the steps and chemicals needed to isolate the desired product. Moreover once isolated, the catalyst can be reused to perform other reactions, and recycling of the catalysts is easier for heterogeneous catalysts than homogeneous species.

In addition to lowering the activation barrier, catalysis can also lead to perfom transformations which employ more sustainable reagents, and thus follow the atom economy principle. Using a reducing reagent such as H₂ instead of NaBH₄ allows to reduce waste generated by ensuring that most of the atoms part of the reagents are incorporated in the final product.

A main interest of light-trigered reactions lies in the energy consumption. Exploiting photons as a source of energy has been at the center of many studies in academia and in the industry, and numerous homogeneous and heterogeneous catalysts have been reported in an effort to achieve that goal. First, photochemistry is a promising venue for milder and greener reaction conditions.^{88, 89} Photons are abundant non-toxic and non-costly reagents, leading to lower energy consumption and reduced environmental impact compared to thermal processes. Using milder conditions is also of interest to avoid thermal degradation of the substrates under high temperatures. Another advantage of photocatalysis is to access reaction pathways otherwise prevented under thermal conditions.⁹⁰ For example, ${}^{1}O_{2}$ is a powerful oxidant which can be used to drive oxidations and couplings under mild conditions, and its formation is possible thanks to the simple energy transfer from an excited state.^{31, 91} ${}^{1}O_{2}$ can even be consider as a green oxidant as oxygen gas is highly abundant, and no pollutant byproducts are formed during its formation and use.

Moreover, the development of electronic technologies such as light emiting diodes (LEDs) and ultra focused lasers has provided scientists with new tools to better study photo-active structures and develop applications for light-driven catalysts. LED technology has enabled chemists to conceive new set ups to fully exploit the catalytic capacities of such photo-responsive materials, owing to this energy-efficient, safe and cheap production of photons in high quantities.⁹² Another advantage of LEDs is that it leads to an increase in temperature smaller than the one observed with light bulbs, therefore using LEDs over traditional light bulbs saves energy required for cooling. This cost-saving and highly efficient technology

proved to be a turning point in the field of photocatalysis, and has allowed to envision industrialization of photocatalysts.

1.4 Scope and contribution to original knowledge of the presented research

This thesis highlights a one-of-a-kind type of photocatalysts: plasmonic nanoparticles. In the light of recently reported catalysts based on plasmonic materials, this new kind of photo-active materials holds great promises. Indeed, plasmonic nanoparticles offer a new venue for the design of photocatalysts owing to their unique interaction with light that leads to the formation of highly energetic electrons, and enhancement of the electric field in their vicinity.

While the number of elements featuring a plasmon excitation wavelength in the visible is restricted, their range of applications in catalysis seems immense owing to the large variety of plasmon active-based materials which can be synthesized. Early studies in the field of plasmon-mediated catalysis focused on inorganic transformations, photodegradation and activation of small molecules, this emerging kind of photocatalytic nanomaterials feature appealing catalytic properties to mediate heterogeneous organic catalytic reactions under mild conditions.

The introduction chapter details how heterogeneous photocatalysis could play a pivotal role in the developement of greener processes. The different systems studies in this thesis investigated how plasmonic materials can be used to drive chemical transformation using visible light under mild reaction conditions by exploiting the catalytic properties of these unique photoactive materials. The materials developed proved to be efficient nano photocatalysts and demonstrate the versatility and potential of plasmon-mediated

49

catalysts. The work presented in this thesis also provide a deeper understanding of how plasmon-active catalysts participate in organic transformations.

An extensive review of the optical properties of plasmonic nanoparticles, and their synthesis are detailed in chapter 2. The performances of these photocatalytic nanomaterials for a wide range of organic transformations, and the mecanisms by which they can participate in catalytic reactions are also highlighted in this chapter. This chapter highlights pioneer studies as well as recent developments in the field of plasmonics, and includes contributions from the chemistry, physics, nanoscience, engineering fields. An effort was made to include organic, photochemical, physical and computation studies in order to provide a wider understanding of the emerging and complex field of plasmonic to a large range of readers, thus giving tools to reseachers from various background to engage in the development of plasmon-driven catalysts. This review is aimed to serve as a seminal reference for researchers in the field interested in organic transformations catalyzed by plasmonically active systems.

Hot electron-mediated catalysis is one of the main mecanisms driving plasmon-mediated organic transformations, and has also been employed by many groups for artificial photosynthesis, also called water splitting. Heterometallic systems based on PNPs coupled with TiO₂ proved to be highly efficient for the formation of H₂ upon visible light irridiation. The variety of bimetallic materials used for photocatalytic water splitting, and the role of the plasmonic metal and the semiconductor for this transformation are reviewed in chapter 3. Photo-driven water spliting is the holy grail oh chemical transformations and has been the focus of intensite studies involving plasmonic materials. This chapter details key studies focussing on the development of photocatalysts for H₂ production with Cu, Ag or Au-based NPs, as well as mechanistic explanations often overlooked in previous reviews and original publications. This chapter aimed to be a must-read for researchers developping hybrid TiO2-plasmonic photocatalysts for water spliting as it provides an overview of recent development in the field, and includes chemical, physical and engineering contributions.

Also, it lays out an accessible description of the mechanisms and the SPR-induced effect on the photocatalytic processes.

Chapter 4 focuses on Ag nanocubes as hydrogenation and oxidation catalysts for carbonyls. Ag intrinsic catalytic properties under thermal condictions are limited, yet SPR and hot electrons granted unique catalytic capacity to these NPs which were used to drive hydrogenations and oxidations using molecular oxygen and hydrogen under mild conditions *via* hot electrons. This chapter focuses on the synthesis and characterization of these nanocatalysts, as well as their use in continuous flow reactor. In this chapter, we have shown that free standing plasmonic NPs can act as hydrogenation and oxidation photocatalysts using green reagents, namely H_2 and O_2 . This chapter is important because it highlights that a metal commonly hard to activate, Ag in our case, has the potential to be efficient and versatile when activated by light to drive industrially relevant reactions. This work was the first example of atmospheric pressure reduction catalysis with Ag. Moreover, this chapter serves as a proof of concept for heterogenous and multiphasic photochemical transformations in a continuous flow reactor.

In chapter 5, we report a photoactive bimetallic catalyst exploiting the enhancement of the electric field in the vicinity of PNPs to drive oxdications. Ag@SiO₂ NPs were used to boost the photoactiviy of [Ru(bpy)₃]²⁺ towards the oxidation of alkenes *via* ¹O₂. The immobilization of this homogeneous catalyst led to an increase in emission and photocatalytic performance. The synthesis, characterization and catalytic activity of this field-enhancement mediated nanocatalyst are discussed. This chapter is the first study of the distance-dependant activity of field enhanced-driven photocatalysts for organic transformations. It provides important information for the development of nanocatalyst exploiting the SPR-induced field enhancement, which has been used in rare occasions for organic reactions. The luminescence and photocatalytic studies have been complemented with both experimental and computational EELS studies, in order to provide extensive physical and photochemical information about such novel nanocatalysts. Such a thorough

study of field enhanced-triggered catalysts is unprecedented and showed that more work is needed to fully understand such plasmon-active nanomaterials.

Chapter 6 investigated how the design of PNPs decorated with photocatalysts affects the luminescence and catalytic activity of nanomaterials with dual properties. Rose Bengal, Methylene Blue and $[Ru(bpy)_3]^{2+}$ were immobilized on Ag@SiO₂ NPs to evaluate their performances, and underline how a careful design of these decorated plasmonic nanoantenna is crucial to maximize the photocatalytic activity.⁹ In this chapter, other photoactive species were investigated to further explore the potential the plasmon-driven catalysts and extend our understanding of the impact of field enhancement of the catalytic activity of decorated PNPs. The species used, Rose Bengal, Methylene Blue and $[Ru(bpy)_3]^{2+}$, are common photocatalysts. This study provides crucial information in regard to their boosted activity when immobilized on Ag NPs when varying the silica thickness. This chapter details the first distance-dependence analysis of the luminescence and photoactivity of several species immobilized on plasmon-active nanocatalysts and paved the way for the developed of thoroughly designed SPR-driven hybrid nano photocatalysts. It also gave access to time-dependant data on such systems, for the first time.

Chapter 7 summarizes the main conclusions of the different chapters and how SPRactivated Ag NPs were used to drive different photocatalytic transformations by exploiting various mechanisms. This chapter also highlights the importance nanomaterials design can have on the activity of catalysts. Suggestions of further analysis and experiments to conduct are also detailed in this chapter. This section mentions which steps would be required for plasmon-driven catalysis to raise more interest among the organic chemistry community, and gain notoriety as an appealing sustainable alternative to common solvothermal methods.

1.5 References

1. Ciamician, G., The Photochemistry of the Future. *Science* **1912**, *36* (926), 385-394.

2. Palmisano, G.; Augugliaro, V.; Pagliaro, M.; Palmisano, L., Photocatalysis: A Promising Route for 21st Century Organic Chemistry. *Chemical Communications* **2007**, (33), 3425-3437.

3. Roth, H. D., The Beginnings of Organic Photochemistry. *Angewandte Chemie International Edition in English* **1989**, *28*(9), 1193-1207.

4. Albini, A.; Fagnoni, M., 1908: Giacomo Ciamician and the Concept of Green Chemistry. *ChemSusChem* **2008**, *1*(1-2), 63-66.

5. Acar, C.; Dincer, I.; Naterer, G. F., Review of Photocatalytic Water-Splitting Methods for Sustainable Hydrogen Production. *International Journal of Energy Research* **2016**, *40* (11), 1449-1473.

6. Jafari, T.; Moharreri, E.; Amin, A. S.; Miao, R.; Song, W.; Suib, S. L., Photocatalytic Water Splitting—the Untamed Dream: A Review of Recent Advances. *Molecules* **2016**, *21* (7), 900.

7. Fajrina, N.; Tahir, M., A Critical Review in Strategies to Improve Photocatalytic Water Splitting Towards Hydrogen Production. *International Journal of Hydrogen Energy* **2019**, *44*(2), 540-577.

8. Nicewicz, D. A.; Nguyen, T. M., Recent Applications of Organic Dyes as Photoredox Catalysts in Organic Synthesis. ACS Publications: 2014.

9. Nicewicz, D. A.; MacMillan, D. W., Merging Photoredox Catalysis with Organocatalysis: The Direct Asymmetric Alkylation of Aldehydes. *Science* **2008**, *322* (5898), 77-80.

10. Al-Mamun, M.; Kader, S.; Islam, M.; Khan, M., Photocatalytic Activity Improvement and Application of Uv-Tio2 Photocatalysis in Textile Wastewater Treatment: A Review. *Journal of Environmental Chemical Engineering* **2019**, *7*(5), 103248.

11. Ahmed, S. N.; Haider, W., Heterogeneous Photocatalysis and Its Potential Applications in Water and Wastewater Treatment: A Review. *Nanotechnology* **2018**, *29* (34), 342001.

12. Ge, J.; Zhang, Y.; Heo, Y.-J.; Park, S.-J., Advanced Design and Synthesis of Composite Photocatalysts for the Remediation of Wastewater: A Review. *Catalysts* **2019**, *9*(2), 122.

13. Romero, N. A.; Nicewicz, D. A., Organic Photoredox Catalysis. *Chemical reviews* **2016**, *116*(17), 10075-10166.

14. Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J., Visible Light Photoredox-Controlled Reactions of N-Radicals and Radical Ions. *Chemical Society Reviews* **2016**, *45* (8), 2044-2056.

15. Schweitzer, C.; Schmidt, R., Physical Mechanisms of Generation and Deactivation of Singlet Oxygen. *Chemical reviews* **2003**, *103*(5), 1685-1758.

16. Ghogare, A. A.; Greer, A., Using Singlet Oxygen to Synthesize Natural Products and Drugs. *Chem. Rev.* **2016**, *116*(17), 9994-10034.

17. Ravelli, D.; Fagnoni, M.; Albini, A., Photoorganocatalysis. What For? *Chemical Society Reviews* **2013**, *42*(1), 97-113.

18. Ravelli, D.; Protti, S.; Fagnoni, M., Carbon–Carbon Bond Forming Reactions Via Photogenerated Intermediates. *Chemical reviews* **2016**, *116* (17), 9850-9913.

19. Schultz, D. M.; Yoon, T. P., Solar Synthesis: Prospects in Visible Light Photocatalysis. *Science* **2014**, *343*(6174).

20. Yoon, T. P.; Ischay, M. A.; Du, J., Visible Light Photocatalysis as a Greener Approach to Photochemical Synthesis. *Nat. Chem.* **2010**, *2*(7), 527-532.

21. Hoffmann, N., Photochemical Reactions as Key Steps in Organic Synthesis. *Chemical Reviews* **2008**, *108*(3), 1052-1103.

22. Karkas, M. D.; Porco Jr, J. A.; Stephenson, C. R., Photochemical Approaches to Complex Chemotypes: Applications in Natural Product Synthesis. *Chemical Reviews* **2016**, *116*(17), 9683-9747.

23. Shaw, M. H.; Twilton, J.; MacMillan, D. W., Photoredox Catalysis in Organic Chemistry. *The Journal of organic chemistry* **2016**, *81*(16), 6898-6926.

24. Zhou, D.; Chen, Z.; Gao, T.; Niu, F.; Qin, L.; Huang, Y., Hydrogen Generation from Water Splitting on Tio2 Nanotube-Array-Based Photocatalysts. *Energy Technology* **2015**, *3* (9), 888-895.

25. Fox, M. A.; Dulay, M. T., Heterogeneous Photocatalysis. *Chemical reviews* **1993**, *93* (1), 341-357.

26. Sharma, S.; Sharma, A., Recent Advances in Photocatalytic Manipulations of Rose Bengal in Organic Synthesis. *Org. Biomol. Chem.* **2019**, *17*(18), 4384-4405.

27. Hari, D. P.; König, B., Synthetic Applications of Eosin Y in Photoredox Catalysis. *Chemical Communications* **2014**, *50*(51), 6688-6699.

28. Joshi-Pangu, A.; Lévesque, F. o.; Roth, H. G.; Oliver, S. F.; Campeau, L.-C.; Nicewicz, D.; DiRocco, D. A., Acridinium-Based Photocatalysts: A Sustainable Option in Photoredox Catalysis. *The Journal of Organic Chemistry* **2016**, *81*(16), 7244-7249.

29. Chen, Y.; Li, A.; Huang, Z.-H.; Wang, L.-N.; Kang, F., Porphyrin-Based Nanostructures for Photocatalytic Applications. *Nanomaterials* **2016**, *6* (3), 51.

30. Ravelli, D.; Fagnoni, M., Dyes as Visible Light Photoredox Organocatalysts. *ChemCatChem* **2012**, *4*(2), 169-171.

31. DeRosa, M. C.; Crutchley, R. J., Photosensitized Singlet Oxygen and Its Applications. *Coordination Chemistry Reviews* **2002**, *233*, 351-371.

32. You, Y., Chemical Tools for the Generation and Detection of Singlet Oxygen. *Organic & biomolecular chemistry* **2018**, *16*(22), 4044-4060.

33. Pibiri, I.; Buscemi, S.; Piccionello, A. P.; Pace, A., Photochemically Produced Singlet Oxygen: Applications and Perspectives. *ChemPhotoChem* **2018**, *2*(7), 535-547.

34. Fukuzumi, S.; Ohkubo, K., Organic Synthetic Transformations Using Organic Dyes as Photoredox Catalysts. *Organic & Biomolecular Chemistry* **2014**, *12*(32), 6059-6071.

35. Teegardin, K.; Day, J. I.; Chan, J.; Weaver, J., Advances in Photocatalysis: A Microreview of Visible Light Mediated Ruthenium and Iridium Catalyzed Organic Transformations. *Org. Proc. Res. Dev.* **2016**, *20*(7), 1156-1163.

36. Michelin, C. m.; Hoffmann, N., Photosensitization and Photocatalysis—Perspectives in Organic Synthesis. *ACS Catalysis* **2018**, *8*(12), 12046-12055.

37. Narayanam, J. M.; Stephenson, C. R., Visible Light Photoredox Catalysis: Applications in Organic Synthesis. *Chemical Society Reviews* **2011**, *40*(1), 102-113.

38. Arias-Rotondo, D. M.; McCusker, J. K., The Photophysics of Photoredox Catalysis: A Roadmap for Catalyst Design. *Chemical Society Reviews* **2016**, *45* (21), 5803-5820.

39. Guo, S.; Chen, K.-K.; Dong, R.; Zhang, Z.-M.; Zhao, J.; Lu, T.-B., Robust and Long-Lived Excited State Ru (Ii) Polyimine Photosensitizers Boost Hydrogen Production. *ACS Catalysis* **2018**, *8*(9), 8659-8670.

40. Parada, G. A.; Fredin, L. A.; Santoni, M.-P.; Jäger, M.; Lomoth, R.; Hammarström, L.; Johansson, O.; Persson, P.; Ott, S., Tuning the Electronics of Bis (Tridentate) Ruthenium (Ii) Complexes with Long-Lived Excited States: Modifications to the Ligand Skeleton Beyond Classical Electron Donor or Electron Withdrawing Group Decorations. *Inorganic Chemistry* **2013**, *52*(9), 5128-5137.

41. Krinsky, N. I., Singlet Oxygen in Biological Systems. *Trends in Biochemical Sciences* **1977**, *2*(2), 35-38.

42. Abdel-Shafi, A. A.; Worrall, D. R.; Ershov, A. Y., Photosensitized Generation of Singlet Oxygen from Ruthenium (Ii) and Osmium (Ii) Bipyridyl Complexes. *Dalton Transactions* **2004**, (1), 30-36.

43. Abdel-Shafi, A. A.; Beer, P. D.; Mortimer, R. J.; Wilkinson, F., Photosensitized Generation of Singlet Oxygen from (Substituted Bipyridine) Ruthenium (Ii) Complexes. *Helvetica Chimica Acta* **2001**, *84*(9), 2784-2795.

44. Gutiérrez, M. I.; Martínez, C. G.; García-Fresnadillo, D.; Castro, A. M.; Orellana, G.; Braun, A. M.; Oliveros, E., Singlet Oxygen (1δg) Production by Ruthenium (Ii) Complexes in Microheterogeneous Systems. *The Journal of Physical Chemistry A* **2003**, *107*(18), 3397-3403.

45. Adam, W.; Brünker, H.-G.; Kumar, A. S.; Peters, E.-M.; Peters, K.; Schneider, U.; von Schnering, H. G., Diastereoselective Singlet Oxygen Ene Reaction (Schenck Reaction) and Diastereoselective Epoxidations of Heteroatom-Substituted Acyclic Chiral Olefins: A Mechanistic Comparison. *Journal of the American Chemical Society* **1996**, *118* (8), 1899-1905.

46. Prein, M.; Adam, W., The Schenck Ene Reaction: Diastereoselective Oxyfunctionalization with Singlet Oxygen in Synthetic Applications. *Angewandte Chemie International Edition in English* **1996**, *35*(5), 477-494.

47. Amara, Z.; Bellamy, J. F.; Horvath, R.; Miller, S. J.; Beeby, A.; Burgard, A.; Rossen, K.; Poliakoff, M.; George, M. W., Applying Green Chemistry to the Photochemical Route to Artemisinin. *Nat. Chem.* **2015**, *7*(6), 489-495.

48. Markham, S. C., Photocatalytic Properties of Oxides. ACS Publications: 1955.

49. Fujishima, A.; Honda, K., Electrochemical Photolysis of Water at a Semiconductor Electrode. *nature* **1972**, *238*(5358), 37-38.

50. Kudo, A.; Miseki, Y., Heterogeneous Photocatalyst Materials for Water Splitting. *Chemical Society Reviews* **2009**, *38*(1), 253-278.

51. Pelaez, M.; Nolan, N. T.; Pillai, S. C.; Seery, M. K.; Falaras, P.; Kontos, A. G.; Dunlop, P. S.; Hamilton, J. W.; Byrne, J. A.; O'shea, K., A Review on the Visible Light Active Titanium

Dioxide Photocatalysts for Environmental Applications. *Applied Catalysis B: Environmental* **2012**, *125*, 331-349.

52. Serpone, N.; Emeline, A., Semiconductor Photocatalysis: Past, Present, and Future Outlook. ACS Publications: 2012.

53. Li, S.; Shelar, D. P.; Hou, C.-C.; Chen, Q.-Q.; Deng, P.; Chen, Y., Wo3 Nanospheres with Improved Catalytic Activity for Visible Light Induced Cross Dehydrogenative Coupling Reactions. *Journal of Photochemistry and Photobiology A: Chemistry* **2018**, *363*, 44-50.

54. Mills, A.; Davies, R. H.; Worsley, D., Water Purification by Semiconductor Photocatalysis. *Chemical Society Reviews* **1993**, *22*(6), 417-425.

55. Demyanenko, A. V.; Bogomolov, A. S.; Dozmorov, N. V.; Svyatova, A. I.; Pyryaeva, A. P.; Goldort, V. G.; Kochubei, S. A.; Baklanov, A. V., Singlet Oxygen 1o2 in Photocatalysis on Tio2. Where Does It Come From? *The Journal of Physical Chemistry* **C2019**, *123*(4), 2175-2181.

56. Daimon, T.; Nosaka, Y., Formation and Behavior of Singlet Molecular Oxygen in Tio2 Photocatalysis Studied by Detection of near-Infrared Phosphorescence. *The Journal of Physical Chemistry* C**2007**, *111*(11), 4420-4424.

57. Moniz, S. J.; Shevlin, S. A.; Martin, D. J.; Guo, Z.-X.; Tang, J., Visible-Light Driven Heterojunction Photocatalysts for Water Splitting-a Critical Review. *Energy & Environmental Science* **2015**, *8*(3), 731-759.

58. Ni, M.; Leung, M. K.; Leung, D. Y.; Sumathy, K., A Review and Recent Developments in Photocatalytic Water-Splitting Using Tio2 for Hydrogen Production. *Renewable and Sustainable Energy Reviews* **2007**, *11*(3), 401-425.

59. Tang, J.; Durrant, J. R.; Klug, D. R., Mechanism of Photocatalytic Water Splitting in Tio2. Reaction of Water with Photoholes, Importance of Charge Carrier Dynamics, and Evidence for Four-Hole Chemistry. *Journal of the American Chemical Society* **2008**, *130* (42), 13885-13891.

60. Kisch, H., Semiconductor Photocatalysis—Mechanistic and Synthetic Aspects. *Angewandte Chemie International Edition* **2013**, *52*(3), 812-847.

61. de Aberasturi, D. J.; Serrano-Montes, A. B.; Liz-Marzán, L. M., Modern Applications of Plasmonic Nanoparticles: From Energy to Health. *Adv. Opt. Mater.* **2015**, *3*(5), 602-617.

62. Song, M.; Wang, D.; Peana, S.; Choudhury, S.; Nyga, P.; Kudyshev, Z. A.; Yu, H.; Boltasseva, A.; Shalaev, V. M.; Kildishev, A. V., Colors with Plasmonic Nanostructures: A Full-Spectrum Review. *Applied Physics Reviews* **2019**, *6* (4), 041308.

63. Masson, J.-F., Surface Plasmon Resonance Clinical Biosensors for Medical Diagnostics. *ACS sensors* **2017**, *2*(1), 16-30.

64. Cheng, L.; Wang, C.; Feng, L.; Yang, K.; Liu, Z., Functional Nanomaterials for Phototherapies of Cancer. *Chemical reviews* **2014**, *114*(21), 10869-10939.

65. Wang, D.; Wang, W.; Knudson, M. P.; Schatz, G. C.; Odom, T. W., Structural Engineering in Plasmon Nanolasers. *Chemical reviews* **2017**, *118*(6), 2865-2881.

66. Clavero, C., Plasmon-Induced Hot-Electron Generation at Nanoparticle/Metal-Oxide Interfaces for Photovoltaic and Photocatalytic Devices. *Nature Photonics* **2014**, *8*(2), 95-103.

67. Kuppe, C.; Rusimova, K. R.; Ohnoutek, L.; Slavov, D.; Valev, V. K., "Hot" in Plasmonics: Temperature-Related Concepts and Applications of Metal Nanostructures. *Advanced Optical Materials* **2020**, *8*(1), 1901166. 68. Cardinal, M. F.; Vander Ende, E.; Hackler, R. A.; McAnally, M. O.; Stair, P. C.; Schatz, G. C.; Van Duyne, R. P., Expanding Applications of Sers through Versatile Nanomaterials Engineering. *Chemical Society Reviews* **2017**, *46* (13), 3886-3903.

69. Gellé, A.; Jin, T.; de la Garza, L.; Price, G. D.; Besteiro, L. V.; Moores, A., Applications of Plasmon-Enhanced Nanocatalysis to Organic Transformations. *Chemical Reviews* **2019**, *120*(2), 986-1041.

70. Moores, A.; Goettmann, F., The Plasmon Band in Noble Metal Nanoparticles: An Introduction to Theory and Applications. *New J. Chem.* **2006**, *30*(8), 1121-1132.

71. Brongersma, M. L.; Halas, N. J.; Nordlander, P., Plasmon-Induced Hot Carrier Science and Technology. *Nature nanotechnology* **2015**, *10*(1), 25-34.

72. Zhang, Z.; Zhang, C.; Zheng, H.; Xu, H., Plasmon-Driven Catalysis on Molecules and Nanomaterials. *Accounts of chemical research* **2019**, *52*(9), 2506-2515.

73. Zhang, Y.; He, S.; Guo, W.; Hu, Y.; Huang, J.; Mulcahy, J. R.; Wei, W. D., Surface-Plasmon-Driven Hot Electron Photochemistry. *Chemical reviews* **2017**, *118* (6), 2927-2954.

74. Mukherjee, S.; Libisch, F.; Large, N.; Neumann, O.; Brown, L. V.; Cheng, J.; Lassiter, J. B.; Carter, E. A.; Nordlander, P.; Halas, N. J., Hot Electrons Do the Impossible: Plasmon-Induced Dissociation of H2 on Au. *Nano letters* **2013**, *13*(1), 240-247.

75. Swearer, D. F.; Zhao, H.; Zhou, L.; Zhang, C.; Robatjazi, H.; Martirez, J. M. P.; Krauter, C. M.; Yazdi, S.; McClain, M. J.; Ringe, E., Heterometallic Antenna– Reactor Complexes for Photocatalysis. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113*(32), 8916-8920.

76. Gellé, A.; Moores, A., Water Splitting Catalyzed by Titanium Dioxide Decorated with Plasmonic Nanoparticles. *Pure and Applied Chemistry* **2017**, *89*(12), 1817-1827.

77. Planas, O.; Macia, N.; Agut, M.; Nonell, S.; Heyne, B., Distance-Dependent Plasmon-Enhanced Singlet Oxygen Production and Emission for Bacterial Inactivation. *J. Am. Chem. Soc.* **2016**, *138* (8), 2762-2768.

78. Clark, J. H., Green Chemistry: Challenges and Opportunities. *Green Chemistry* **1999**, *1*(1), 1-8.

79. Anastas, P. T.; Warner, J. C., Principles of Green Chemistry. *Green chemistry: Theory and practice* **1998**, 29-56.

80. Taylor, D. A., Principles into Practice Setting the Bar for Green Chemistry. National Institute of Environmental Health Sciences: 2010.

81. Sheldon, R. A., Green Chemistry and Resource Efficiency: Towards a Green Economy. *Green Chemistry* **2016**, *18*(11), 3180-3183.

82. Sanderson, K., It's Not Easy Being Green: In the Past Two Decades, the Green-Chemistry Movement Has Helped Industry Become Much Cleaner. But Mindsets Change Slowly, and the Revolution Still Has a Long Way to Go. *Nature* **2011**, *469*(7328), 18-21.

83. Roschangar, F.; Colberg, J.; Dunn, P. J.; Gallou, F.; Hayler, J. D.; Koenig, S. G.; Kopach, M. E.; Leahy, D. K.; Mergelsberg, I.; Tucker, J. L., A Deeper Shade of Green: Inspiring Sustainable Drug Manufacturing. *Green Chemistry* **2017**, *19*(1), 281-285.

84. Poliakoff, M.; Fitzpatrick, J. M.; Farren, T. R.; Anastas, P. T., Green Chemistry: Science and Politics of Change. *Science* **2002**, *297* (5582), 807-810.

85. Sheldon, R. A., Metrics of Green Chemistry and Sustainability: Past, Present, and Future. *ACS Sustainable Chemistry & Engineering* **2018**, *6*(1), 32-48.

86. Roschangar, F.; Sheldon, R.; Senanayake, C., Overcoming Barriers to Green Chemistry in the Pharmaceutical Industry-the Green Aspiration Level[™] Concept. *Green Chemistry* **2015**, *17*(2), 752-768.

87. Anastas, P. T.; Kirchhoff, M. M.; Williamson, T. C., Catalysis as a Foundational Pillar of Green Chemistry. *Applied Catalysis A: General* **2001**, *221*(1-2), 3-13.

88. Albini, A.; Fagnoni, M., Green Chemistry and Photochemistry Were Born at the Same Time. *Green Chemistry* **2004**, *6*(1), 1-6.

89. Marzo, L.; Pagire, S. K.; Reiser, O.; König, B., Visible-Light Photocatalysis: Does It Make a Difference in Organic Synthesis? *Angewandte Chemie International Edition* **2018**, *57*(32), 10034-10072.

90. Zhou, Q. Q.; Zou, Y. Q.; Lu, L. Q.; Xiao, W. J., Visible-Light-Induced Organic Photochemical Reactions through Energy-Transfer Pathways. *Angewandte Chemie International Edition* **2019**, *58*(6), 1586-1604.

91. Ogilby, P. R., Singlet Oxygen: There Is Indeed Something New under the Sun. *Chemical Society Reviews* **2010**, *39*(8), 3181-3209.

92. Jo, W.-K.; Tayade, R. J., New Generation Energy-Efficient Light Source for Photocatalysis: Leds for Environmental Applications. *Industrial & Engineering Chemistry Research* **2014**, *53*(6), 2073-2084.

Transition

Following this introduction of green chemistry and photocatalysis and plasmonic nanoparticles, organic transformations catalyzed by plasmon-based nanostructures are reviewed. This chapter aimed at highlighting the variety of photo-nanocatalysts and organic transformations that can benefit from SPR-induced catalytic activity



This chapter is adapted from a published article. The American Chemical Society granted permission to reprint the published article, as did all co-authors.

Alexandra Gellé, Tony Jin, Luis de la Garza, Lucas V. Besteiro and Audrey Moores Applications of Plasmon-Enhanced Nanocatalysis for Organic Transformations, Chemical Reviews, 2020, 120, 2, 986.

2.1 Introduction

In 2017 in the United States, 46% of the energy used in industry was used towards the bulk chemical production and petrochemical refining.⁹³ Only less than 8% of the energy used in US industry is coming from renewable resources,⁹³ thus making industry a major contributor to greenhouse gases emission.⁹⁴

For over a century, photochemistry has been envisaged as an opportunity to perform transformations using light as the source of energy.95 The Italian chemist Giacomo Ciamician first described his vision of replacing fossil burning by sunshine for chemicals production. The last two decades in particular have seen tremendous developments in the field of photochemistry, making light a viable alternative energy source in a foreseeable future in the context of organic chemistry.⁹⁶ Photocatalysis is seen as a major opportunity in the organic chemistry community as it allows controlling organic transformation in a precise fashion, typically via radical chemistry. In a typical scheme, visible-light-absorbing transition metal complexes, such as tris(bipyridine)Ru (II) or tris(2-phenylpyridine) Ir(III) have been used as dyes, in order to harvest photons enabling single electron transitions.¹⁹ These have been successfully used for instance towards singlet oxygen activation, and opened interesting paths in total synthesis.⁴⁷ Besides, intense research efforts have been devoted to photocatalysis relying on the use of metal oxide semiconductors, such as TiO₂, ZnS or CdS.²⁵ In such systems, light excitation at energies above the material band gap produces an electron-hole pair and triggers a variety of redox reactions, most notably in the area of photocatalytic water splitting, as proven by Fujishima and Honda in 1972.^{49, 97, 98} Other applications for photocatalysis are also seen, as highlighted in reviews found elsewhere.^{8, 12, 13} ^{25, 99, 100} In other approaches, metal free, organic dyes have also been utilized successfully in a number of organic transformations.¹³ In an effort to expand upon this capability into new types of photocatalysts, researchers have looked into harnessing the powers of plasmonic nanoparticles (PNPs). PNPs are now being applied to a range of applications from solar radiation conversion¹⁰¹ to sensing and from high efficient telecom and datacom to high density memories.¹⁰² Following pioneer studies on plasmon-mediated catalysis from the early 2000s, LSPR-mediated catalysis emerged over the last decade as a

new field at the interface of photocalysis and nanocatalysis. One of the early report of LSPR-induced catalysis by Tian and Tatsuma focused on the oxidation of methanol and ethanol under visible-light irradiation using Au NPs as sensitizers for titanium dioxide films.¹⁰³ The term "plasmonic photocatalysis" was coined few years later by Awazu *et al.* who reported the photodecomposition of methylene blue mediated by Ag NPs embedded in TiO₂.¹⁰⁴ In the framework of this chapter, we will use indifferently plasmonic photocatalysis and plasmon-enhanced catalysis. Taking inspiration from these early works, a variety of PNP-based catalysts have been studied, extending the scope of reactions photocatalyzed by LSPR.

In this chapter, we are focusing on the use of PNP in organic transformations. Many nanoparticles, especially metal nanoparticles, have been reported as effective catalysts for such reactions.¹⁰⁵⁻¹⁰⁷ Nanoparticles became very popular as catalysts in the late 1990s, as they were viewed as bridging the gap between homogeneous and heterogeneous catalysis.¹⁰⁵ In particular nanoparticles offer a number of advantages in the context of catalysis. As one can control the size, shape, crystallinity properties and composition of nanoparticles, nanocatalysts have rapidly emerged as tunable, reactive and selective catalysts.¹⁰⁸ They can be easily immobilized without compromising their catalytic activity and are thus great systems to develop flow solutions.¹⁰⁹ Importantly, other properties of nanoparticles have been exploited in the context of catalysis to afford synergistic, or complementary effects. For instance, magnetic nanoparticles allow access to easily recyclable catalysts.^{110, 111} Optical properties of nanoparticles, among which plasmonic properties, are also salient features, and they offer a chance to positively affect catalysis. By the careful selection of both nanocatalysts and studied reactions, plasmon-enhanced catalysis has allowed the development of catalysts which are typically more active and/or more selective than comparable systems which are not light activated. This chapter will highlight such examples.

2.2 Mechanisms of plasmon-enhanced nanocatalysis

2.2.1 Principles of localized surface plasmon resonance

The plasmonic properties of metal nanoparticles (NPs) have been exploited for centuries, in particular for aesthetic reasons. A number of nanoparticles syntheses, of Ag and Au in particular, have been discovered and developed, motivated by the vivid colors featured by these nanomaterials, arising from their plasmonic properties. It has been associated with magical properties and thus a topic of fascination. Since Antiquity, craftsmen have developed methods to fabricate plasmonic NPs (PNPs), which we now find in a number of artifacts. The Lycurgus Cup dates back to the 4th century Roman Empire and features dichroic properties from the presence of AuAg alloy NPs.¹¹² The red stained glasses in gothic churches of the Middle Ages, or bohemian glasses in the 17th century are other iconic artifacts made of *Au ruby* glasses, a material produced by the reduction *in situ*, inside molten glass, of Au ions into well-defined nanoparticles.¹¹³

2.2.2 LSPR theories and properties

Only in the early 20th century did theories start to be developed, with the aim to predict and understand the collective properties of colloidal suspensions. One of hurdles faced then in theorizing the optical properties of metal NPs was the ability to describe the dielectric properties of metal NPs disseminated in a matrix with an effective dielectric medium ε_m .^{114, 115} A major stepping stone in this endeavor was the development by Gustav Mie in 1908 of a general theory for the scattering of nanoparticles, which he obtained from a purely analytical solution of the Maxwell equations for spherical systems.¹¹⁶ As such, it provides a general tool for calculating the intensity of the interaction of light with small spherical scatterers of any arbitrary material. The strength of the Mie formalism lies in the absence of approximations. Yet one can find useful to study certain regimes that allow for practical simplifications to the theoretical approach. One particularly relevant example for the

purposes of this chapter is the quasi-static regime, which is well adapted for NPs with sizes significantly smaller than the wavelength of the light impinging on them. Within this regime, one can obtain the extinction of the NP as coming from its dipolar moment, resulting from its polarizability. Such perspective results in an expression of the extinction cross section for a small spherical NP given in Equation 2-1.¹¹⁷

$$C_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{2/3}}{\lambda} \frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2}$$

Equation 2-1 -Extinction cross section for a small spherical NP, where ε m is the dielectric function of the medium, ε_1 and ε_2 the real and imaginary part of the metal's permittivity, and λ the wavelength of incident light.

Regardless of the approach, the theoretical modeling of plasmonic nanoparticles can be used in combination with experimental values for permittivity, or those obtained from theoretical models. One particularly relevant example is the Drude model,¹¹⁸ which describes the conductivity of a metal in terms of the kinetic properties of a classical gas of electrons moving against the background of the ionic lattice of the material. As of today, the Drude model is still routinely invoked to estimate the dielectric response of different materials, and used in the numerical solution of the Maxwell equations for arbitrary particle geometries using modern computational techniques.

It is beyond the scope of this chapter to provide extensive derivations of these models, and they can be found elsewhere.^{70, 119-122} In the following we focus on the description of salient facts to help the readers relate plasmonic theories with application in catalysis. These models are helpful because they enable a description of the electric field in and around PNPs, the energetics of the electrons in such systems, and thermal dissipation around the particles, all parameters of paramount importance in the context of catalysis.

For the chemists willing to apply plasmonic phenomena in catalysis, perhaps the most effective way to describe the localized surface plasmon resonance (LSPR) is *via* a tutorial

model.⁷⁰ This model provides a better intuition of the physics behind the phenomenon. There, the position of an electron in a PNP is described by:

$$m\frac{d^2\boldsymbol{r}}{dt^2} + \frac{m}{\tau}\frac{d\boldsymbol{r}}{dt} + m\omega_0^2\boldsymbol{r} = qE_{ext}(t)$$

Equation 2-2 - Position of an electron in a PNP, where m is the mass of the electron, τ is a phenomenological relaxation time or mean free time between electronic collisions with the background, ω_0 is a frequency, and E_{ext} is the external magnetic field driving the charge movement.

This equation can be identified as one describing a harmonic oscillator, damped by a Joule damping term in dr/dt,¹²³ with a resonance frequency ω_{ib} corresponding to the highest amplitude in r. Such large displacement translates, in the aggregate picture, to a greater accumulation of charge at the surface of the particle and a stronger enhancement of its near field. At resonance frequency ω_{ib} , the plasmon band appears, and the extinction cross section of the particle is maximum.

This provides an intuitive framework to understand the LSPR. Essentially, inside PNPs, conducting electrons are mobile electrons (Drude free electrons), meaning that they can move through the metal when guided by external forces, such as any incident EM waves (Figure 2-1A). This movement will be hindered, however, by collisions with the ionic background which are modeled by the friction term in **Error! Reference source not found**. (dr/dtterm). These conduction electrons collectively behave as a coherent electronic cloud. When exposed to an incident oscillating EM field (E_{ext} in **Error! Reference source not found**.), this cloud oscillates in reaction to combination of the external field and the resulting Coulombic forces generated due to the charge displacement. Illuminating the system results in the polarization of the nanoparticle, with charges accumulating at opposite ends of its structure. These charges create a depolarization field that creates a restoring force on the electron cloud ($m\omega\sigma^2$ factor in **Error! Reference source not found**.) being the restoring constant in this tutorial model). Here an analogy can be drawn with a

macroscopic oscillator in the form of a spring attached to a mass (Figure 2-1B). The damping term represents the energy loss occurring due to absorption during the process and it is responsible for broadening the LSPR band, equivalently to the spectrum of a damped spring.

As mentioned above, at resonance, the collective oscillation of the electron cloud causes near-field EM enhancement at the vicinity of the PNPs. This occurs because the polarization and depolarization fields are in phase, which is the fundamental characteristic of the plasmonic resonance, and increases the amplitude of the electric field near the regions of accumulating the charge, i.e. the particle surfaces. This explains why this phenomenon was coined as a "localized" (as it is supported in a confined, localized particle, as opposed to a continuous metal-dielectric interface) and "surface" (as this is where the charges are actually localized) effect, yet it is important to bear in mind that the phenomenon results from a collective oscillation of all conductive electrons in the PNPs. This explains that the absorption due to the Joule effect, although most intense at the regions with a large field intensity, does occur throughout the metal volume. The enhancement of the electric field is one of the major properties of plasmonic resonances, and it is highly localized, mostly existing a few nanometers around the PNPs surface.¹²⁴ This has been harnessed in sensing^{125, 126} and spectroscopy, in particular in surface enhanced Raman spectroscopy¹²⁷ and plasmon enhanced fluorescence,^{128, 129} but also for near field microscopy, whereby the resolution limit inherent to visible light is overcome by the strong light confinement enabled by the LSPR.¹²⁴



Figure 2-1 – A) Depiction of the dynamics of a PNP during irradiation. The diagram shows a snapshot of a nanoparticle excited at a frequency below that of resonance, at which the carriers follow the changes in electric field orientation. The excitation is caused by the incoming electric field (orange), while the restoring electric field is generated by the out-ofequilibrium surface charges (green) and the ionic network causes damping (purple, with the direction of the arrow assuming that the electrons already moving downwards in the diagram). Importantly, if the external field oscillates at the frequency of the resonant mode of the particle, both external and restoring fields will sync, greatly enhancing the total field in and around the particle. If the external field disappears, the charge oscillation in the particle will continue until dampened by the friction-like losses. Figure adapted from Ref.¹³⁰ Copyright American Chemical Society B) The electron cloud can be understood as behaving like a harmonic oscillator, in analogy to a macroscopic oscillator such as a spring attached to a mass driven by an external oscillating force (orange), to which the spring responds with a restoring force (green) when expanded or contracted. Friction with the supporting surface will also cause damping (purple). Reproduced from ref ⁶⁹. Copyright 2020 American Chemical Society.

Other important effects of the LSPR result from the damping phenomena taking place in PNPs. As mentioned above, there are several types of damping effects.¹³¹ The non-radiative damping is caused by processes transferring the plasmon energy into the immediate surroundings of the PNP or the PNP itself. These include collisions of the mobile

67

electrons with the background ions, and the excitation of single electron-hole pairs through the excitation of interband transitions in the metal.¹³² Because of the role of electron transitions in non-radiative damping, the band configuration and the Fermi level of the metal are key parameters in the problem. Different metals thus behave differently, both in terms of their natural resonance frequency, but also regarding to their intrinsic losses at different parts of the EM spectrum.¹³² Now, although we are characterizing the nonradiative losses in plasmonic materials as a purely negative contribution, the truth is that they can be utilized for scientific and technological purposes. Firstly, these loss mechanisms may cause heating, as the energy present in the electronic kinetic energy (or electronic degrees of freedom) is transferred to the metal lattice.¹³³ This phenomenon is, for instance, extensively used in the research of new techniques to deliver targeted photothermal cancer therapy^{134, 135} and, perhaps more relevantly for the purposes of this chapter, to drive higher reaction rates.^{136, 137} Secondly, the intraband transitions characteristic of plasmonic excitation may give rise, upon the decay of the plasmon, to the generation of hot carriers, i.e. carriers with energy levels up to the total energy of the incoming photon above the Fermi energy.^{71, 138} They receive their name because of having energies above what a thermal distribution of electrons at ambient temperature would enable. These hot carriers can relax internally or be exploited at the PNP surface for chemistry: this is an important manifold towards applications in, for instance, solar harvesting and photodetection.^{71, 138}

The LSPR phenomenon is strongly dependent on the size and shape the PNP. As the particle grows in size, its polarizability increases and the plasmon band is further broadened by opening a radiative decay channel. This becomes accessible as the nanoparticle experiences stronger dipolar modes, from which the plasmon can spontaneously reemit a photon in the far field, which amounts to the scattering of the incident light.¹³² Small spherical PNPs can be easily modeled as an oscillating dipole. Elongated nanoparticles, such as rods, feature two plasmonic modes, one in the longitudinal, one in the lateral direction, and two characteristic LSPR bands are observed in absorption.¹³⁹ As the shape becomes more complicated, and especially if the structure involves tips and edges, the local EM field around these features becomes very intense. These so-called *hot spots* are important, as

they cause large enhancements of the LSPR properties locally. Similarly hot spots are also observed between two nanoparticles in close proximity (less than a NP diameter away from one another), for instance in 2D arrangements of PNPs,¹²⁴ or in nanocavities.¹⁴⁰ Based on this, plasmonics has developed into a research field of its own, where nanoparticle structures can be designed and manipulated to obtain the desired field enhancement at specific locations, following the concept of plasmon hybridization.¹⁴¹ This concept was introduced as an analogy to one of the molecular orbital hybridization to predict optical properties of metallic nanostructures beyond the spherical, film and cubic pre-existing models.¹⁴¹ It has since been applied to a variety of complex plasmonic structures including nanoshell, nanorice, nanomatryushkas (a nanoshell embedded within a nanoshell), as well as multiparticle plasmons like dimers, trimers and quadrumers.¹⁴² Plasmon hybridization can be seen as a tool to predict and analyze the LSPR properties of complex structures by deconvoluting them into nanostructures with simple geometry and them combining the optical properties of these easily-modelled structures.

2.2.3 LSPR and catalysis

In previous sections, we have focused on the critical properties of the optical excitation of PNP and outlined the fundamental mechanism supporting plasmonic resonances. Here we will explicitly describe the different aspects that have brought plasmonic nanoparticles to the forefront of research on photocatalytic, including the description of the mechanisms arising from illuminating PNPs and how they can assist catalytic reactions.¹⁴³ In 2017 Liz-Marzan and coworkers wrote a review on LSPR modeling in which they list the properties of PNPs.¹²³ This framework allows to clearly delineate why PNPs are appealing systems to assist catalytic reactions (

Table 2-1).

Table 2-1 - PNP properties and relevance to catalysis

Entry	Property of plasmonic	Relevance of these properties to catalysis				
	nanoparticle					
1	Plasmons interact strongly with	Light enables more efficient energy delivery				
	light, in a specific fashion	than thermal means in catalysis and is				
		associated with better selectivities PNPs provide the means to target photocatalysis events spectrally and spatially, resulting in				
		an appealing framework to favor reactivity				
		and selectivity in chemical events				
2	They are robust against	In industry, heterogeneous catalysts are				
	imperfections, inhomogeneities,	preferred as they allow easy recovery. The				
	and environmental noise	ability to use metal nanoparticles and the				
		resilience of the plasmon band against				
		impurities or small changes in the PNP is an				
		advantage in this context.				
3	Their operation frequency is	In catalysis, this property can be exploited to				
	sensitive to their geometry and	tweak optical properties to match				
	the dielectric environment	application needs.				
4	The optical electric field is greatly	Local field enhancement is at the heart of the				
	amplified near a nanoparticle	different processes that can drive chemical				
	when irradiated by light tuned to	reactions around the PNPs, from direct				
	one of its plasmon resonances	promotion of molecular excitation to the				
		injection of hot plasmonic electrons.				
5	The optical enhancement can be	The confinement of the plasmon effect is				
	confined down to a nanometer-	interesting because it means that the energy				
	sized region, much smaller than	of the system is concentrated where it				
	the incident light wavelength	matters: at the surface of the catalysts.				
		Furthermore, by spatially focusing light's				
		energy and creating loci of higher energy				

	density	they	allow	photocatalysis	under
	lower radiation intensity.				

Based on the description of LSPR phenomenon, there are three main properties of excited PNPs which are relevant in the context of catalysis: the ability for the LSPR to cause local heating, the ability for the LSPR to cause local field enhancement, and finally the ability for the LSPR to provide charge carriers (Figure 2-2). These three effects induced by irradiation of PNP at the resonance frequency are concomitant, and one or more properties can be harvested to drive chemical transformations, depending on the nature of the nanoparticles and the reactants.



Figure 2-2 - Schematic of the three properties on a PNP arising from LSPR, their general applications, and their applications specifically in the context of catalysis. All these effects take place in a given PNP, yet their respective intensity and relevance to catalysis may vary greatly as a function of the PNP design. The general applications, specifically in the context of catalysis of PNP, are given in relation to these three main effects.

2.2.4 LSPR characterization

The LSPR as described above causes strong absorption and scattering in the spectral region of the LSPR band, which ranges from ultra violet (UV) to near infrared (NIR), depending on the metal and PNP morphology, including shape and size. Traditionally, this property can be measured by acquiring UV-visible-NIR extinction spectra. The LSPR is then characterized by its peak position and width, which both depend on the metal, the shape and size of the PNPs as well as the surrounding medium.¹⁴⁴ This measurement however provides an average signal of the collection of PNPs in the solution, in all possible orientations. In order to gain better insight into the local effect of the LSPR on a specific nanoparticle, the technique of choice is energy electron loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM). Essentially, in a STEM experiment a sample is scanned by a focused electron beam. EELS allows analyzing the energy spectrum of any such electron collected after interaction with the sample. Typically, two main types of data are available: for a given point, an energy spectrum can be provided, while for a STEM image, one can overlay a map of EELS intensity at a given energy onto the STEM image, using a color code (Figure 2-3).¹⁴⁵ EELS allows for visualization at sub-angstrom resolution of spatial symmetries controlling the excitation of plasmonic modes at the surface of the object under scrutiny.¹⁴⁵ EELS also allows for the filtering of the signal in terms of energy, thus providing a unique view on the different symmetries of plasmonic modes as a function of the energy, with excellent energy resolution as well. This technique has become fairly mainstream now and many catalysis application articles nowadays feature LSPR characterization by this method.¹⁴⁶ A full description of how this method works for studying LSPR, and applications have been extensively reviewed in a recent publication by Camden and co-workers.¹⁴⁵


Figure 2-3 - A) HAADF–STEM image of a Ag nanoprism with 78-nm-long sides; B) EEL spectra acquired at corner A before (original data) and after deconvolution (Deconvoluted). After deconvolution, resonances (here, one peaked at 1.75 eV) in the ultraviolet/near-infrared domain are more clearly resolved C) EELS mapping. Each EELS mapping corresponds to a specific energy, provided on the image. The colour scale, common to the three maps, is linear and in arbitrary units. Reprinted with permission from¹⁴⁷. Copyright 2007 Nature Publishing.

2.3 Design of plasmon-enhanced nanocatalysts

Since Faraday first reported the synthesis of colloidal Au NPs *via* reduction of chloroauric acid by phosphorus,¹⁴⁸ methods to obtain plasmonic NPs have been extensively investigated. Over the years, the synthesis of monodisperse and shape-controlled NPs has raised an increasing amount of research interest. As new applications for plasmonic NPs

are being continuously discovered, the precise and reproducible fabrication of well-defined nanostructures is a lasting concern. In catalysis in particular, plasmonic NPs have to be tailor-made to optimize their optical properties and surface chemistry, thus maximizing their photocatalytic performances. Indeed, altering the morphology of nanocrystals influence their excitation wavelengths, extinction coefficients, surface area, facets and undercoordinated surface atoms, which can all influence the catalytic performances.

This section describes the synthesis of coinage metals and aluminum free-standing PNPs. Plasmonic nanoparticles can also be immobilized on supporting structures made of silica and other semiconductors, or be coupled with transition metals in bimetallic or alloy structures. We aimed at illustrating the flexibility and versatility of PNP synthesis and variety of available structures to suggest to the reader all the tailoring possibilities when designing plasmon-based catalysts, and the implications of the morphology of PNPs on catalytic efficiency.

2.3.1 Design of free-standing plasmonic NPs

The solution-phase synthesis of metallic NPs is well documented.¹⁴⁹ It can be achieved by either decomposition or reduction of a precursor into zero-valent species, which then assemble to form nanostructures. The reduction route is more frequently used to obtain Au and Ag NPs, from HAuCl₄ and AgNO₃ precursors respectively, when reduced by sodium borohydride, sodium citrate or alcohols.¹⁵⁰ This synthetic scheme is particularly appealing to control the resulting NP size, but also direct the process towards well defined shapes, a feature particularly appealing for plasmonic NPs. This synthesis proceeds first *via* the nucleation of clusters, called seeds, formed by few ions and/or atoms.¹⁵¹ The seed size is well defined because, past a critical size, structural fluctuations are energetically too costly.¹⁵² The growth of the seeds into nanocrystals is controlled by a dynamic interplay: the energy of the bulk of the NP decreases as the structure enlarges, whereas the surface energy increases with size.¹⁵³ A variety of morphologies can be obtained by tuning the

reaction conditions, such as the ratio between the metal precursor and the reducing agent, the reagent concentrations, the solvent nature and the temperature. Another key reaction parameter towards the shape-controlled synthesis of NPs is the capping agent used. The ligand used to passivate the surface of the NPs can prevent aggregation and influence the suspendability of the synthesized structures in solvents. They also play a pivotal role during the synthesis and towards the design of nanocrystals by directing particle growth to the desired shape.¹⁵⁴⁷⁰ Surface capping modifies the free energies of specific crystallographic planes. This alters the relative growth rates of the different facets, which leads to facet-selective growth and therefore different nanostructure morphologies.¹⁵²

Early reports of the synthesis of plasmonic NPs from the 20th century¹⁵⁵⁻¹⁵⁷ describe the use of sodium citrate as both reducing and capping agent to obtain quasi-spherical nanostructures with (111) facets.^{158, 159} By the early 2000s, several groups had already proved they mastered the synthesis of anisotropic plasmonic NPs. The development of non-spherical structures led to new optical properties from the visible range to the NIR, which have picked the curiosity of scientists and opened the possibilities of new applications in nanomedicine,⁶⁴ biosensors,^{160, 161} spectroscopy⁶⁸ and catalysis.¹⁶²

2.3.1.1 Polyol synthesis of Ag and Au PNPs

Ag nanocrystals have been reported in numerous morphologies, including cubes,¹⁶³ tetrahedrons,¹⁶⁴ rods,¹⁶⁵ plates,¹⁶⁶ decahedrons,¹⁶⁷ and stars¹⁶⁸ to only mention a few. Most of these syntheses rely on the so-called polyol process, which consist of the injection of AgNO₃ and polyvinylpyrrolidone (PVP) in preheated ethylene glycol. Xia and coworkers have extensively studied the synthesis and growth mechanisms of Ag NPs. They reported the synthesis of Ag NCs,^{163, 169} right bipyramids,¹⁷⁰ nanobars¹⁷¹ and nanorice¹⁷¹ *via* modified polyol processes (Figure 2-4). In a typical polyol synthesis, ethylene glycol or 1,5-pentanediol serves as both solvent and reducing agent.¹⁷² The active reductant species was found to be glycoaldehyde, formed *via in situ* oxidation of ethylene glycol.¹⁷³ The advantage

of this method lies in the precise control of the NP growth by tailoring the amount of capping agent used, typically PVP with high molecular weight. In the polyol method, the reducing agent and capping agent are distinct species, which allows more control over reaction parameters, compared to early citrate-based methods. Ag NCs were obtained by simultaneous injection of the metal precursor and PVP in preheated ethylene glycol containing hydrochloric acid.^{169, 174} Preferential binding of PVP on (100) facets via 2pyrrolidone ring induces shape-controlled synthesis of anisotropic Ag PNPs,^{175, 176} exhibiting various morphology and aspect ratio depending on the amount and nature of halides ions added. For example, varying the initial concentration of Ag precursor, while keeping the ratio Ag/PVP the same, lead to the formation of Ag nanowires instead of NCs.¹⁷⁷ Yet using NaBr used instead of HCl lead to the growth of right bipyramids.¹⁷⁰ Moreover, for a bromide ion concentration twice higher, nanobars were obtained.¹⁷¹ This demonstrates that upon addition of an oxidative etchant, such as halide ions, or the use of capping agents binding preferentially on selected facets of interest can also alter the growth of nanocrystals and afford anisotropic nanostructures. Such methods are described in the review by Ghosh and Manna.¹⁷⁸ Recent studies by the Rioux group investigated the influence of ions present in solution, upon the addition of HCl, during the synthesis of Ag NCs. According to their experiments and calculations, HNO₃ is formed in situ and control the kinetics of AgNO₃ reduction and AgCl NCs are also formed but subsequently decompose to finally give Ag NCs covered with Cl^{-,150, 179} Xia group noticed that when the solution of nanobars was left incubated in a solution of PVP in water for a week, the extremities of the PNPs became rounded and slowly turned into nanorice structures.¹⁷¹ This interesting observation highlights the asset and drawback of plasmonic nanocrystals; fine tuning can be achieved yet they are fragile and sensitive nanostructures.





Figure 2-4 - Description of PNPs growth via a polyol process, light-mediated synthesis, and nanosphere lithography with the variety of morphologies obtained. (A, C–I) Reproduced with permission from ref ¹⁵⁰. Copyright 2007 American Chemical Society. (B) Reproduced with permission from ref ¹⁸⁰. Copyright 2009 American Chemical Society. (J) Reproduced with permission from ref ¹⁵⁰. Copyright 2011 American Chemical Society. (K, L) Reproduced from ref ¹⁸¹. Copyright 2003 Nature. (M) Reproduced from ref ¹⁸². Copyright 2010 American Chemical Society.

Au and Ag both exhibit *face-centered cubic* (fcc) arrangements, yet using PVP as a capping agent does not form (100)-based Au nanocrystals, as usually observed for PVP-capped Ag NPs, but rather favors formation of structures enclosed by (111) facets such as octahedrons, truncated tetrahedrons, icosahedrons and decahedrons.^{183, 184} Though upon the addition of CI or Br ions, formation of (100) faceted Au NCs is observed.^{185, 186}

Sections detailing the synthesis methods pictured in Figure 1-1 and for hybrid PNPs are reviewed in the original publication by Gellé et al.⁶⁹ but were not included in this thesis for the sake of length.

2.4 Application of LSPR to organic transformations

2.4.1 Oxidation reactions

Oxidation reactions are fundamental steps in many key reactions in both industry and academia. Organic precursors containing aldehydes, ketones, carboxylic acids, and imines are invaluable building blocks with key functionalities.¹⁸⁷ The necessity in creating these molecules are of utmost importance. While there are non-catalytic methods in doing so, many are energy intensive or involve harsh oxidants such as permanganate,188 dichromate,¹⁸⁹ and oxone¹⁹⁰ as sources of oxidants. Catalysis has been a powerful means to drastically improve atom economy. In other cases, oxidation reactions require the use of an excess of organic solvents with homogeneous metal contaminants, which also proves to be a detriment.¹⁹¹ Works have focused on using relatively benign oxidants such as hydrogen peroxide as oxidants.¹⁹² Ideally however, the most economical, environmentally benign, and abundant oxidant that can be used is O₂ gas, which produces water as the only byproduct.¹⁹³ Though, one of the main problems with catalytic aerobic oxidation include activation of the O₂ substrate, which is a major challenge to overcome.¹⁹⁴ The activation of O₂ through a plasmon-mediated pathway is a fundamental advantage of LSPR-enhanced oxidation reactions.¹⁹⁵ This section will provide a detailed scope on the catalytic ability of currently developed plasmonic nanomaterials used for the oxidation reaction, as well as give insight onto possible mechanisms of oxidation through the LSPR effect. The oxidation of alcohols and aldehydes will be covered, oxidation of amines to their azo-bearing substituent, as well as the epoxidation of alkenes will be mainly covered. Scheme 2-1 depicts the general reactions that will be covered below.



Scheme 2-1 - Oxidation of alcohols, alkenes and aromatics, amines, and carbon monoxide

2.4.1.1 Oxidation of alcohols

In 2005, Tian and Tatsuma demonstrated the ability of Au NPs supported by TiO₂ to oxidize methanol and ethanol while also reducing oxygen, making it the first reported photocatalytic oxidation through LSPR.¹⁰³ From this pioneer work, there has been a cascade of studies done on plasmon-mediated catalytic oxidation reactions.¹⁶² Interestingly, Au NPs embedded on TiO₂ were originally considered as catalysts for photodegradation reactions such as the decomposition of methyl-tert-butyl ether and phenol.^{196, 197} However, as many recognized the versatility of these photoactive nanostructures for use in organic transformations such as oxidation reactions, studies shifted towards using these species as photocatalysts for organic transformations. Initial work in LSPR-driven oxidations studied the Au-TiO₂ hybrid system in order to deduce the mechanism of photoactivity. The work of Ohtani and coworkers in 2009 first showed the ability of Au NPs supported on TiO₂ to oxidize isopropanol into acetone, as they confirmed that photoabsorption caused by the LSPR of the Au NPs enhanced catalytic activity.¹⁹⁸ They speculated that the Au NPs could potentially donate electrons into the TiO₂ conduction band that can reduce molecular oxygen, while the hole left behind on the Au could potentially oxidize isopropanol. A follow-up study further confirmed the role of the LSPR of Au in the photocatalytic ability of the Au@TiO₂ nanostructure, while optimizing properties such as the size of Au and TiO₂ particulates, the crystalline structure of TiO₂, and various synthetic methods.¹⁹⁹

Following this, the PNPs supported on metal oxide catalytic system were studied extensively as catalysts for other oxidation reactions, along with changing various parameters of the system such as NP composition and shape, metal-oxide support, and size of both components. Tada and coworkers developed a similar Au NP supported by TiO₂ nanosystem, in which they tested photocatalytic aerobic oxidation of cinnamyl alcohol.²⁰⁰ In 2012, Shiraishi and coworkers fabricated Au NPs at the interface between rutile and anatase TiO₂ particulates, which promoted electron-injection from the Au NPs into the anatase TiO₂ phase, which is the active site for O₂ reduction and subsequently alcohol

dehydrogenation.²⁰¹ While, Kominami and coworkers contrasted the TiO₂ semiconducting support with that of a CeO₂ support.²⁰² The Au@CeO₂ system displayed superior photocatalytic rate and yield towards the selective oxidation of benzyl alcohol to benzaldehyde, with no side-products such as benzoic acid or CO₂. Further results from the same group included a synthetic method in order to tailor size of the Au NP, demonstrating that larger Au NPs increased the rate of reaction, while also revealing the selective oxidation of *p*-aminobenzyl alcohol to *p*-aminobenzaldehyde.²⁰³ Another study by Tian and coworkers replaced Au NPs with Pt NPs, leading to increased reaction rate, however it is noted that the Pt NPs are supported by a TiO₂ film instead of TiO₂ particulates.²⁰⁴ Au NPs have also been fabricated by Ye and coworkers to which they supported with TiO₂, enabling the oxidation of isopropanol to acetone.²⁰⁵ Lately, Idriss and co-workers replaced Au with Ag NPs supported by TiO₂ to plasmonically catalyze the oxidation of aliphatic alcohols such as ethanol to acetaldehyde, studying the effects of temperature and the role of the LSPR of Ag NPs at elevated temperatures.²⁰⁶ It is seen that at above 500 K, thermal energy within the system is sufficient such that LSPR local heat contribution of the Ag NPs have minimal impact on the catalytic performances.

Bare plasmonic nanoparticles have also demonstrated the ability to facilitate oxidation reactions. In 2011, the Scaiano group proved the ability of aqueous colloidal Au nanoparticles with no support as a prominent catalyst for the oxidation of sec-phenethyl and benzyl alcohols.²⁰⁷ However, it is to be noted that the oxidant is hydrogen peroxide. Work done by the same group explored using various other supports for the Au NPs such as hydrotalcite (HT), Al₂O₃, and ZnO in order to make the colloidal Au NP suspensions easier to retrieve after reaction as well as promoting efficient shuttling of electrons within the material to improve photocatalytic behavior for benzyl alcohol oxidation.²⁰⁸ In 2017, our group reported the oxidation of aldehydes to carboxylic acids with Ag NCs with excellent yield and selectivity.²⁰⁹

Studies have been also done towards employing alloyed bimetallic nanoparticles for use in oxidation reactions, in hopes of improving photocatalytic activity. Shiraishi and coworkers

81

used AuCu bimetallic alloy NPs loaded onto TiO₂ as a plasmonic catalyst for the oxidation of isopropanol.²¹⁰ This bimetallic nanostructure promoted the formation of acetone at a faster rate than that of individual Au or Cu NPs. Further, AuPd bimetallic NPs became the center of many groups attention and were studied in photocatalytic oxidation of benzyl alcohol derivatives to their respective benzaldehyde,²¹¹⁻²¹³ as well as methanol oxidation to methyl formate.²¹⁴

Work has also been done in the oxidation of glucose to gluconic acid, as first reported by Xiong and co-workers in 2014 as a model reaction in order to study the plasmonic hot electron behavior in relation to the Schottky junction created between Pd NCs and TiO₂ semiconductor.²¹⁵

Recent work has shown substantial interest in selective catalytic oxidation of glycerol to valuable products, as glycerol is the main byproduct produced in the formation of biodiesel.²¹⁶ In 2015, Tüysüz and coworkers demonstrated the ability that Au and AuCu bimetallic NPs supported on SiO₂ and TiO₂ could plasmonically catalyze the oxidation of glycerol to dihydroxyacetone with excellent selectivity (90% for AuCu alloy NPs).^{217, 218} Due to synergistic effects between Au and Cu, they discovered increased enhancement with the bimetallic AuCu alloy system. Studies done by the Yang group in 2018 have shown the photocatalytic activity of AuCu-CuS core-shell nanoparticles supported on anodic TiO₂ nanocavity arrays, in which they attribute hot electron generation and photothermal heating from the CuS shell to be the enhancing factors in the relatively high yield and selectivity of dihydroxyacetone.²¹⁹ Jradi and coworkers explored the effects of Au NPs supported by either TiO₂ or Al₂O₃ in the oxidation of glycerol.²²⁰Excellent yields, up to 90%, were observed, yet glyceric acid was reported as the main product with a lower selectivity (60%) than in the study by the Tüysüz group using Au NPs@TiO₂.²²¹

Generally, LSPR of PNPs enhance the catalytic aerobic oxidation *via* three processes: 1) adsorption and activation of O_2 *via* hot electron transfer from the PNP; 2) oxidization of the substrate by the hot holes created in parallel with the hot electron, and 3) photothermal contributions localized at the surface of the material caused by electron-phonon

interactions.²²²⁻²²⁴ These three processes are seen to occur congruently as a consequence of light excitation at the SPR mode of the plasmonic NPs. To improve hot carrier separation, metal-oxide support may be added to form a Mott-Schottky junction, as seen by very recent works done by the groups of Liu and Boltersdorf.^{223,224} It can be seen in Figure 2-5 that with LSPR activation, the complete cleavage of the O-H bond of the reactant (in this case a primary alcohol) can be propagated *via* hot hole formation and prolonged lifetimes of the hot electrons/holes spurred on by the synergistic effects of alloying and metal oxide support.²²³ Hydrogen abstraction can then occur which reduces oxygen into hydrogen peroxide, while the oxidized aldehyde is formed.



Figure 2-5 - (a) Schematic of synergistic catalytic processes for alcohol aerobic oxidation on PtCu@TiO2 NB in dark. B) Schematic of hot carrier enhanced synergistic catalysis catalytic processes for alcohol aerobic oxidation on PtCu@TiO2 NB under visible light. The inset at center shows an energy band diagram for hot carrier generation and transfer at the PtCu@TiO2 NB interface. Reproduced with permission from ²²³. Copyright 2017 John Wiley and Sons.

It is also seen that the proposed mechanism for bare NPs has slight variations, as proposed recently by Li and coworkers.²²² With use of DFT calculations and synchrotron techniques, they propose that hot electrons generated from LSPR can be injected into the LUMO $2\pi^*$ anti orbital of adsorbed oxygen, thereby activating it into an anionic O_2^- radical species, while electrons from the HOMO of adsorbed reactants can be injected into a hot hole in order to facilitate both the oxidation of the product via formation of hydrogen peroxide as well as desorption of the Au-O bond that can regenerate the active site of the catalyst. Further electron paramagnetic resonance experiments done by Zhang and coworkers theorized that plasmonic hot holes can act to mildly oxidize the reactant alcohol to form a carbon-centered radical that can more easily be oxidized by anionic O2⁻ species induced by hot electrons.²²⁵ Other groups have used techniques such as Kelvin probe force microscopy (KPFM) to elucidate the possible mechanism of the hot electrons in plasmonic oxidation reactions.²²⁶ With this, they found that by varying the aerobic and anaerobic conditions of Ag NPs on semiconducting polypyyrole wire, they could monitor the oppositely changed charge states of the Ag NP at the nanoscale, visualizing the effects that hot electron generation has on adsorbed O_2 .

With these techniques in mind however, it is to be considered that each of these methodologies in interpreting the role of the LSPR is associated with only the respective nanosystem that each group has chosen to use. Only a more in-depth scope and further analysis of multiple types of nanosystems will allow to draw a conclusive, unified vision. With more research, better deductions can be made on how to create plasmonic nanostructures to be even more efficient at heterogeneous plasmonic catalysis, along with narrowing down key parameters that can promote the various steps in the reaction.

Although outside the scope of this chapter, it is important to note that LSPR is also seen to enhance electrocatalytic oxidation reactions such as the ethylene glycol oxidation reaction (EGOR), as well as the oxygen evolution reaction (OER). A few examples are provided herein. Du and coworkers fabricated AuAg nanobowls for use as light absorbers on modified electrodes, using these for the EGOR under visible light.²²⁷ PtAg nanodendrites prepared by the same group also exhibited enhanced electrocatalytic activity of EGOR

84

when used in modified electrodes.²²⁸ Jin and coworkers fabricated Au NPs supported by a Co/Ni metal organic framework (MOF), inducing boosted electrocatalytic activity for the OER.²²⁹ The authors postulate from their findings that photogenerated holes from the Au NPs directly oxidize Ni²⁺ and Co²⁺ to Ni³⁺ and Co³⁺, which are more reactive for the OER. Exciting new applications can be applied to these recent studies such as the use of plasmonic AgAu NPs to enhance the electrooxidation of glycerol in a direct alcohol fuel cell (DAFC), as exemplified by Minteer and coworkers.²²¹ They saw a 100% increase in power density associated with plasmonic Au and Ag nanoparticles embedded on electrodes, which they attribute to the hot electron effect as well as hole generation for reduction of glycerol.

2.4.1.2 Oxidation of alkenes and aromatics

Ethylene is the most produced chemical in the petrochemical industry, with much work being done into making it a valuable feedstock to create more applicable chemicals.²³⁰ Among them, the epoxidation of ethylene to ethylene oxide (EO) is considered amongst the most important heterogeneously catalyzed reactions in industry²³¹ as EO is a common precursor for ethylene glycol, which is used in the production of antifreeze, polyethylene and polyethylene terephthalate (PET).²³² As such, Ag oxides almost exclusively dominate in industry as the main source of catalyst, in which oxygen gas (10-30 bar) and high temperatures (200-300 °C) are used.^{232, 233} The use of high temperatures can be seen as detrimental, due to the high cost associated with it at the industrial scale, the recyclability of the catalyst, and the decrease in selectivity at high temperatures due to ease in activation of products on the catalyst.²³⁴ The design of efficient catalytic systems that employ light as the energy source instead of heat, along with increasing selectivity towards ethylene oxide and halting further oxidation into CO₂ and water, are paramount objectives in this field.

In 2011, the Linic group revealed the distinct role of the LSPR of Ag NCs in the photocatalytic oxidation of ethylene to ethylene oxide.²³⁴ This is among the first cases of using LSPR for the enhancement of epoxidation reactions, as it was demonstrated that the sharp vertices of the NCs played a crucial role in the plasmon-induced dissociation of O_2 .

Further studies by the same group used Cu NPs to mediate the oxidation of propylene to propylene oxide, controlling the selectivity through the switching of Cu metal and Cu₂O through varying the light intensity induced onto the system.²³⁵

Further developments of this field have also been done recently in 2018 by Jain and coworkers, in which they used surface-enhanced Raman spectroscopy (SERS) in order to deduce the formation of graphene substituents on the surface of Ag NPs when exposed to ethylene gas.²³⁶ They saw graphene to be highly active catalytic component in the system and played a key part in the epoxidation of ethylene. These results were exemplified with experimental catalytic testing with as-synthesized graphene-sheets embedded on Ag NPs on an Al₂O₃ support, complimented by DFT calculations on key steps such as O₂ absorption enhanced by hot electron transfer from the LSPR of Ag NPs.

Along with these key papers in studying the reaction mechanism, selectivity, and parameters that affect catalytic activity for epoxidation, many papers have used the epoxidation reaction only as part of their scope in order to deduce the range of catalytic activity of their catalyst. Yamashita and coworkers grafted a well-known photo catalyst, tris(bipyridine)Ru(II) complex, onto plasmonic Ag NPs coated by a SiO₂ layer. They saw activity enhancement under light activation in the epoxidation of styrene and α -methyl styrene, *via* a field enhancement mechanism.²³⁷

Aside from the oxidation of alkenes, direct oxidation of aromatic species has been described early on in the literature. Selective oxidation of benzene to phenol has been seen by the Ogawa lab as early as $2010.^{238}$ Interestingly, they saw that with the addition of the product -phenol- to the reaction mixture, it enhanced the reaction rate of phenol formation from benzene under visible-light radiation and an Au NP on a modified titanate TiO₃²⁻ support. Other works include the oxidation of 9-anthraldehyde to anthraquinone by the Scaiano group, in which they used a nanostructure consisting of Au NPs supported on nanocrystalline diamond.²³⁹ They discovered that even in air, the oxidation of the anthraldehyde complex could take place with the photocatalyst, to which they owed the

activation of O_2 in the air to form an anionic O_2^- species. Huang and coworkers also evidenced oxidation of benzene to phenol by using various plasmonic metals supported by Ti O_2 .²⁴⁰ A recent study has also proven the oxidation of a sp³-hybridized C-H bond by through plasmonics with a nanomaterial composed of Ag NPs embedded on tungsten oxide (WO₃) nanosheets, however it is to note that tert-butylhydroperoxide was used as an oxidant.²⁴¹

While these initial studies demonstrate the ability plasmonic-enhancement has towards obtaining high catalytic rate and selectivity at more benign conditions, this particular field is seen to not have much attention with respect to its other oxidation reaction counterparts.

2.4.1.3 Oxidation of amines

Oxidation products of amines, such as iminium or azo substituents, have many applications to the production of dyes, pigments, pharmaceutical synthetic intermediates, and nitrogen containing biologically active compounds.^{242, 243} However, several industrial procedures in synthesizing these products involve stoichiometric amounts of harmful and explosive additives.²⁴⁴ Plasmonic photocatalysis is seen as a method in order to address these intrinsic problems, in which aerobic oxidation under visible light mitigates the need for harmful oxidants and thermal conditions.

The oxidation of amines to imines was first reported by Tada and coworkers following their work on the oxidation of alcohols using their Au@TiO₂ photocatalyst.²⁴⁵ They saw imine product formation from benzyl amine, which was the first known aerobic oxidation of amines at the time. It is remarkable to note however that with the addition of acetonitrile as a solvent, a remarkable increase in yield but decrease in selectivity was seen, as the major product formed was the benzaldehyde, not the imine. In a follow-up paper, the same group employed the use of a Au-Cu core-shell system supported by TiO₂, which further enhanced the photocatalytic ability of benzylamine oxygenation to the aldehyde.²⁴⁶ The authors

attributed this great increase to the effects of the thin Cu shell around the Au, greatly enhancing the charge-separation from the plasmonically excited Au hot electrons to the TiO₂ support.

Guo and coworkers fabricated a graphene-stabilized Cu NP nanosystem in which they demonstrated exceptional yield and selectivity for the plasmon-enhanced oxidative homocoupling of benzylic amine into an imine, along with also confirming the catalyzed oxidation of secondary amines with the same system.²⁴⁷ ¹⁶² They proposed a mechanism in which the amine is oxygenated into an aldehyde first, followed by a condensation with a second molecule of benzylamine to form the coupled imine product. Interestingly, this nanostructure of Cu NPs stabilized by graphene, allowed the oxygenation of into the imine derivative instead of a complete stop in oxidation at the benzaldehyde as seen by Tada and coworkers, mentioned earlier. Zhu and coworkers have also demonstrated plasmonic catalytic ability of their PdAu bimetallic alloy system on the oxidation of benzyl amine to imines.²¹² The oxidation of *p*-aminothiophenol (PATP) to dimercaptoazobenzene (DMAB) has been a widely studied reaction for plasmonic photocatalysis in recent years. Camargo and coworkers demonstrated selective oxidation of p-aminothiophenol (PATP) to either dimercaptoazobenzene (DMAB) or p-nitrothiophenol (PNTP), based on whether or not the Au NPs were supported by TiO₂, as well as UV-illumination.²⁴⁸ They illustrated that with bare Au NPs, they saw oxidation of PATP to DMAB, while with the TiO₂ support, they saw no catalytic effect until they employed UV light, to which they saw oxidation to PNTP. Further studies by the same group utilized a nanorattle system in which Au NPs were encapsulated within a hollow AgAu bimetallic alloy shell.²⁴⁹ SERS experiments with the plasmonic aerobic oxidation of PATP to DMAB proved the effectiveness of this nanocomposite over traditional pure Au or Ag NPs, with enhanced hot electron generation and increased electromagnetic field hot spot intensity. From this model test, it was then seen that this nanomaterial could effectively catalyze the oxidation of aniline to azobenzene. Other works include Wang and coworkers that used MnO₂ as the metal oxide support for Au NPs, which saw enhanced plasmonic oxidation of PATP to DMAB.²⁵⁰

Theoretical work as performed by Zhao *et al.* has demonstrated that oxygen activation is the rate-determining step for aerobic O₂ activation and PATP oxidation, which is agreed upon by other studies.^{195, 251-253} It is theorized that hot electron generation from the LSPR of Ag can activate oxygen to lower the activation energy for hydrogen abstraction, which is the key step for oxidation of PATP to yield DMAB. Fascinatingly, the same group compared Ag to Au and saw a stark difference in catalytic ability, as Ag had a higher average hot electron energy level than Au, leading to increased facility to activate the O₂ antiorbital.²⁵¹ Contrasting this, Sun and coworkers devised a method using graphene mediated SERS (G-SERS) and a bias voltage in order to elucidate the role of hot holes generated by Au NPs supported by monolayered graphene sheets.²⁵⁴ It was seen that by tuning the gate voltage to a negative bias, the oxidation of PATP to DMAB increased, as seen in the G-SERS measurements. They hypothesized from this evidence that the plasmon-driven oxidation reaction of PATP was mainly driven by hot holes, and not hot electrons.

2.4.1.4 Oxidation of carbon monoxide

The removal of poisonous carbon monoxide from oxidized environments such as household heating, industrial production, and the starting of an engine are of utmost importance in order to maintain current indoor and outdoor air quality.²⁵⁵ A common popular example of how poisonous fumes are mitigated is with the use of a catalytic converter, commonly found in modern commercially produced cars. The catalyst that is mainly associated with this is Pt, however with drawbacks such as abundance and catalytic ability only above 200 °C, motivation to find another suitable CO conversion catalyst is prevalent.^{256, 257} Haruta *et al.* first demonstrated the ability of colloidal Au NPs to catalyze CO oxidation back in the 1990s and effectively initiated the entire field of Au NP catalysis, at a time when Au was still considered a completely inert metal.¹⁴⁹ Recent works have shown the effect of using MgO and Mg(OH)₂ effectively catalyzing CO oxidation below 0 °C.^{258, 259} However, low catalytic ability from 20 – 175 °C is seen.²⁵⁵ Thus, Liu and coworkers demonstrated the effect of using light irradiation on the same Au NPs supported on Mg(OH)₂ developed by Jia *et al.* and demonstrate how the LSPR of Au caused enhanced catalytic activity. They

observed that increased reaction rates were seen above 20°C, while proposing the ratedetermining step to be the desorption of surface carbonates poisoning the catalyst between 20 – 175 °C, to which the generation of hot electrons and local heating from the plasmonic Au NPs can remove.

A whole suite of nanomaterials have been synthesized and tested for plasmonic photooxidation of CO by Park and coworkers.²⁶⁰⁻²⁶³ Throughout their work, it is noted that direct hot electron transfer is likely the main plasmonic mechanism associated with such enhancement. For example, with the use of hexoctahedral Au NPs supported by Cu₂O, hot electron injection into the metal oxide followed by oxidation of the CO followed a Marsvan Krevelen type mechanism.^{262, 264} Other systems such as Au NPs supported by ZIF-8 modified TiO₂ studied by Fu and coworkers have also been demonstrated to oxidize CO.²⁶⁵ The authors postulate that the ZIF-8 MOF decreased the amount of aggregation of Au NPs decorated on TiO₂, while also proposing that the MF acts as a "electron-transfer mediator" between the plasmonic Au NPs and TiO₂, effectively enhancing hot electron generation and injection into TiO₂, which in turn can promote the oxidation of CO.

2.4.2 Reduction reactions

2.4.2.1 Reduction of alkenes and alkynes

LSPR activation of H₂ through field enhancement was also explored. Halas and coworkers studied the hydrogenation of acetylene using Pd@Al NPs (Scheme 2-2). As discussed in section 2.3, the Al NPs served as antennae to harvest light while catalytic events took place at the surface of photoactivated Pd islands.²⁶⁶⁻²⁶⁸ This system illustrates how plasmon-enhanced catalysis can affect nanoparticle reactivity. Under thermal activation, Pd@Al NPs hydrogenates acetylene into a mixture of ethylene and ethane, with ethylene:ethane ratios ranging between 6 and 10 across a range of temperatures. Ethylene is a more valuable product. In contrast, plasmon-activation of Pd@Al NPs increased the selectivity for the

partial hydrogenation to ethylene all the way to a ratio of 37 under high white light irradiation. The selectivity observed under light irradiation is shown to be due to an increased desorption rate of hydrides into H2 at the surface of Pd NPs compared to the thermal counterparts.

Partial hydrogenation of phenylacetylene provided further evidences of LSPR-induced improved selectivity for transition metals immobilized on PNPs.²⁶⁹ Camargo and coworkers demonstrated that Au@AgPt nanorattle structures exhibited increased selectivity for C-C triple bond over double bonds, leading to selective semi-hydrogenation of phenylacetylene to styrene rather than ethylbenzene (Scheme 2-2). Nanorattles are core-shell NPs including a dielectric spacer between the two metals exhibiting a strong field enhancement in the particles inner cavity.^{249, 270} Specifically Au@AgPt is composed of an Au plasmonic core and an ultrathin catalytic shell of Ag-Pt alloy. It exhibited higher performances than the Au@Ag@Pt core-shell counterpart. The nanorattles are believed to enable higher reactivity owing to the plasmon hybridization between the Au core and the plasmonic-catalytic shell. Indeed, DFT and experiments confirmed field enhancement effect inside the nanorattle structures. Discrimination between C-C triple bond and double bond was due to referential adsorption of acetylene over styrene because of stronger localized interactions between C-C triple bonds and the Pt surface compared to the ones with double bonds.

The hydrogenation of styrene to ethylbenzene catalyzed by Pd-Ag NPs was reported by Zhao et al²⁷¹ (Scheme 2-2). Local heating was proven to be responsible for the reaction rate increase as similar yields were obtained in the dark at 70 °C and under light irradiation at room temperature. The Scott group reported the hydrogenation of 2-methyl-3-buten-2-ol using Pd@Au nanotriangles at 0.34 atm.²⁷² 42% conversion was observed upon LSPR excitation whereas only 18% was observed in the dark at the same temperature.

2.4.2.2 Reduction of aldehydes and ketones

The transfer hydrogenation of cinnamaldehyde with 2-propanol over Au@SiC NPs was reported by Hao *et al.* and showed formation of acetone and 100 % selectivity for cinnamyl alcohol at 20 °C with visible-light irradiation²⁷³ (Scheme 2-2). Other industrially relevant unsaturated alcohols such as crotyl alcohol and 2-penten-1-ol were selectively produced from the corresponding α , β -unsaturated aldehydes. Using Au or the SiC support alone with light irradiation, cinnamyl alcohol was formed in low yield with poor selectivity, reinforcing the importance of structural design and both the plasmonically active metal and the semiconductor for efficient charge carriers separation for maximized performance. The mechanism proposed includes oxidation of propanol on positive sites at Au surface generated by hot electron injection into the semiconductor, which thus formed acetone and activate hydrogens available for reduction of carbonyls. α , β -unsaturated aldehydes were believed to adsorb selectively with the C=O bond at the interface between Au and SiC, thus favoring the reduction of the carbonyl by electron-rich catalytically active sites at the metal junction.

Beyond transfer hydrogenation, the reduction of H₂ has been hindered by the poor performance of Au and Ag towards activating this molecule, because of the high Fermi level in these metals.²⁷⁴ A promising result was disclosed by the Halas group in 2014, when they observed LSPR-induced dissociation of hydrogen gas under ambient conditions at the surface of Au NPs, operating through a hot electron mechanism.^{74, 275} It was later proven that Al₂O₃@Al PNPs could also mediated hydrogen gas dissociation *via* hot electrons transfer.²⁷⁶

Plasmon-mediated photodissociation of H₂ was further exploited in catalysis by Moores and coworkers for hydrogenation of carbonyls under mild conditions using Ag NCs (Scheme 2-2). Reduction of aldehydes and ketones was performed at 1 atm of H₂ and 80 °C and showed excellent selectivity towards C=O over C=C bonds. Ag-based catalysis had been previously reported for reduction of carbonyls but harsh conditions are usually required to induced heterolytic hydrogen gas dissociation²⁷⁴ whereas homoleptic cleavage of H₂ at the surface of Ag NCs was promoted by plasmon-activation at atmospheric pressure. H₂ dissociation *via* hot electron transfer from Ag surface to σ^* orbitals was followed by transfer of thus formed photoactivated hydrogens to the substrates adsorbed at the surface of the PNPs and finally gave the corresponding alcohols with good to excellent yields.(Figure 2-6)



Figure 2-6: Proposed mechanism for the hydrogenation of carbonyl compounds with H_2 catalyzed by Ag NCs. From reference ²⁰⁹. Copyright 2017 American Chemical Society.

2.4.2.3 Reduction of nitro compounds

Since the first report of the Pal group on the catalytic activity of coinage metals for the reduction of nitro aromatics²⁷⁷ to the corresponding amines in 2001, a variety of Aubased²⁷⁸⁻²⁸⁰ and Ag-based²⁸¹⁻²⁸³ nanocatalyst have been extensively reported, using H₂ or sodium borohydride as a reductant (Scheme 2-2). To only mention a few, a variety of

coinage metal PNPS as well as alloy NPs²⁸⁴⁻²⁸⁸ and bimetallic NPs^{289, 290} showed visiblelight-driven photoactivity for the reduction of nitro aromatics as well as magnetically recyclable plasmonic.²⁹¹⁻²⁹³ Studies by Barbosa *et al.* using Au NPs supported on TiO₂ and SiO₂ for reduction of nitro compounds by either H₂ or NaBH₄ revealed that both the nature of the reductant and the support influenced the reaction pathway under light irradiation.²⁹⁴ The reduction of nitro aromatics *via* photogenerated hot electrons can also lead to the formation of azo compounds as reported by Zhu²⁹² and Tada groups²⁹⁵ and others using coinage metals PNPs. Azo compounds were also obtained *via* plasmon-induced coupling of amino moieties.^{296, 297} Using Ag-Cu alloy NPs, Liu *et al.* showed the reduction of nitroaromatics could also lead selectively to azoxy compounds, while in presence of Ag NPs the azo compound was formed.²⁹⁸

Further, Guo and coworkers have demonstrated plasmonic photocatalytic N-N reductive coupling of nitrobenzenes by using Cu₂O nanoparticles supported on graphene sheets.²⁹⁹ There, the graphene sheets helped stabilize the plasmonic Cu₂O nanoparticles, which exhibit a LSPR peak at 560 nm. Interestingly, this nanosystem demonstrates unique selectivity towards the degree of reduction of nitrobenzene, as it is seen that increasing the reaction temperature imparts preferential selectivity from azoxybenzene to azobenzene, and further to aniline. The authors attribute this selectivity to the lower activation barrier that the conversion of nitrobenzene to azobenzene has than to azobenzene. Thus, thermal energy is imparted into the Cu₂O NPs, causing a higher population of hot electrons that can interact with adsorbed reactants and promote the reaction towards further reduction.

Interestingly, a large number of plasmon-induced nitro-compounds transformations have been initially observed *via* SERS measurements in the early 2000s. Huang *et al.* were surely surprised to observe the formation of new bonds, mediated by the measurements they were undertaking, as they were running SERS experiments on para-aminothiophenol immobilized on Ag surface.³⁰⁰ Since then, a variety of SERS-induced reactions, *via* either field enhancement or hot electrons, have been reported as reviewed by Ren *et al.* (Scheme

94

2-2).³⁰¹ Other analytical methods such as tip-enhanced Raman scattering (TERS) have shown to induced organic transformations.^{302, 303} Commonly observed SERS-induced reduction are the transformation of nitro compounds to amino counterparts at Ag^{304} and $Au^{280, 305, 306}$ surfaces or the formation of azobenzene from nitro and amino compounds using $Ag^{307, 308}$ or Au.³⁰⁹



Scheme 2-2: Reduction of organic compounds by PNPs

2.4.3 C-C and C-N Bond-Forming Coupling Reactions

The ability to break and form C-C bonds are crucial tools in a chemist's arsenal for the design and production of molecules. Since the development of nickel-catalyzed C-C coupling between conjugated aryl and alkenyl halides and Grignard reagents by Kumada in 1972,³¹⁰ there has been a cascade of research efforts in developing more efficient and novel techniques inducing C-C coupling. Seminal advancements include the work of Akira Suzuki, Ei-Ichi Negishi, and Richard Heck, who were awarded the 2010 Nobel Prize in Chemistry through their discovery of the use of Pd catalysts for cross-couplings, reactions now routinely used in both industry and academia settings. Many catalytic systems of homogeneous metal complexes have been rigorously studied by tuning the parameters of both the metal and ligand, leading to optimized catalytic ability.³¹¹Conversely, efforts have been devoted to developing this reaction heterogeneously with great success.^{312, 313} However, with using heterogeneous catalyst systems for cross-coupling reactions, there comes a cost of increased reaction temperature needed to drive the reaction forward.³¹² For example, a heterogeneous PdO system supported on various types of carbon materials such as graphene oxide and single-walled carbon nanotubes have been used to catalyze Heck-coupling at 150 °C.³¹⁴ In order to mitigate this extra energy cost in heat, plasmonic photocatalysis is seen to be a strong alternative to traditional heterogeneous catalyst systems, as will be discussed in the following section.³¹⁵ Specifically, cross-coupling reactions to form C-C bonds will first be discussed, with focus on the Suzuki-Miyaura reaction along with other reactions such as Sonogashira, Heck, and Ullmann reactions. Further, C-N and N-N coupling reactions will be covered, along with tandem reactions such as A³ coupling. A recent review by Gu and coworkers covers the plasmonic C-C coupling photocatalysis with Pd.³¹⁵ While many of these nanosystems include the use of Pd, we will also cover a wider variety of coupling reactions not limited to traditional Pd-catalyzed C-C coupling reactions, such A³ coupling,³¹⁶ N-N coupling,²⁹⁹ Friedel-crafts alkylation,³¹⁷ and gas-phase C₂ hydrocarbon generation.³¹⁸



Scheme 2-3 - Coupling reactions catalyzed by PNPs

2.4.3.1 Suzuki-Miyaura coupling reactions

Much of the initial work done in the field of applying plasmonic to C-C couplings involve implementing the Suzuki-Miyaura reaction as the model coupling reaction, based on the stability of the reagents, the functional group compatibility, and the simplicity of the reaction implementation.

A number of systems have been developed based around enhancing Pd through light activation and charge transfer, such as photosensitizer complexes³¹⁹ and semiconductors.³¹⁵ This area has already seen an extensive array of research by using cocatalysts with Pd, while Pd itself is known to initiate cascade radical reactions involving photoinitiated single electron transfer.³²⁰ However, many of these systems have key flaws such as poor absorption in the visible region by semiconductors, and also being homogeneous catalysts in the case of photosensitizer systems.³²¹ Due to this, much work has shifted towards Pd catalysts that are coupled with plasmonic metals that allow for both heterogeneity of the catalyst and visible-light photocatalytic activity towards cross-coupling reactions in particular.

Zhu and coworkers first demonstrated the plasmonic-catalyzed Suzuki-Miyaura coupling reaction.²¹² Using a PdAu bimetallic alloy nanoparticle system as catalysts, they showed that light activation was crucial for the system to catalyze the coupling reaction, since an enhancement from 37% to 97% yield was upon irradiation of the reaction mixture with broadband spectrum of light. Alloying was crucial too, as the physical mixture of individual Pd and Au nanoparticles failed to afford the same enhancement. They later proved the synergistic effects of using Pd as the active site for catalysis and Au to enhance the nanomaterial ability to generate hot electrons.³²² It is known that oxidative addition is the rate-determining step in heterocatalytic Suzuki coupling reactions.³²³ Thus, it was proposed that the generation of hot electrons help in cleaving the carbon-halogen bond in order to induce either the formation of a phenyl radical, or the ability to form a pseudo aryl-Pd iodide intermediate complex, which can proceed through the rest of the coupling

reaction through a well-documented process.^{324, 325} Recent work done by Buskens and coworkers have demonstrated that a thermal mechanism is also possible.³²⁶ By using Pd NP-decorated Au NRs, the authors compared the conversion over time plots of heating the reaction mixture with illuminating the reaction mixture, with both reaching a plateau of the same temperature. Through the plotting of Arrhenius plots, they arrived at a similar activation energy for both experiments, detailing the correlation between normal heating and photothermal heating of the Au NRs.

At nearly the same time as the Zhu group, two other groups developed similar AuPd bimetallic systems as plasmonic photocatalysts for Suzuki-Miyaura coupling. Yan and coworkers fabricated a core-shell type nanomaterial with Au nanorods decorated with Pd NPs preferentially along the longitudinal axes of the rod, while the ends remained naked.³²⁷ They used Au nanorods for the tunability of the LSPR peak wavelength and strong absorption across the solar spectrum. Contrary to Zhu's alloyed system, who witnessed a damping of the overall LSPR upon an increased in Pd incorporation, the Au nanorods retained a strong absorption upon decoration with Pd NPs, along with a red-shift in their plasmon band. This may be due to the different nanostructure architectures associated with these systems. From this, it seems that the composition and overall architecture of the nanosystem both affect the overall LSPR properties. From their study, Yan proposed a mechanism where both hot electron injection as well as photothermal heating contributed to the photocatalytic system. Huang and coworkers also developed a similar bimetallic system of AuPd "nanowheels" analogues to the system of Yan, in which a unique aspect of their work involves their one-pot synthetic strategy in preparing these nanostructures.²¹³

From these three pioneering studies, many efforts in tuning this Au-Pd system were made by way of size, shape, nanostructure, and composition. Qu and coworkers implement a CeO₂ nanorod semiconductor as a support for Pd-Au core-shells, in which they propose that CeO₂ can generate charge carriers that can also transfer into the Au-Pd system, along with hot electron generation from Au.³²⁸ Further, a system designed by the group of Yamashita demonstrate the effectiveness of using SiO₂ as a support for Au nanorods

99

decorated with Pd NPs.³²⁹ Zhang and coworkers corroborated the effects of using TiO₂ as a support for AuPd alloy nanoparticles, in which they theorize that the photogenerated electrons migrate toward electropositive Au in order to stabilize the Au after it participates in hot electron injection into Pd.³³⁰ In all of these cases with a metal oxide support, it is seen that the photogenerated electron transfer towards the Au-Pd nanosystems, while the hole can activate the borane substrate as part of the catalytic cycle. However, it is to be noted that there is no concrete evidence currently that can describe the proposed mechanism of photogenerated charge carriers from TiO₂ by visible light. With this said, more research must be done in elucidating these hypotheses.

Along with tuning the support of the AuPd system, Scott and co-workers looked at modifying the shape of the PNPs. They fabricated Au nanotriangles in order to improve the plasmonic effects through the presence of hot spots at the NP tips.²⁷² They reported enhanced reaction yield under light irradiation for the Suzuki coupling reaction, associating it mainly with photothermal heating of the catalyst. While, Wang and coworkers discovered a way to selectively place Pd nanoparticles at the tips of Au nanobipyramids, which increased photocatalytic activity was attributed, again, to the enhancement of the local field at the tips of the Au nanobipyramids.³³¹ Su *et al.* fabricated Pd nanodendrites that preferentially adsorbed onto the longitudinal modes of Au nanorods.³³² The authors proposed that this method can create more catalytically active sites due to the larger surface area of the nanodendrites structure. With this, it is seen their nanomaterial exhibited remarkable reactivity under laser light irradiation at the specific LSPR band, which proved that the LSPR of the nanostructure directly involved in the photocatalytic ability.

Recently, an in-depth study by Kiwi-Minsker and coworkers on an Au-Pd core-shell nanosystem stabilized with hyper-cross-linked polystyrene (HPS) discussed some possible mechanisms for the cross-coupling process.³³³ ²⁴⁹ They observed the presence of both Pd^{II} and Pd⁰ species, which is consistent with the traditional Pd catalyzed thermal cross coupling cycle,³³⁴ which starts with the oxidative addition of the aryl halide substrates.^{323, 249}

³³⁴ ^{239, 250} The authors hypothesize that electron donation from Au to Pd under light irradiation facilitates the oxidative addition step, to which they see a photocatalytic enhancement as opposed to under dark conditions.

Tang and coworkers developed a unique system involving a Pd nanoarray on top of Au nanorods, referred to as PdAu superstructure (SS).³³⁵ This SS was analyzed by the finite difference time domain (FDTD) method and shown to possess a more concentrated enhancement of the electric field at the boundaries of the individual Pd nanoparticles, as compared to the other Pd@Au nanosystems. Transient absorption spectroscopic measurements also indicated that the decay time of hot electrons on the PdAu SS are longer with respect to other systems such as Au nanorods surrounded by a film of Pd, or Pd nanodendrites. From this, it is seen this PdAu SS complex possesses intrinsically higher catalytic activity than the other types of Pd-Au structures, due to the intrinsically higher enhanced electric field as well as enhanced lifetime of the hot-electrons.

Verma *et al.* have also reported the use of Ag as the plasmonic component for heterogeneous photocatalysis with Pd.³³⁶ The bimetallic nanoparticles were supported by mesoporous silica, and the bimetallic PNPs exhibited an LSPR band even with the incorporation of the support. From this, it is seen through the catalytic testing that the PdAg system exhibited better reactivity than Ag alone for the Suzuki-Miyaura coupling reaction. Interestingly, work was also done on how the PdAg and PdAu systems catalyzed the decomposition of ammonium borane, and it was found that the PdAg nanostructure displayed increased catalytic reactivity with regard to the PdAu nanostructure. Thus, it is seen that catalytic activity of plasmonic nanomaterial systems is reaction specific.

Another study showed how Pd itself can have the ability to conduct plasmonic photocatalysis on Suzuki-coupling reactions. Teranishi and coworkers developed a facile and efficient method in making hexagonal nanoplates of Pd, which showed exquisite tunability in the longitudinal LSPR mode by varying the edge length of the hexagonal plates.³³⁷ They further proposed a mechanism in which hot electrons generated by the

LSPR can promote the dissociation of the aryl halide substrate, while the photogenerated hole activate the phenylboronic substrate.

Recently, it was also shown that the Suzuki coupling reaction can be catalyzed by non-Pd systems, as demonstrated by Bhalla and coworkers with their Ag-Cu₂O core-shell nanostructure.³³⁸ It is demonstrated that the plasmonic Ag component enhances the reactivity of this system as compared with bare Cu₂O nanoparticles, although no detailed studies are done in addressing the mechanism of how the plasmonic Ag is contributing to the enhancement.

2.4.3.2 Other C-C coupling reactions

While the bulk of catalytic coupling reactions by plasmonics have been done using the Suzuki-Miyaura reaction as the model reaction, other studies have focused on using plasmonic enhancement to drive other C-C couplings.

Zhu and coworkers expanded on their work with AuPd bimetallic alloy nanoparticles on reactions such as Sonogashira, Stille, Hiyama, Ullmann, and Buchwald-Hartwig cross-couplings. It is seen that light activation enhances all of the coupling reactions.³³⁹ A proposed mechanism suggests that since the splitting of the aryl halide C-X bond is the rate determining step of the reactions, plasmonic enhancement via hot electron injection can induce electron density into the LUMO of the C-X aryl halide bond, thus increasing reaction rate, which is similar to the proposal by Kiwi-Minsker as stated above.³³³

The work of Guo and coworkers explored how their Pd NPs supported on carbon nanocoils can photocatalyze Heck cross-coupling reactions.³⁴⁰ At 40 °C, enhanced reaction yield is seen while the reaction mixture is irradiated with broadband visible light. The authors attribute this to an enhanced electron-rich Pd surface site due to hot electron generation, which is beneficial for the oxidation step. Since the LSPR of Pd small NPs is deep within the UV region, the hot electron generation is attributed to interband transitions.

The Scaiano group studied plasmonic photocatalysis of the Friedel-Crafts alkylation of anisole with benzyl chloride with a niobium oxide shell encapsulating a plasmonic Au core.³¹⁷ In this scheme, the plasmonic properties of Au under light irradiation are used to create local heating and improve the catalytic activity of Nb₂O₅, even though the overall temperature of the reaction mixture only reached 80°C. The same group explored the reductive C-C dimerization of bromobenzene by supported Au NPs on TiO₂ *via* a free-radical mechanism that is enhanced through LSPR.³⁴¹ Radical trapping experiments proved that the mechanism occurs through radical coupling rather than nucleophilic substitution, while control experiments demonstrate the importance of the plasmonic Au and light irradiation. A proposed mechanism involves hot electron injection from Au to the TiO₂ support, which can be transferred to the alkyl halide, creating a carbon-centered free radical and halide anion.

Recent work by Jain and coworkers have demonstrated gas-phase reduction of CO_2 into methane and further C-C coupling to form ethane via plasmonic photocatalysis.³¹⁸ They correlated the increased production of hydrocarbons with the generation of hot electrons at the surface of Au NPs. Further, they used a Poisson statistical method in order to analyze the probability of two radicalized CO_2 .⁻ being adsorbed on the same Au NP, thus coupling to form the C₂H₆ intermediate.

2.4.3.3 C-N Coupling reactions

In 2013, Luque and coworkers have released pioneering work for demonstrating the amidation of benzaldehyde and morpholine at room temperature *via* plasmonic photocatalysis.³⁴² Through plasmonic heating, it is seen that their SiO₂-supported Au NPs could catalyze the amidation process by providing internal heating to the reaction system. They proposed a mechanism in which plasmonic heating upon irradiation at the plasmonic wavelength of Au NPs (532 nm) caused adsorbed morpholine entities at the surface of Au NPs to desorb faster, thus increasing the reaction rate.

2.4.3.4 A³ Coupling reactions

The aldehyde, amine and alkyne coupling, so called A³ coupling, was first discovered by C.J. Li and coworkers and is a very atom-economical way to access propargylamines.³⁴³ The only reported case of plasmonic A³ coupling was done by the Scaiano group with Au NPs supported on ZnO.³¹⁶ They showed that the synergistic effects between the Au NPs and ZnO metal oxide semiconductor were crucial in the formation of alkynyl-metal and hydride-metal complexes, due to ZnO relatively high basicity compared with other metal oxides such as Al₂O₃ and TiO₂. High yields of the proparglymine product could be obtained in 2 hours at room temperature under green LED light irradiation, which are the mildest conditions for A³ coupling to our knowledge. Photothermal effects as well as hot electron injection were both speculated to be the origin of such catalytic ability.

In short, while plasmonically enhanced coupling reactions have not been researched as extensively as other organic transformations, important studies have demonstrated their viability in competing with other energy-intensive C-C coupling processes. Importantly most works in this area rely on the use of alloy systems based on Au and Pd. Much work can be done in further detailing the possible mechanisms of enhancement that LSPR allows, as well as demonstrating how certain nanoscale parameters favor such enhancements. In particular, it will be important to better detail the interplay between the catalysts surface and possible soluble homogeneous catalytic species, which are known to play a role in C-C couplings. Such efforts will allow for a greener approach in syntheses that requires extensive coupling steps in product formation such as the pharmaceutical industry, while also imploring more economic advantages in atom-efficiency and energy demand.

2.5 Conclusion

Plasmonic properties of coinage metals have been exploited for centuries, and the underlying physics phenomenon leading to the vivid and intriguing colors of solution of colloids nanoparticles have been identified and modeled in the early 20th century. The nature and morphology of PNPs synthesized have been steadily expanding, and lead to nanocrystals exhibiting various properties which have been extensively exploited in the field of SERS, photothermal therapy, and few inorganic catalysis applications such as water splitting and CO₂ reduction. Due to their strong interaction with light, application of PNPs in visible-light-driven organic catalysis has been the focus of intense studies over the last decade.

In this chapter, we briefly explained the LSPR phenomenon and its appealing characteristics for catalysis. Upon light excitation, PNPs feature unique behavior arising from the collective oscillation of their electrons, leading to three main properties: local heat generation, enhancement of the local field and formation of highly energetic charge carriers at the surface.

Careful engineering of the features of nanocatalysts is expected to maximize their efficiency for plasmon-mediated transformations. Section 3 describes the multiple synthetic pathways reported to access various plasmonic nanostructures with or without support, and also coupled with transition metals in bimetallic nanostructures or alloys. We then suggested how to tailor the nature and morphology of PNPs in order to achieve desired reactivity and maximize their efficiency for a given LSPR-mediated mechanism. These works demonstrate that careful engineering of PNPs in regard to the substrate of interest will further extend the range of plasmon-catalyzed organic transformations.

So far, PNPs have proven to be efficient catalysts for oxidation, reduction, coupling and polymerization reactions, while often requiring milder conditions than previously reported

nanomaterials. LSPR-excitation can achieve activation of O₂ and H₂ at atmospheric pressure, hence offering sustainable alternatives to commonly employed oxidants and reducing agents such as NaBH₄, while avoiding the use of homogeneous transition metal complexes which are challenging to recycle. Coupling of plasmonic materials with transition metals, in bimetallic structures or alloys, showed increased efficiency upon visible-light irradiation for couplings reactions. Also, the use of PNPs as catalysts in polymerization reactions has been shown to be useful in a vast array of applications. The potential for the development of novel polymer-metal systems, molecular probing, and numerous other applications reported here demonstrate the versatility of catalytic LSPR.

2.6 References

13. Romero, N. A.; Nicewicz, D. A., Organic Photoredox Catalysis. *Chemical reviews* **2016**, *116*(17), 10075-10166.

19. Schultz, D. M.; Yoon, T. P., Solar Synthesis: Prospects in Visible Light Photocatalysis. *Science* **2014**, *343*(6174).

25. Fox, M. A.; Dulay, M. T., Heterogeneous Photocatalysis. *Chemical reviews* **1993**, *93* (1), 341-357.

47. Amara, Z.; Bellamy, J. F.; Horvath, R.; Miller, S. J.; Beeby, A.; Burgard, A.; Rossen, K.; Poliakoff, M.; George, M. W., Applying Green Chemistry to the Photochemical Route to Artemisinin. *Nat. Chem.* **2015**, *7*(6), 489-495.

49. Fujishima, A.; Honda, K., Electrochemical Photolysis of Water at a Semiconductor Electrode. *nature* **1972**, *238*(5358), 37-38.

64. Cheng, L.; Wang, C.; Feng, L.; Yang, K.; Liu, Z., Functional Nanomaterials for Phototherapies of Cancer. *Chemical reviews* **2014**, *114*(21), 10869-10939.

68. Cardinal, M. F.; Vander Ende, E.; Hackler, R. A.; McAnally, M. O.; Stair, P. C.; Schatz, G. C.; Van Duyne, R. P., Expanding Applications of Sers through Versatile Nanomaterials Engineering. *Chemical Society Reviews* **2017**, *46* (13), 3886-3903.

69. Gellé, A.; Jin, T.; de la Garza, L.; Price, G. D.; Besteiro, L. V.; Moores, A., Applications of Plasmon-Enhanced Nanocatalysis to Organic Transformations. *Chemical Reviews* **2019**, *120*(2), 986-1041.

70. Moores, A.; Goettmann, F., The Plasmon Band in Noble Metal Nanoparticles: An Introduction to Theory and Applications. *New J. Chem.* **2006**, *30*(8), 1121-1132.

71. Brongersma, M. L.; Halas, N. J.; Nordlander, P., Plasmon-Induced Hot Carrier Science and Technology. *Nature nanotechnology* **2015**, *10*(1), 25-34.

74. Mukherjee, S.; Libisch, F.; Large, N.; Neumann, O.; Brown, L. V.; Cheng, J.; Lassiter, J. B.; Carter, E. A.; Nordlander, P.; Halas, N. J., Hot Electrons Do the Impossible: Plasmon-Induced Dissociation of H2 on Au. *Nano letters* **2013**, *13*(1), 240-247.

93. Chavez, S.; Aslam, U.; Linic, S., Design Principles for Directing Energy and Energetic Charge Flow in Multicomponent Plasmonic Nanostructures. *ACS Energy Lett.* **2018**, *3*(7), 1590-1596.

94. Burnham, A.; Han, J.; Clark, C. E.; Wang, M.; Dunn, J. B.; Palou-Rivera, I., Life-Cycle Greenhouse Gas Emissions of Shale Gas, Natural Gas, Coal, and Petroleum. *Environmental Science & Technology* **2012**, *46*(2), 619-627.

95. Armaroli, N.; Balzani, V., The Future of Energy Supply: Challenges and Opportunities. *Angewandte Chemie-International Edition* **2007**, *46* (1-2), 52-66.

96. Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C., Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chemical Reviews* **2013**, *113*(7), 5322-5363.

97. Ni, M.; Leung, M. K. H.; Leung, D. Y. C.; Sumathy, K., A Review and Recent Developments in Photocatalytic Water-Splitting Using Tio2 for Hydrogen Production. *Renewable & Sustainable Energy Reviews* **2007**, *11*(3), 401-425.

98. Hisatomi, T.; Kubota, J.; Domen, K., Recent Advances in Semiconductors for Photocatalytic and Photoelectrochemical Water Splitting. *Chemical Society Reviews* **2014**, *43*(22), 7520-7535.

99. Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W., Environmental Applications of Semiconductor Photocatalysis. *Chemical Reviews* **1995**, *95*(1), 69-96.

100. Han, F.; Kambala, V. S. R.; Srinivasan, M.; Rajarathnam, D.; Naidu, R., Tailored Titanium Dioxide Photocatalysts for the Degradation of Organic Dyes in Wastewater Treatment: A Review. *Applied Catalysis a-General* **2009**, *359*(1-2), 25-40.

101. Smith, J. G.; Faucheaux, J. A.; Jain, P. K., Plasmon Resonances for Solar Energy Harvesting: A Mechanistic Outlook. *Nano Today* **2015**, *10*(1), 67-80.

102. Papaioannou, S.; Kalavrouziotis, D.; Vyrsokinos, K.; Weeber, J. C.; Hassan, K.; Markey, L.; Dereux, A.; Kumar, A.; Bozhevolnyi, S. I.; Baus, M.; Tekin, T.; Apostolopoulos, D.; Avramopoulos, H.; Pleros, N., Active Plasmonics in Wdm Traffic Switching Applications. *Scientific Reports* **2012**, *2*.

103. Tian, Y.; Tatsuma, T., Mechanisms and Applications of Plasmon-Induced Charge Separation at Tio2 Films Loaded with Gold Nanoparticles. *Journal of the American Chemical Society* **2005**, *127*(20), 7632-7637.

104. Awazu, K.; Fujimaki, M.; Rockstuhl, C.; Tominaga, J.; Murakami, H.; Ohki, Y.; Yoshida, N.; Watanabe, T., A Plasmonic Photocatalyst Consisting of Silver Nanoparticles Embedded in Titanium Dioxide. *J. Am. Chem. Soc.* **2008**, *130*(5), 1676-1680.

105. Astruc, D.; Lu, F.; Aranzaes, J. R., Nanoparticles as Recyclable Catalysts: The Frontier between Homogeneous and Heterogeneous Catalysis. *Angewandte Chemie-International Edition* **2005**, *44*(48), 7852-7872.

106. Fihri, A.; Bouhrara, M.; Nekoueishahraki, B.; Basset, J. M.; Polshettiwar, V., Nanocatalysts for Suzuki Cross-Coupling Reactions. *Chemical Society Reviews* **2011**, *40* (10), 5181-5203.

107. Polshettiwar, V.; Varma, R. S., Green Chemistry by Nano-Catalysis. *Green Chem.* **2010**, *12*(5), 743-754.

108. Roldan Cuenya, B., Synthesis and Catalytic Properties of Metal Nanoparticles: Size, Shape, Support, Composition, and Oxidation State Effects. *Thin Solid Films* **2010**, *518*(12), 3127-3150.

109. Ricciardi, R.; Huskens, J.; Verboom, W., Nanocatalysis in Flow. *Chemsuschem* **2015**, *8*(16), 2586-2605.

110. Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H. B.; Bouhrara, M.; Bassett, J. M., Magnetically Recoverable Nanocatalysts. *Chemical Reviews* **2011**, *111*(5), 3036-3075.

111. Hudson, R.; Feng, Y. T.; Varma, R. S.; Moores, A., Bare Magnetic Nanoparticles: Sustainable Synthesis and Applications in Catalytic Organic Transformations. *Green Chemistry* **2014**, *16*(10), 4493-4505.

112. Gonella, F.; Mazzoldi, P., *Handbook of Nanostructured Materials and Nanotechnology*. Elsevier: 2000.

113. Louis, C., Gold Nanoparticles in the Past: Before the Nanotechnology Era. In *Gold Nanoparticles for Physics, Chemistry and Biology*, 2012.
114. Garnett, J. M., Colours in Metal Glasses and in Metallic Films. *Philos. Trans. R. Soc. London* **1904**, *203*, 359-371.

115. Garnett, J. M., Colours in Metal Glasses, in Metallic Films, and in Metallic Solutions. *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character* **1906**, *205*, 387-401.

116. Mie, G., Beiträge Zur Optik Trüber Medien, Speziell Kolloidaler Metallösungen. *Annalen der Physik* **1908**, *330*(3), 377-445.

117. Kreibig, U.; Vollmer, M., *Optical Properties of Metal Clusters*. Springer: Berlin, 1995.
118. Drude, P., Zur Elektronentheorie Der Metalle. *Annalen der Physik* **1900**, *306* (3),

566-613.

119. Solis, D. M.; Taboada, J. M.; Obelleiro, F.; Liz-Marzan, L. M.; García de Abajo, F. J., Toward Ultimate Nanoplasmonics Modeling. *Acs Nano* **2014**, *8*(8), 7559-7570.

120. Maier, S. A., *Plasmonics: Fundamentals and Applications*. Springer Science & Business Media: 2007.

121. Pelton, M.; Bryant, G. W., *Introduction to Metal-Nanoparticle Plasmonics*. Wiley: 2013.

122. van de Hulst, H. C., *Light Scattering by Small Particles*. Dover Publications: 1981.

123. Yu, R.; Liz-Marzán, L. M.; García de Abajo, F. J., Universal Analytical Modeling of Plasmonic Nanoparticles. *Chemical Society Reviews* **2017**, *46* (22), 6710-6724.

124. Merlen, A.; Lagugné-Labarthet, F., Imaging the Optical near Field in Plasmonic Nanostructures. *Applied spectroscopy* **2014**, *68*(12), 1307-1326.

125. Moores, A.; Le Floch, P., Metal Nanoparticle Plasmon Band as a Powerful Tool for Chemo and Biosensing. In *Biosensing Using Nanomaterials*, Merkoçi, A., Ed. Wiley & Sons: 2009; pp 137-170.

126. Anker, J. N.; Hall, P.; Lyandres, O.; Shah, N. C.; Zhao, J.; Van Duyne, R. P., Biosensing with Plasmonic Nanosensors. In *Nanoscience and Technology*, Nature, Ed. 2010; pp 308-319.

127. Moskovits, M., Surface-Enhanced Raman Spectroscopy: A Brief Retrospective. *Journal of Raman Spectroscopy* **2005**, *36* (6-7), 485-496.

128. Tam, F.; Goodrich, G. P.; Johnson, B. R.; Halas, N. J., Plasmonic Enhancement of Molecular Fluorescence. *Nano Letters* **2007**, *7*(2), 496-501.

129. Bauch, M.; Toma, K.; Toma, M.; Zhang, Q.; Dostalek, J., Plasmon-Enhanced Fluorescence Biosensors: A Review. *Plasmonics* **2014**, *9*(4), 781-799.

130. Willets, K. A.; Duyne, R. P. V., Localized Surface Plasmon Resonance Spectroscopy and Sensing. *Annual Review of Physical Chemistry* **2007**, *58*(1), 267-297.

131. Sonnefraud, Y.; Verellen, N.; Sobhani, H.; Vandenbosch, G. A. E.; Moshchalkov, V. V.; Van Dorpe, P.; Nordlander, P.; Maier, S. A., Experimental Realization of Subradiant, Superradiant, and Fano Resonances in Ring/Disk Plasmonic Nanocavities. *ACS Nano* **2010**, *4*(3), 1664-1670.

132. Zorić, I.; Zäch, M.; Kasemo, B.; Langhammer, C., Gold, Platinum, and Aluminum Nanodisk Plasmons: Material Independence, Subradiance, and Damping Mechanisms. *ACS Nano* **2011**, *5*(4), 2535-2546.

133. Govorov, A. O.; Richardson, H. H., Generating Heat with Metal Nanoparticles. *Nano today* **2007**, *2*(1), 30-38.

134. Lal, S.; Clare, S. E.; Halas, N. J., Nanoshell-Enabled Photothermal Cancer Therapy: Impending Clinical Impact. *Accounts of Chemical Research* **2008**, *41*(12), 1842-1851.

135. Huang, X.; Jain, P. K.; El-Sayed, I. H.; El-Sayed, M. A., Plasmonic Photothermal Therapy (Pptt) Using Gold Nanoparticles. *Lasers in medical science* **2008**, *23*(3), 217-218.

136. Xiao, M.; Jiang, R.; Wang, F.; Fang, C.; Wang, J.; Jimmy, C. Y., Plasmon-Enhanced Chemical Reactions. *J. Mater. Chem. A* **2013**, *1*(19), 5790-5805.

137. Qiu, J. J.; Wei, W. D., Surface Plasmon-Mediated Photothermal Chemistry. *Journal of Physical Chemistry C***2014**, *118*(36), 20735-20749.

138. Hartland, G. V.; Besteiro, L. V.; Johns, P.; Govorov, A. O., What's So Hot About Electrons in Metal Nanoparticles? *ACS Energy Letters* **2017**, *2*(7), 1641-1653.

139. Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C., The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *The Journal of Physical Chemistry B* **2003**, *107*(3), 668-677.

140. Chikkaraddy, R.; de Nijs, B.; Benz, F.; Barrow, S. J.; Scherman, O. A.; Rosta, E.; Demetriadou, A.; Fox, P.; Hess, O.; Baumberg, J. J., Single-Molecule Strong Coupling at Room Temperature in Plasmonic Nanocavities. *Nature* **2016**, *535*, 127-130.

141. Prodan, E.; Radloff, C.; Halas, N. J.; Nordlander, P., A Hybridization Model for the Plasmon Response of Complex Nanostructures. *Science* **2003**, *302*(5644), 419-422.

142. Wang, H.; Brandl, D. W.; Nordlander, P.; Halas, N. J., Plasmonic Nanostructures: Artificial Molecules. *Accounts of Chemical Research* **2007**, *40*(1), 53-62.

143. Enoch, S.; Bonod, N., *Plasmonics: From Basics to Advanced Topics*. Springer: 2012.

144. Liz-Marzan, L. M., Tailoring Surface Plasmons through the Morphology and Assembly of Metal Nanoparticles. *Langmuir* **2006**, *22*(1), 32-41.

145. Wu, Y. Y.; Li, G. L.; Camden, J. P., Probing Nanoparticle Plasmons with Electron Energy Loss Spectroscopy. *Chemical Reviews* **2018**, *118*(6), 2994-3031.

146. Brodusch, N.; Demers, H.; Gellé, A.; Moores, A.; Gauvin, R., Electron Energy-Loss Spectroscopy (Eels) with a Cold-Field Emission Scanning Electron Microscope at Low Accelerating Voltage in Transmission Mode. *Ultramicroscopy* **2018**, *203*, 21-36.

147. Nelayah, J.; Kociak, M.; Stéphan, O.; de Abajo, F. J. G.; Tencé, M.; Henrard, L.; Taverna, D.; Pastoriza-Santos, I.; Liz-Marzán, L. M.; Colliex, C., Mapping Surface Plasmons on a Single Metallic Nanoparticle. *Nature Physics* **2007**, *3*(5), 348-353.

148. Faraday, M., On the Color of Colloidal Gold. *Phil. Trans. R. Soc. London* **1857**, *147*, 145-181.

149. Daniel, M.-C.; Astruc, D., Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology. *Chemical reviews* **2004**, *104*(1), 293-346.

150. Rycenga, M.; Cobley, C. M.; Zeng, J.; Li, W.; Moran, C. H.; Zhang, Q.; Qin, D.; Xia, Y., Controlling the Synthesis and Assembly of Silver Nanostructures for Plasmonic Applications. *Chemical reviews* **2011**, *111*(6), 3669-3712.

151. Thanh, N. T. K.; Maclean, N.; Mahiddine, S., Mechanisms of Nucleation and Growth of Nanoparticles in Solution. *Chemical Reviews* **2014**, *114*(15), 7610-7630.

152. Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E., Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angewandte Chemie International Edition* **2009**, *48*(1), 60-103.

153. LaMer, V. K.; Dinegar, R. H., Theory, Production and Mechanism of Formation of Monodispersed Hydrosols. *Journal of the American Chemical Society* **1950**, *72*(11), 4847-4854.

154. Kang, H.; Buchman, J. T.; Rodriguez, R. S.; Ring, H. L.; He, J.; Bantz, K. C.; Haynes, C. L., Stabilization of Silver and Gold Nanoparticles: Preservation and Improvement of Plasmonic Functionalities. *Chemical Reviews* **2019**, *119*(1), 664-699.

155. Lee, P.; Meisel, D., Adsorption and Surface-Enhanced Raman of Dyes on Silver and Gold Sols. *The Journal of Physical Chemistry* **1982**, *86*(17), 3391-3395.

156. Henglein, A.; Giersig, M., Formation of Colloidal Silver Nanoparticles: Capping Action of Citrate. *The Journal of Physical Chemistry B***1999**, *103*(44), 9533-9539.

157. Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A., Chemistry and Properties of Nanocrystals of Different Shapes. *Chemical Reviews* **2005**, *105*(4), 1025-1102.

158. Turkevich, J.; Stevenson, P. C.; Hillier, J., A Study of the Nucleation and Growth Processes in the Synthesis of Colloidal Gold. *Discussions of the Faraday Society* **1951**, *11* (0), 55-75.

159. Frens, G., Controlled Nucleation for the Regulation of the Particle Size in Monodisperse Gold Suspensions. *Nature physical science* **1973**, *241* (105), 20-22.

160. Mayer, K. M.; Hafner, J. H., Localized Surface Plasmon Resonance Sensors. *Chemical Reviews* **2011**, *111*(6), 3828-3857.

161. Turner, A. P. F., Biosensors: Sense and Sensibility. *Chemical Society Reviews* **2013**, *42* (8), 3184-3196.

162. Gellé, A.; Moores, A., Plasmonic Nanoparticles: Photocatalysts with a Bright Future. *Current Opinion in Green and Sustainable Chemistry* **2019**, *15*, 60-66.

163. Sun, Y.; Xia, Y., Shape-Controlled Synthesis of Gold and Silver Nanoparticles. *Science* **2002**, *298* (5601), 2176-2179.

164. Zhou, J.; An, J.; Tang, B.; Xu, S.; Cao, Y.; Zhao, B.; Xu, W.; Chang, J.; Lombardi, J. R., Growth of Tetrahedral Silver Nanocrystals in Aqueous Solution and Their Sers Enhancement. *Langmuir* **2008**, *24*(18), 10407-10413.

165. Ditlbacher, H.; Hohenau, A.; Wagner, D.; Kreibig, U.; Rogers, M.; Hofer, F.; Aussenegg, F. R.; Krenn, J. R., Silver Nanowires as Surface Plasmon Resonators. *Physical review letters* **2005**, *95*(25), 257403.

166. Chen, S.; Carroll, D. L., Synthesis and Characterization of Truncated Triangular Silver Nanoplates. *Nano Letters* **2002**, *2*(9), 1003-1007.

167. Pietrobon, B.; Kitaev, V., Photochemical Synthesis of Monodisperse Size-Controlled Silver Decahedral Nanoparticles and Their Remarkable Optical Properties. *Chemistry of Materials* **2008**, *20*(16), 5186-5190.

168. Liu, X.; Huang, R.; Zhu, J., Functional Faceted Silver Nano-Hexapods: Synthesis, Structure Characterizations, and Optical Properties. *Chemistry of Materials* **2008**, *20*(1), 192-197.

169. Wiley, B.; Herricks, T.; Sun, Y.; Xia, Y., Polyol Synthesis of Silver Nanoparticles: Use of Chloride and Oxygen to Promote the Formation of Single-Crystal, Truncated Cubes and Tetrahedrons. *Nano Letters* **2004**, *4*(9), 1733-1739.

170. Wiley, B. J.; Xiong, Y.; Li, Z.-Y.; Yin, Y.; Xia, Y., Right Bipyramids of Silver: A New Shape Derived from Single Twinned Seeds. *Nano letters* **2006**, *6*(4), 765-768.

171. Wiley, B. J.; Chen, Y.; McLellan, J. M.; Xiong, Y.; Li, Z.-Y.; Ginger, D.; Xia, Y., Synthesis and Optical Properties of Silver Nanobars and Nanorice. *Nano letters* **2007**, *7*(4), 1032-1036.

172. Wiley, B.; Sun, Y.; Xia, Y., Synthesis of Silver Nanostructures with Controlled Shapes and Properties. *Accounts of chemical research* **2007**, *40*(10), 1067-1076.

173. Skrabalak, S. E.; Wiley, B. J.; Kim, M.; Formo, E. V.; Xia, Y., On the Polyol Synthesis of Silver Nanostructures: Glycolaldehyde as a Reducing Agent. *Nano letters* **2008**, *8*(7), 2077-2081.

174. Im, S. H.; Lee, Y. T.; Wiley, B.; Xia, Y. N., Large-Scale Synthesis of Silver Nanocubes: The Role of Hcl in Promoting Cube Perfection and Monodispersity. *Angewandte Chemie-International Edition* **2005**, *44*(14), 2154-2157.

175. Al-Saidi, W. A.; Feng, H. J.; Fichthorn, K. A., Adsorption of Polyvinylpyrrolidone on Ag Surfaces: Insight into a Structure-Directing Agent. *Nano Letters* **2012**, *12*(2), 997-1001. 176. Saidi, W. A.; Feng, H. J.; Fichthorn, K. A., Binding of Polyvinylpyrrolidone to Ag Surfaces: Insight into a Structure-Directing Agent from Dispersion-Corrected Density Functional Theory. *Journal of Physical Chemistry C* **2013**, *117*(2), 1163-1171.

177. Sun, Y.; Yin, Y.; Mayers, B. T.; Herricks, T.; Xia, Y., Uniform Silver Nanowires Synthesis by Reducing Agno3 with Ethylene Glycol in the Presence of Seeds and Poly(Vinyl Pyrrolidone). *Chemistry of Materials* **2002**, *14*(11), 4736-4745.

178. Ghosh, S.; Manna, L., The Many "Facets" of Halide Ions in the Chemistry of Colloidal Inorganic Nanocrystals. *Chemical reviews* **2018**, *118*(16), 7804-7864.

179. Chen, Z.; Balankura, T.; Fichthorn, K. A.; Rioux, R. M., Revisiting the Polyol Synthesis of Silver Nanostructures: Role of Chloride in Nanocube Formation. *ACS Nano* **2019**, *13*(2), 1849-1860.

180. Cobley, C. M.; Rycenga, M.; Zhou, F.; Li, Z.-Y.; Xia, Y., Controlled Etching as a Route to High Quality Silver Nanospheres for Optical Studies. *The Journal of Physical Chemistry C***2009**, *113*(39), 16975-16982.

181. Jin, R.; Cao, Y. C.; Hao, E.; Métraux, G. S.; Schatz, G. C.; Mirkin, C. A., Controlling Anisotropic Nanoparticle Growth through Plasmon Excitation. *Nature* **2003**, *425* (6957), 487-490.

182. Haynes, C. L.; Van Duyne, R. P., Nanosphere Lithography: A Versatile Nanofabrication Tool for Studies of Size-Dependent Nanoparticle Optics. *The Journal of Physical Chemistry* B **2001**, *105* (24), 5599-5611.

183. Kim, F.; Connor, S.; Song, H.; Kuykendall, T.; Yang, P., Platonic Gold Nanocrystals. *Angewandte Chemie International Edition* **2004**, *43*(28), 3673-3677.

184. Li, C.; Shuford, K. L.; Park, Q.-H.; Cai, W.; Li, Y.; Lee, E. J.; Cho, S. O., High-Yield Synthesis of Single-Crystalline Gold Nano-Octahedra. *Angewandte Chemie International Edition* **2007**, *46* (18), 3264-3268.

185. Seo, D.; Park, J. C.; Song, H., Polyhedral Gold Nanocrystals with Oh Symmetry: From Octahedra to Cubes. *Journal of the American Chemical Society* **2006**, *128* (46), 14863-14870.

186. Seo, D.; Yoo, C. I.; Park, J. C.; Park, S. M.; Ryu, S.; Song, H., Directed Surface Overgrowth and Morphology Control of Polyhedral Gold Nanocrystals. *Angewandte Chemie* **2008**, *120*(4), 775-779.

187. Magano, J.; Dunetz, J. R., Large-Scale Carbonyl Reductions in the Pharmaceutical Industry. *Organic Process Research & Development* **2012**, *16*(6), 1156-1184.

188. Evans, W. L.; Day, J. E., The Oxidation of Ethyl Alcohol by Means of Potassium Permanganate. *Journal of the American Chemical Society* **1916**, *38*(2), 375-381.

189. Lee, D. G.; Spitzer, U. A., Aqueous Dichromate Oxidation of Primary Alcohols. *The Journal of Organic Chemistry* **1970**, *35*(10), 3589-3590.

190. Travis, B. R.; Sivakumar, M.; Hollist, G. O.; Borhan, B., Facile Oxidation of Aldehydes to Acids and Esters with Oxone. *Organic Letters* **2003**, *5*(7), 1031-1034.

191. Han, L.; Xing, P.; Jiang, B., Selective Aerobic Oxidation of Alcohols to Aldehydes, Carboxylic Acids, and Imines Catalyzed by a Ag-Nhc Complex. *Organic Letters* **2014**, *16* (13), 3428-3431.

192. González-Arellano, C.; Campelo, J. M.; Macquarrie, D. J.; Marinas, J. M.; Romero, A. A.; Luque, R., Efficient Microwave Oxidation of Alcohols Using Low-Loaded Supported Metallic Iron Nanoparticles. *ChemSusChem* **2008**, *1* (8-9), 746-750.

193. Mallat, T.; Baiker, A., Oxidation of Alcohols with Molecular Oxygen on Solid Catalysts. *Chemical Reviews* **2004**, *104*(6), 3037-3058.

194. Roduner, E.; Kaim, W.; Sarkar, B.; Urlacher, V. B.; Pleiss, J.; Gläser, R.; Einicke, W.-D.; Sprenger, G. A.; Beifuß, U.; Klemm, E.; Liebner, C.; Hieronymus, H.; Hsu, S.-F.; Plietker, B.; Laschat, S., Selective Catalytic Oxidation of C H Bonds with Molecular Oxygen. *ChemCatChem* **2013**, *5*(1), 82-112.

195. Huang, Y.-F.; Zhang, M.; Zhao, L.-B.; Feng, J.-M.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q., Activation of Oxygen on Gold and Silver Nanoparticles Assisted by Surface Plasmon Resonances. *Angewandte Chemie International Edition* **2014**, *53*(9), 2353-2357.

196. Rodríguez-González, V.; Zanella, R.; del Angel, G.; Gómez, R., Mtbe Visible-Light Photocatalytic Decomposition over Au/Tio2 and Au/Tio2–Al2o3 Sol–Gel Prepared Catalysts. *Journal of Molecular Catalysis A: Chemical* **2008**, *281*(1), 93-98.

197. Li, H.; Bian, Z.; Zhu, J.; Huo, Y.; Li, H.; Lu, Y., Mesoporous Au/Tio2 Nanocomposites with Enhanced Photocatalytic Activity. *Journal of the American Chemical Society* **2007**, *129*(15), 4538-4539.

198. Kowalska, E.; Abe, R.; Ohtani, B., Visible Light-Induced Photocatalytic Reaction of Gold-Modified Titanium(Iv) Oxide Particles: Action Spectrum Analysis. *Chemical Communications* **2009**, (2), 241-243.

199. Kowalska, E.; Mahaney, O. O. P.; Abe, R.; Ohtani, B., Visible-Light-Induced Photocatalysis through Surface Plasmon Excitation of Gold on Titania Surfaces. *Physical Chemistry Chemical Physics* **2010**, *12*(10), 2344-2355.

200. Naya, S.-i.; Inoue, A.; Tada, H., Self-Assembled Heterosupramolecular Visible Light Photocatalyst Consisting of Gold Nanoparticle-Loaded Titanium(Iv) Dioxide and Surfactant. *Journal of the American Chemical Society* **2010**, *132*(18), 6292-6293.

201. Tsukamoto, D.; Shiraishi, Y.; Sugano, Y.; Ichikawa, S.; Tanaka, S.; Hirai, T., Gold Nanoparticles Located at the Interface of Anatase/Rutile Tio2 Particles as Active Plasmonic Photocatalysts for Aerobic Oxidation. *Journal of the American Chemical Society* **2012**, *134* (14), 6309-6315.

202. Tanaka, A.; Hashimoto, K.; Kominami, H., Selective Photocatalytic Oxidation of Aromatic Alcohols to Aldehydes in an Aqueous Suspension of Gold Nanoparticles

Supported on Cerium(Iv) Oxide under Irradiation of Green Light. *Chemical Communications* **2011**, *47*(37), 10446-10448.

203. Tanaka, A.; Hashimoto, K.; Kominami, H., Preparation of Au/Ceo2 Exhibiting Strong Surface Plasmon Resonance Effective for Selective or Chemoselective Oxidation of Alcohols to Aldehydes or Ketones in Aqueous Suspensions under Irradiation by Green Light. *Journal of the American Chemical Society* **2012**, *134*(35), 14526-14533.

204. Zhai, W.; Xue, S.; Zhu, A.; Luo, Y.; Tian, Y., Plasmon-Driven Selective Oxidation of Aromatic Alcohols to Aldehydes in Water with Recyclable Pt/Tio2 Nanocomposites. *ChemCatChem* **2011**, *3*(1), 127-130.

205. Liu, L.; Ouyang, S.; Ye, J., Gold-Nanorod-Photosensitized Titanium Dioxide with Wide-Range Visible-Light Harvesting Based on Localized Surface Plasmon Resonance. *Angewandte Chemie* **2013**, *125* (26), 6821-6825.

206. Nadeem, M. A.; Idriss, H., Photo-Thermal Reactions of Ethanol over Ag/Tio2 Catalysts. The Role of Silver Plasmon Resonance in the Reaction Kinetics. *Chemical Communications* **2018**, *54*(41), 5197-5200.

207. Hallett-Tapley, G. L.; Silvero, M. J.; González-Béjar, M.; Grenier, M.; Netto-Ferreira, J. C.; Scaiano, J. C., Plasmon-Mediated Catalytic Oxidation of Sec-Phenethyl and Benzyl Alcohols. *The Journal of Physical Chemistry* **C2011**, *115* (21), 10784-10790.

208. Hallett-Tapley, G. L.; Silvero, M. J.; Bueno-Alejo, C. J.; González-Béjar, M.; McTiernan, C. D.; Grenier, M.; Netto-Ferreira, J. C.; Scaiano, J. C., Supported Gold Nanoparticles as Efficient Catalysts in the Solventless Plasmon Mediated Oxidation of Sec-Phenethyl and Benzyl Alcohol. *The Journal of Physical Chemistry* C2013, *117*(23), 12279-12288.

209. Landry, M. J.; Gellé, A.; Meng, B. Y.; Barrett, C. J.; Moores, A., Surface-Plasmon-Mediated Hydrogenation of Carbonyls Catalyzed by Silver Nanocubes under Visible Light. *ACS Catalysis* **2017**, *7*(9), 6128-6133.

210. Sugano, Y.; Shiraishi, Y.; Tsukamoto, D.; Ichikawa, S.; Tanaka, S.; Hirai, T., Supported Au–Cu Bimetallic Alloy Nanoparticles: An Aerobic Oxidation Catalyst with Regenerable Activity by Visible-Light Irradiation. *Angewandte Chemie* **2013**, *125* (20), 5403-5407.

211. Jiang, T.; Jia, C.; Zhang, L.; He, S.; Sang, Y.; Li, H.; Li, Y.; Xu, X.; Liu, H., Gold and Gold– Palladium Alloy Nanoparticles on Heterostructured Tio2 Nanobelts as Plasmonic Photocatalysts for Benzyl Alcohol Oxidation. *Nanoscale* **2015**, *7*(1), 209-217.

212. Sarina, S.; Zhu, H.; Jaatinen, E.; Xiao, Q.; Liu, H.; Jia, J.; Chen, C.; Zhao, J., Enhancing Catalytic Performance of Palladium in Gold and Palladium Alloy Nanoparticles for Organic Synthesis Reactions through Visible Light Irradiation at Ambient Temperatures. *Journal of the American Chemical Society* **2013**, *135*(15), 5793-5801.

213. Huang, X.; Li, Y.; Chen, Y.; Zhou, H.; Duan, X.; Huang, Y., Plasmonic and Catalytic Aupd Nanowheels for the Efficient Conversion of Light into Chemical Energy. *Angewandte Chemie* **2013**, *125* (23), 6179-6183.

214. Colmenares, J. C.; Lisowski, P.; Łomot, D.; Chernyayeva, O.; Lisovytskiy, D., Sonophotodeposition of Bimetallic Photocatalysts Pd-Au/Tio2: Application to Selective Oxidation of Methanol to Methyl Formate. *ChemSusChem* **2015**, *8*(10), 1676-1685.

215. Long, R.; Mao, K.; Gong, M.; Zhou, S.; Hu, J.; Zhi, M.; You, Y.; Bai, S.; Jiang, J.; Zhang, Q.; Wu, X.; Xiong, Y., Tunable Oxygen Activation for Catalytic Organic Oxidation: Schottky

Junction Versus Plasmonic Effects. *Angewandte Chemie International Edition* **2014**, *53* (12), 3205-3209.

216. Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F., Improved Utilisation of Renewable Resources: New Important Derivatives of Glycerol. *Green Chemistry* **2008**, *10* (1), 13-30.

217. Schünemann, S.; Dodekatos, G.; Tüysüz, H., Mesoporous Silica Supported Au and Aucu Nanoparticles for Surface Plasmon Driven Glycerol Oxidation. *Chemistry of Materials* **2015**, *27*(22), 7743-7750.

218. Dodekatos, G.; Tüysüz, H., Plasmonic Au/Tio2 Nanostructures for Glycerol Oxidation. *Catalysis Science & Technology* **2016**, *6*(19), 7307-7315.

219. Guo, L.; Sun, Q.; Marcus, K.; Hao, Y.; Deng, J.; Bi, K.; Yang, Y., Photocatalytic Glycerol Oxidation on Auxcu-Cus@Tio2 Plasmonic Heterostructures. *Journal of Materials Chemistry A* **2018**, *6* (44), 22005-22012.

220. Chehadi, Z.; Girardon, J.-S.; Capron, M.; Dumeignil, F.; Jradi, S., Thermoplasmonic-Induced Energy-Efficient Catalytic Oxidation of Glycerol over Gold Supported Catalysts Using Visible Light at Ambient Temperature. *Applied Catalysis A: General* **2019**, *572*, 9-14. 221. Rasmussen, M.; Serov, A.; Artyushkova, K.; Chen, D.; Rose, T. C.; Atanassov, P.; Harris, J. M.; Minteer, S. D., Enhancement of Electrocatalytic Oxidation of Glycerol by Plasmonics. *ChemElectroChem* **2019**, *6*(1), 241-245.

222. Peng, T.; Miao, J.; Gao, Z.; Zhang, L.; Gao, Y.; Fan, C.; Li, D., Reactivating Catalytic Surface: Insights into the Role of Hot Holes in Plasmonic Catalysis. *Small* **2018**, *14* (12), 1703510.

223. Zhang, L.; Jia, C.; He, S.; Zhu, Y.; Wang, Y.; Zhao, Z.; Gao, X.; Zhang, X.; Sang, Y.; Zhang, D.; Xu, X.; Liu, H., Hot Hole Enhanced Synergistic Catalytic Oxidation on Pt-Cu Alloy Clusters. *Advanced Science* **2017**, *4*(6), 1600448.

224. Boltersdorf, J.; Forcherio, G. T.; McClure, J. P.; Baker, D. R.; Leff, A. C.; Lundgren, C., Visible Light-Promoted Plasmon Resonance to Induce "Hot" Hole Transfer and Photothermal Conversion for Catalytic Oxidation. *The Journal of Physical Chemistry C* **2018**, *122*(50), 28934-28948.

225. Li, H.; Qin, F.; Yang, Z.; Cui, X.; Wang, J.; Zhang, L., New Reaction Pathway Induced by Plasmon for Selective Benzyl Alcohol Oxidation on Biocl Possessing Oxygen Vacancies. *Journal of the American Chemical Society* **2017**, *139*(9), 3513-3521.

226. Lee, S.-H.; Jo, J.-S.; Park, J. H.; Lee, S. W.; Jang, J.-W., A Hot-Electron-Triggered Catalytic Oxidation Reaction of Plasmonic Silver Nanoparticles Evidenced by Surface Potential Mapping. *Journal of Materials Chemistry A* **2018**, *6*(42), 20939-20946.

227. Xu, H.; Song, P.; Yan, B.; Wang, J.; Guo, J.; Du, Y., Surface-Plasmon-Enhanced Photo-Electrocatalytic Ethylene Glycol Oxidation Based on Highly Open Auag Nanobowls. *ACS Sustainable Chemistry & Engineering* **2018**, *6*(3), 4138-4146.

228. Xu, H.; Song, P.; Fernandez, C.; Wang, J.; Shiraishi, Y.; Wang, C.; Du, Y., Surface Plasmon Enhanced Ethylene Glycol Electrooxidation Based on Hollow Platinum-Silver Nanodendrites Structures. *Journal of the Taiwan Institute of Chemical Engineers* **2018**, *91*, 316-322.

229. Wang, M.; Wang, P.; Li, C.; Li, H.; Jin, Y., Boosting Electrocatalytic Oxygen Evolution Performance of Ultrathin Co/Ni-Mof Nanosheets Via Plasmon-Induced Hot Carriers. *ACS Applied Materials & Interfaces* **2018**, *10*(43), 37095-37102.

230. Plotkin, J. S. Beyond the Ethylene Steam Cracker. <u>https://www.acs.org/content/acs/en/pressroom/cutting-edge-chemistry/beyond-the-ethylene-steam-cracker.html</u> (accessed February 27, 2019).

231. Jones, T. E.; Wyrwich, R.; Böcklein, S.; Carbonio, E. A.; Greiner, M. T.; Klyushin, A. Y.; Moritz, W.; Locatelli, A.; Menteş, T. O.; Niño, M. A.; Knop-Gericke, A.; Schlögl, R.; Günther, S.; Wintterlin, J.; Piccinin, S., The Selective Species in Ethylene Epoxidation on Silver. *ACS Catalysis* **2018**, *8*(5), 3844-3852.

232. Institute, G. C. Ethylene Oxide Production. <u>https://hub.globalccsinstitute.com/publications/ccs-roadmap-industry-high-purity-co2-</u> <u>sources-sectoral-assessment-%E2%80%93-final-draft-report-2</u> (accessed February 27, 2019).

233. Ozbek, M. O.; Onal, I.; van Santen, R. A., Why Silver Is the Unique Catalyst for Ethylene Epoxidation. *Journal of Catalysis* **2011**, *284*(2), 230-235.

234. Christopher, P.; Xin, H.; Linic, S., Visible-Light-Enhanced Catalytic Oxidation Reactions on Plasmonic Silver Nanostructures. *Nature chemistry* **2011**, *3*(6), 467-472.

235. Marimuthu, A.; Zhang, J.; Linic, S., Tuning Selectivity in Propylene Epoxidation by Plasmon Mediated Photo-Switching of Cu Oxidation State. *Science* **2013**, *339* (6127), 1590-1593.

236. Zhang, X.; Kumari, G.; Heo, J.; Jain, P. K., In situ Formation of Catalytically Active Graphene in Ethylene Photo-Epoxidation. *Nature Communications* **2018**, *9*(1), 3056.

237. Mori, K.; Kawashima, M.; Che, M.; Yamashita, H., Enhancement of the Photoinduced Oxidation Activity of a Ruthenium(Ii) Complex Anchored on Silica-Coated Silver Nanoparticles by Localized Surface Plasmon Resonance. *Angew. Chem.* **2010**, *122* (46), 8780-8783.

238. Ide, Y.; Matsuoka, M.; Ogawa, M., Efficient Visible-Light-Induced Photocatalytic Activity on Gold-Nanoparticle-Supported Layered Titanate. *Journal of the American Chemical Society* **2010**, *132*(47), 16762-16764.

239. Wee, T.-L.; Schmidt, L. C.; Scaiano, J. C., Photooxidation of 9-Anthraldehyde Catalyzed by Gold Nanoparticles: Solution and Single Nanoparticle Studies Using Fluorescence Lifetime Imaging. *The Journal of Physical Chemistry C* **2012**, *116* (45), 24373-24379.

240. Zheng, Z.; Huang, B.; Qin, X.; Zhang, X.; Dai, Y.; Whangbo, M.-H., Facile in Situ Synthesis of Visible-Light Plasmonic Photocatalysts M@Tio2 (M = Au, Pt, Ag) and Evaluation of Their Photocatalytic Oxidation of Benzene to Phenol. *Journal of Materials Chemistry* **2011**, *21*(25), 9079-9087.

241. Xiao, Y.; Liu, J.; Mai, J.; Pan, C.; Cai, X.; Fang, Y., High-Performance Silver Nanoparticles Coupled with Monolayer Hydrated Tungsten Oxide Nanosheets: The Structural Effects in Photocatalytic Oxidation of Cyclohexane. *Journal of Colloid and Interface Science* **2018**, *516*, 172-181.

242. Egli, R.; Peter, A.; Freeman, H., *Colour Chemistry: The Design and Synthesis of Organic Dyes and Pigments*. Springer: 1991.

243. Murahashi, S.-I., Synthetic Aspects of Metal-Catalyzed Oxidations of Amines and Related Reactions. *Angewandte Chemie International Edition in English* **1995**, *34* (22), 2443-2465.

244. Nicolaou, K. C.; Mathison, C. J. N.; Montagnon, T., New Reactions of Ibx: Oxidation of Nitrogen- and Sulfur-Containing Substrates to Afford Useful Synthetic Intermediates. *Angewandte Chemie International Edition* **2003**, *42*(34), 4077-4082.

245. Naya, S.-i.; Kimura, K.; Tada, H., One-Step Selective Aerobic Oxidation of Amines to Imines by Gold Nanoparticle-Loaded Rutile Titanium(Iv) Oxide Plasmon Photocatalyst. *ACS Catalysis* **2013**, *3*(1), 10-13.

246. Sato, Y.; Naya, S.-i.; Tada, H., A New Bimetallic Plasmonic Photocatalyst Consisting of Gold(Core)-Copper(Shell) Nanoparticle and Titanium(Iv) Oxide Support. *APL Materials* **2015**, *3*(10), 104502.

247. Zhai, Z.-Y.; Guo, X.-N.; Jin, G.-Q.; Guo, X.-Y., Visible Light-Induced Selective Photocatalytic Aerobic Oxidation of Amines into Imines on Cu/Graphene. *Catalysis Science & Technology* **2015**, *5*(8), 4202-4207.

248. Wang, J.; Ando, R. A.; Camargo, P. H. C., Controlling the Selectivity of the Surface Plasmon Resonance Mediated Oxidation of P-Aminothiophenol on Au Nanoparticles by Charge Transfer from Uv-Excited Tio2. *Angewandte Chemie* **2015**, *127*(23), 7013-7016.

249. da Silva, A. G. M.; Rodrigues, T. S.; Correia, V. G.; Alves, T. V.; Alves, R. S.; Ando, R. A.; Ornellas, F. R.; Wang, J.; Andrade, L. H.; Camargo, P. H. C., Plasmonic Nanorattles as Next-Generation Catalysts for Surface Plasmon Resonance-Mediated Oxidations Promoted by Activated Oxygen. *Angewandte Chemie International Edition* **2016**, *55* (25), 7111-7115.

250. Zhu, K.; Wang, C.; Camargo, P. H. C.; Wang, J., Investigating the Effect of Mno2 Band Gap in Hybrid Mno2–Au Materials over the Spr-Mediated Activities under Visible Light. *Journal of Materials Chemistry A* **2019**, *7*(3), 925-931.

251. Zhao, L.-B.; Liu, X.-X.; Zhang, M.; Liu, Z.-F.; Wu, D.-Y.; Tian, Z.-Q., Surface Plasmon Catalytic Aerobic Oxidation of Aromatic Amines in Metal/Molecule/Metal Junctions. *The Journal of Physical Chemistry C*2016, *120*(2), 944-955.

252. Wang, J.; Alves, T. V.; Trindade, F. J.; de Aquino, C. B.; Pieretti, J. C.; Domingues, S. H.; Ando, R. A.; Ornellas, F. R.; Camargo, P. H. C., Theoretical Design and Experimental Realization of Quasi Single Electron Enhancement in Plasmonic Catalysis. *Angewandte Chemie* **2015**, *127*(48), 14635-14639.

253. Woodham, A. P.; Meijer, G.; Fielicke, A., Activation of Molecular Oxygen by Anionic Gold Clusters. *Angewandte Chemie International Edition* **2012**, *51*(18), 4444-4447.

254. Lin, W.; Cao, E.; Zhang, L.; Xu, X.; Song, Y.; Liang, W.; Sun, M., Electrically Enhanced Hot Hole Driven Oxidation Catalysis at the Interface of a Plasmon-Exciton Hybrid. *Nanoscale* **2018**, *10*(12), 5482-5488.

255. Novello, P.; Varanasi, C. V.; Liu, J., Effects of Light on Catalytic Activities and Lifetime of Plasmonic Au Catalysts in the Co Oxidation Reaction. *ACS Catalysis* **2019**, *9*(1), 578-586.

256. An, N.; Li, S.; Duchesne, P. N.; Wu, P.; Zhang, W.; Lee, J.-F.; Cheng, S.; Zhang, P.; Jia, M.; Zhang, W., Size Effects of Platinum Colloid Particles on the Structure and Co Oxidation Properties of Supported Pt/Fe2o3 Catalysts. *The Journal of Physical Chemistry C* **2013**, *117*(41), 21254-21262.

257. Bamwenda, G. R.; Tsubota, S.; Nakamura, T.; Haruta, M., The Influence of the Preparation Methods on the Catalytic Activity of Platinum and Gold Supported on Tio2 for Co Oxidation. *Catalysis Letters* **1997**, *44*(1), 83-87.

258. Jia, C.-J.; Liu, Y.; Bongard, H.; Schüth, F., Very Low Temperature Co Oxidation over Colloidally Deposited Gold Nanoparticles on Mg(Oh)2 and Mgo. *Journal of the American Chemical Society* **2010**, *132*(5), 1520-1522.

259. Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N., Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature Far Below 0 °C. *Chemistry Letters* **1987**, *16*(2), 405-408.

260. Lee, S. W.; Lee, C.; Goddeti, K. C.; Kim, S. M.; Park, J. Y., Surface Plasmon-Driven Catalytic Reactions on a Patterned Co3o4/Au Inverse Catalyst. *RSC Advances* **2017**, *7*(88), 56073-56080.

261. Kim, S. M.; Lee, C.; Goddeti, K. C.; Park, J. Y., Hot Plasmonic Electron-Driven Catalytic Reactions on Patterned Metal-Insulator-Metal Nanostructures. *Nanoscale* **2017**, *9*(32), 11667-11677.

262. Lee, S. W.; Hong, J. W.; Lee, H.; Wi, D. H.; Kim, S. M.; Han, S. W.; Park, J. Y., The Surface Plasmon-Induced Hot Carrier Effect on the Catalytic Activity of Co Oxidation on a Cu2o/Hexoctahedral Au Inverse Catalyst. *Nanoscale* **2018**, *10*(23), 10835-10843.

263. Kim, S. M.; Lee, S. J.; Kim, S. H.; Kwon, S.; Yee, K. J.; Song, H.; Somorjai, G. A.; Park, J. Y., Hot Carrier-Driven Catalytic Reactions on Pt–Cdse–Pt Nanodumbbells and Pt/Gan under Light Irradiation. *Nano Letters* **2013**, *13*(3), 1352-1358.

264. Park, J. Y.; Baker, L. R.; Somorjai, G. A., Role of Hot Electrons and Metal-Oxide Interfaces in Surface Chemistry and Catalytic Reactions. *Chemical Reviews* **2015**, *115*(8), 2781-2817.

265. Zhang, Y.; Li, Q.; Liu, C.; Shan, X.; Chen, X.; Dai, W.; Fu, X., The Promoted Effect of a Metal-Organic Frameworks (Zif-8) on Au/Tio2 for Co Oxidation at Room Temperature Both in Dark and under Visible Light Irradiation. *Applied Catalysis B: Environmental* **2018**, *224*, 283-294.

266. Swearer, D. F.; Zhao, H. Q.; Zhou, L. N.; Zhang, C.; Robatjazi, H.; Martirez, J. M. P.; Krauter, C. M.; Yazdi, S.; McClain, M. J.; Ringe, E.; Carter, E. A.; Nordlander, P.; Halas, N. J., Heterometallic Antenna-Reactor Complexes for Photocatalysis. *Proceedings of the National Academy of Sciences of the United States of America* **2016**, *113*(32), 8916-8920. 267. Zhang, C.; Zhao, H.; Zhou, L.; Schlather, A. E.; Dong, L.; McClain, M. J.; Swearer, D. F.; Nordlander, P.; Halas, N. J., Al-Pd Nanodisk Heterodimers as Antenna-Reactor Photocatalysts. *Nano Lett.* **2016**, *16*(10), 6677-6682.

268. Spata, V. A.; Carter, E. A., Mechanistic Insights into Photocatalyzed Hydrogen Desorption from Palladium Surfaces Assisted by Localized Surface Plasmon Resonances. *ACS nano* **2018**, *12*(4), 3512-3522.

269. Quiroz, J.; Barbosa, E. C.; Araujo, T. P.; Fiorio, J. L.; Wang, Y.-C.; Zou, Y.-C.; Mou, T.; Alves, T. V.; de Oliveira, D. C.; Wang, B.; Haigh, S.; Rossi, L.; Camargo, P. H., Controlling Reaction Selectivity over Hybrid Plasmonic Nanocatalysts. *Nano Letters* **2018**, *18* (11), 7289-7297.

270. Schnepf, M. J.; Mayer, M.; Kuttner, C.; Tebbe, M.; Wolf, D.; Dulle, M.; Altantzis, T.; Formanek, P.; Förster, S.; Bals, S.; König, T. A. F.; Fery, A., Nanorattles with Tailored Electric Field Enhancement. *Nanoscale* **2017**, *9*(27), 9376-9385.

271. Zhao, X. Y.; Long, R.; Liu, D.; Luo, B. B.; Xiong, Y. J., Pd-Ag Alloy Nanocages: Integration of Ag Plasmonic Properties with Pd Active Sites for Light-Driven Catalytic Hydrogenation. *Journal of Materials Chemistry A* **2015**, *3*(18), 9390-9394. 272. Gangishetty, M. K.; Fontes, A. M.; Malta, M.; Kelly, T. L.; Scott, R. W. J., Improving the Rates of Pd-Catalyzed Reactions by Exciting the Surface Plasmons of Aupd Bimetallic Nanotriangles. *RSC Advances* **2017**, *7*(64), 40218-40226.

273. Hao, C.-H.; Guo, X.-N.; Pan, Y.-T.; Chen, S.; Jiao, Z.-F.; Yang, H.; Guo, X.-Y., Visible-Light-Driven Selective Photocatalytic Hydrogenation of Cinnamaldehyde over Au/Sic Catalysts. *Journal of the American Chemical Society* **2016**, *138* (30), 9361-9364.

274. Li, A. Y.; Gellé, A.; Segalla, A.; Moores, A., Silver Nanoparticles in Organic Transformations. In *Silver Catalysis in Organic Synthesis*, Li, C. J., Bi, Xihe., Ed. Wiley: 2019. 275. Mukherjee, S.; Zhou, L.; Goodman, A. M.; Large, N.; Ayala-Orozco, C.; Zhang, Y.; Nordlander, P.; Halas, N. J., Hot-Electron-Induced Dissociation of H2 on Gold Nanoparticles Supported on Sio2. *Journal of the American Chemical Society* **2014**, *136*(1), 64-67.

276. Zhou, L.; Zhang, C.; McClain, M. J.; Manavacas, A.; Krauter, C. M.; Tian, S.; Berg, F.; Everitt, H. O.; Carter, E. A.; Nordlander, P.; Halas, N. J., Aluminum Nanocrystals as a Plasmonic Photocatalyst for Hydrogen Dissociation. *Nano Letters* **2016**, *16* (2), 1478-1484.

277. Pradhan, N.; Pal, A.; Pal, T., Catalytic Reduction of Aromatic Nitro Compounds by Coinage Metal Nanoparticles. *Langmuir* **2001**, *17*(5), 1800-1802.

278. Wu, X.-Q.; Wu, X.-W.; Huang, Q.; Shen, J.-S.; Zhang, H.-W., In Situ Synthesized Gold Nanoparticles in Hydrogels for Catalytic Reduction of Nitroaromatic Compounds. *Applied Surface Science* **2015**, *331*, 210-218.

279. Shah, D.; Kaur, H., Resin-Trapped Gold Nanoparticles: An Efficient Catalyst for Reduction of Nitro Compounds and Suzuki-Miyaura Coupling. *Journal of Molecular Catalysis A: Chemical* **2014**, *381*, 70-76.

280. Cui, Q.; Xia, B.; Mitzscherling, S.; Masic, A.; Li, L.; Bargheer, M.; Möhwald, H., Preparation of Gold Nanostars and Their Study in Selective Catalytic Reactions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2015**, *465*, 20-25.

281. Mori, K.; Verma, P.; Hayashi, R.; Fuku, K.; Yamashita, H., Color-Controlled Ag Nanoparticles and Nanorods within Confined Mesopores: Microwave-Assisted Rapid Synthesis and Application in Plasmonic Catalysis under Visible-Light Irradiation. *Chemistry–A European Journal* **2015**, *21*(33), 11885-11893.

282. Pradhan, N.; Pal, A.; Pal, T., Silver Nanoparticle Catalyzed Reduction of Aromatic Nitro Compounds. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2002**, *196* (2-3), 247-257.

283. Vadakkekara, R.; Chakraborty, M.; Parikh, P. A., Reduction of Aromatic Nitro Compounds on Colloidal Hollow Silver Nanospheres. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2012**, *399*, 11-17.

284. Hajfathalian, M.; Gilroy, K. D.; Yaghoubzade, A.; Sundar, A.; Tan, T.; Hughes, R. A.; Neretina, S., Photocatalytic Enhancements to the Reduction of 4-Nitrophenol by Resonantly Excited Triangular Gold-Copper Nanostructures. *The Journal of Physical Chemistry* **C2015**, *119*(30), 17308-17315.

285. He, R.; Wang, Y.-C.; Wang, X.; Wang, Z.; Liu, G.; Zhou, W.; Wen, L.; Li, Q.; Wang, X.; Chen, X.; Zeng, J.; Hou, J. G., Facile Synthesis of Pentacle Gold–Copper Alloy Nanocrystals and Their Plasmonic and Catalytic Properties. *Nature Communications* **2014**, *5*, 4327.

286. Haldar, K. K.; Kundu, S.; Patra, A., Core-Size-Dependent Catalytic Properties of Bimetallic Au/Ag Core-Shell Nanoparticles. *ACS applied materials & interfaces* **2014**, *6* (24), 21946-21953.

287. Wu, W.; Lei, M.; Yang, S.; Zhou, L.; Liu, L.; Xiao, X.; Jiang, C.; Roy, V. A., A One-Pot Route to the Synthesis of Alloyed Cu/Ag Bimetallic Nanoparticles with Different Mass Ratios for Catalytic Reduction of 4-Nitrophenol. *Journal of Materials Chemistry A* **2015**, *3* (7), 3450-3455.

288. Xiao, Q.; Sarina, S.; Waclawik, E. R.; Jia, J.; Chang, J.; Riches, J. D.; Wu, H.; Zheng, Z.; Zhu, H., Alloying Gold with Copper Makes for a Highly Selective Visible-Light Photocatalyst for the Reduction of Nitroaromatics to Anilines. *ACS Catalysis* **2016**, *6* (3), 1744-1753.

289. Vysakh, A.; Babu, C. L.; Vinod, C., Demonstration of Synergistic Catalysis in Au@ Ni Bimetallic Core–Shell Nanostructures. *The Journal of Physical Chemistry* **C2015**, *119*(15), 8138-8146.

290. Essner, J. B.; Laber, C. H.; Baker, G. A., Carbon Dot Reduced Bimetallic Nanoparticles: Size and Surface Plasmon Resonance Tunability for Enhanced Catalytic Applications. *Journal of Materials Chemistry A* **2015**, *3*(31), 16354-16360.

291. Shin, K. S.; Cho, Y. K.; Choi, J.-Y.; Kim, K., Facile Synthesis of Silver-Deposited Silanized Magnetite Nanoparticles and Their Application for Catalytic Reduction of Nitrophenols. *Applied Catalysis A: General* **2012**, *413-414*, 170-175.

292. Zhu, H.; Ke, X.; Yang, X.; Sarina, S.; Liu, H., Reduction of Nitroaromatic Compounds on Supported Gold Nanoparticles by Visible and Ultraviolet Light. *Angewandte Chemie* **2010**, *122*(50), 9851-9855.

293. Wu, Y.; Zhang, T.; Zheng, Z.; Ding, X.; Peng, Y., A Facile Approach to Fe3o4@Au Nanoparticles with Magnetic Recyclable Catalytic Properties. *Materials Research Bulletin* **2010**, *45*(4), 513-517.

294. Barbosa, E. C. M.; Fiorio, J. L.; Mou, T.; Wang, B.; Rossi, L. M.; Camargo, P. H. C., Reaction Pathway Dependence in Plasmonic Catalysis: Hydrogenation as a Model Molecular Transformation. *Chemistry – A European Journal* **2018**, *24*(47), 12330-12339.

295. Naya, S.-i.; Niwa, T.; Kume, T.; Tada, H., Visible-Light-Induced Electron Transport from Small to Large Nanoparticles in Bimodal Gold Nanoparticle-Loaded Titanium(Iv) Oxide. *Angewandte Chemie International Edition* **2014**, *53* (28), 7305-7309.

296. Ding, Q.; Chen, M.; Fang, Y.; Zhang, Z.; Sun, M., Plasmon-Driven Diazo Coupling Reactions of P-Nitroaniline Via –Nh2 or –No2 in Atmosphere Environment. *The Journal of Physical Chemistry C* **2017**, *121*(9), 5225-5231.

297. Zhao, L.-B.; Zhang, M.; Huang, Y.-F.; Williams, C. T.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q., Theoretical Study of Plasmon-Enhanced Surface Catalytic Coupling Reactions of Aromatic Amines and Nitro Compounds. *The Journal of Physical Chemistry Letters* **2014**, *5*(7), 1259-1266.

298. Liu, Z.; Huang, Y.; Xiao, Q.; Zhu, H., Selective Reduction of Nitroaromatics to Azoxy Compounds on Supported Ag–Cu Alloy Nanoparticles through Visible Light Irradiation. *Green Chemistry* **2016**, *18*(3), 817-825.

299. Guo, X.; Hao, C.; Jin, G.; Zhu, H.-Y.; Guo, X.-Y., Copper Nanoparticles on Graphene Support: An Efficient Photocatalyst for Coupling of Nitroaromatics in Visible Light. *Angewandte Chemie International Edition* **2014**, *53*(7), 1973-1977.

300. Huang, Y.-F.; Zhu, H.-P.; Liu, G.-K.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q., When the Signal Is Not from the Original Molecule to Be Detected: Chemical Transformation of Para-Aminothiophenol on Ag During the Sers Measurement. *Journal of the American Chemical Society* **2010**, *132*(27), 9244-9246.

301. Ren, X.; Cao, E.; Lin, W.; Song, Y.; Liang, W.; Wang, J., Recent Advances in Surface Plasmon-Driven Catalytic Reactions. *RSC Advances* **2017**, *7*(50), 31189-31203.

302. Bailo, E.; Deckert, V., Tip-Enhanced Raman Scattering. *Chemical Society Reviews* **2008**, *37*(5), 921-930.

303. Hartman, T.; Wondergem, C. S.; Kumar, N.; van den Berg, A.; Weckhuysen, B. M., Surface-and Tip-Enhanced Raman Spectroscopy in Catalysis. *The journal of physical chemistry letters* **2016**, *7*(8), 1570-1584.

304. Kundu, S.; Mandal, M.; Ghosh, S. K.; Pal, T., Photochemical Deposition of Sers Active Silver Nanoparticles on Silica Gel and Their Application as Catalysts for the Reduction of Aromatic Nitro Compounds. *Journal of colloid and interface science* **2004**, *272* (1), 134-144.

305. Xie, W.; Walkenfort, B.; Schlücker, S., Label-Free Sers Monitoring of Chemical Reactions Catalyzed by Small Gold Nanoparticles Using 3d Plasmonic Superstructures. *Journal of the American Chemical Society* **2012**, *135*(5), 1657-1660.

306. Ren, X.; Tan, E.; Lang, X.; You, T.; Jiang, L.; Zhang, H.; Yin, P.; Guo, L., Observing Reduction of 4-Nitrobenzenthiol on Gold Nanoparticles in Situ Using Surface-Enhanced Raman Spectroscopy. *Physical Chemistry Chemical Physics* **2013**, *15*(34), 14196-14201.

307. Zhang, Z.; Kinzel, D.; Deckert, V., Photo-Induced or Plasmon-Induced Reaction: Investigation of the Light-Induced Azo-Coupling of Amino Groups. *The Journal of Physical Chemistry* **C2016**, *120*(37), 20978-20983.

308. Cho, F.-H.; Kuo, S.-C.; Lai, Y.-H., Surface-Plasmon-Induced Azo Coupling Reaction between Nitro Compounds on Dendritic Silver Monitored by Surface-Enhanced Raman Spectroscopy. *RSC Advances* **2017**, *7*(17), 10259-10265.

309. Huang, Y.-F.; Wu, D.-Y.; Zhu, H.-P.; Zhao, L.-B.; Liu, G.-K.; Ren, B.; Tian, Z.-Q., Surface-Enhanced Raman Spectroscopic Study of P-Aminothiophenol. *Physical Chemistry Chemical Physics* **2012**, *14*(24), 8485-8497.

310. Tamao, K.; Sumitani, K.; Kumada, M., Selective Carbon-Carbon Bond Formation by Cross-Coupling of Grignard Reagents with Organic Halides. Catalysis by Nickel-Phosphine Complexes. *Journal of the American Chemical Society* **1972**, *94*(12), 4374-4376.

311. Lundgren, R. J.; Stradiotto, M., Addressing Challenges in Palladium-Catalyzed Cross-Coupling Reactions through Ligand Design. *Chemistry – A European Journal* **2012**, *18*(32), 9758-9769.

312. Mpungose, P.; Vundla, Z.; Maguire, G.; Friedrich, H., The Current Status of Heterogeneous Palladium Catalysed Heck and Suzuki Cross-Coupling Reactions. *Molecules* **2018**, *23*(7), 1676-1699.

313. Hussain, I.; Capricho, J.; Yawer, M. A., Synthesis of Biaryls Via Ligand-Free Suzuki-Miyaura Cross-Coupling Reactions: A Review of Homogeneous and Heterogeneous Catalytic Developments. *Advanced Synthesis & Catalysis* **2016**, *358* (21), 3320-3349.

314. Lakshminarayana, B.; Mahendar, L.; Ghosal, P.; Satyanarayana, G.; Subrahmanyam, C., Nano-Sized Recyclable Pdo Supported Carbon Nanostructures for Heck Reaction: Influence of Carbon Materials. *Chemistryselect* **2017**, *2*(9), 2700-2707.

315. Gu, Q.; Jia, Q.; Long, J.; Gao, Z., Heterogeneous Photocatalyzed C–C Cross-Coupling Reactions under Visible-Light and near-Infrared Light Irradiation. *ChemCatChem* **2019**, *11* (2), 669-683.

316. González-Béjar, M.; Peters, K.; Hallett-Tapley, G. L.; Grenier, M.; Scaiano, J. C., Rapid One-Pot Propargylamine Synthesis by Plasmon Mediated Catalysis with Gold Nanoparticles on Zno under Ambient Conditions. *Chemical Communications* **2013**, *49*(17), 1732-1734.

317. Dos Santos, C. G.; Marquez, D. T.; Crites, C.-O. L.; Netto-Ferreira, J. C.; Scaiano, J. C., Plasmon Heating Mediated Friedel-Crafts Alkylation of Anisole Using Supported Aunp@Nb2o5 Catalysts. *Tetrahedron Letters* **2017**, *58*(5), 427-431.

318. Yu, S.; Wilson, A. J.; Heo, J.; Jain, P. K., Plasmonic Control of Multi-Electron Transfer and C–C Coupling in Visible-Light-Driven Co2 Reduction on Au Nanoparticles. *Nano letters* **2018**, *18*(4), 2189-2194.

319. Hopkinson, M. N.; Sahoo, B.; Li, J.-L.; Glorius, F., Dual Catalysis Sees the Light: Combining Photoredox with Organo-, Acid, and Transition-Metal Catalysis. *Chemistry – A European Journal* **2014**, *20*(14), 3874-3886.

320. Liu, Q.; Dong, X.; Li, J.; Xiao, J.; Dong, Y.; Liu, H., Recent Advances on Palladium Radical Involved Reactions. *ACS Catalysis* **2015**, *5*(10), 6111-6137.

321. Wu, X.; Jaatinen, E.; Sarina, S.; Zhu, H. Y., Direct Photocatalysis of Supported Metal Nanostructures for Organic Synthesis. *Journal of Physics D: Applied Physics* **2017**, *50*(28), 283001.

322. Xiao, Q.; Sarina, S.; Jaatinen, E.; Jia, J.; Arnold, D. P.; Liu, H.; Zhu, H., Efficient Photocatalytic Suzuki Cross-Coupling Reactions on Au–Pd Alloy Nanoparticles under Visible Light Irradiation. *Green Chemistry* **2014**, *16*(9), 4272-4285.

323. Eremin, D. B.; Ananikov, V. P., Understanding Active Species in Catalytic Transformations: From Molecular Catalysis to Nanoparticles, Leaching, "Cocktails" of Catalysts and Dynamic Systems. *Coordination Chemistry Reviews* **2017**, *346*, 2-19.

324. Thathagar, M. B.; ten Elshof, J. E.; Rothenberg, G., Pd Nanoclusters in C C Coupling Reactions: Proof of Leaching. *Angewandte Chemie International Edition* **2006**, *45* (18), 2886-2890.

325. MacQuarrie, S.; Horton, J. H.; Barnes, J.; McEleney, K.; Loock, H.-P.; Crudden, C. M., Visual Observation of Redistribution and Dissolution of Palladium During the Suzuki-Miyaura Reaction. *Angewandte Chemie International Edition* **2008**, *47*(17), 3279-3282.

326. Verkaaik, M.; Grote, R.; Meulendijks, N.; Sastre, F.; Weckhuysen, B. M.; Buskens, P., Suzuki-Miyaura Cross-Coupling Using Plasmonic Pd-Decorated Au Nanorods as Catalyst: A Study on the Contribution of Laser Illumination. *ChemCatChem* **2019**, *11*, 1-8.

327. Wang, F.; Li, C.; Chen, H.; Jiang, R.; Sun, L.-D.; Li, Q.; Wang, J.; Yu, J. C.; Yan, C.-H., Plasmonic Harvesting of Light Energy for Suzuki Coupling Reactions. *Journal of the American Chemical Society* **2013**, *135*(15), 5588-5601.

328. Zhang, S.; Chang, C.; Huang, Z.; Ma, Y.; Gao, W.; Li, J.; Qu, Y., Visible-Light-Activated Suzuki-Miyaura Coupling Reactions of Aryl Chlorides over the Multifunctional Pd/Au/Porous Nanorods of Ceo2 Catalysts. *ACS Catalysis* **2015**, *5* (11), 6481-6488.

329. Wen, M.; Takakura, S.; Fuku, K.; Mori, K.; Yamashita, H., Enhancement of Pd-Catalyzed Suzuki-Miyaura Coupling Reaction Assisted by Localized Surface Plasmon Resonance of Au Nanorods. *Catalysis Today* **2015**, *242*, 381-385.

330. Han, D.; Bao, Z.; Xing, H.; Yang, Y.; Ren, Q.; Zhang, Z., Fabrication of Plasmonic Au-Pd Alloy Nanoparticles for Photocatalytic Suzuki-Miyaura Reactions under Ambient Conditions. *Nanoscale* **2017**, *9*(18), 6026-6032.

331. Zhu, X.; Jia, H.; Zhu, X.-M.; Cheng, S.; Zhuo, X.; Qin, F.; Yang, Z.; Wang, J., Selective Pd Deposition on Au Nanobipyramids and Pd Site-Dependent Plasmonic Photocatalytic Activity. *Advanced Functional Materials* **2017**, *27*(22), 1700016.

332. Su, G.; Jiang, H.; Zhu, H.; Lv, J.-J.; Yang, G.; Yan, B.; Zhu, J.-J., Controlled Deposition of Palladium Nanodendrites on the Tips of Gold Nanorods and Their Enhanced Catalytic Activity. *Nanoscale* **2017**, *9*(34), 12494-12502.

333. Nemygina, N. A.; Nikoshvili, L. Z.; Tiamina, I. Y.; Bykov, A. V.; Smirnov, I. S.; LaGrange, T.; Kaszkur, Z.; Matveeva, V. G.; Sulman, E. M.; Kiwi-Minsker, L., Au Core-Pd Shell Bimetallic Nanoparticles Immobilized within Hyper-Cross-Linked Polystyrene for Mechanistic Study of Suzuki Cross-Coupling: Homogeneous or Heterogeneous Catalysis? *Organic Process Research & Development* **2018**, *22*(12), 1606-1613.

334. Kozuch, S.; Shaik, S., A Combined Kinetic–Quantum Mechanical Model for Assessment of Catalytic Cycles: Application to Cross-Coupling and Heck Reactions. *Journal of the American Chemical Society* **2006**, *128*(10), 3355-3365.

335. Guo, J.; Zhang, Y.; Shi, L.; Zhu, Y.; Mideksa, M. F.; Hou, K.; Zhao, W.; Wang, D.; Zhao, M.; Zhang, X.; Lv, J.; Zhang, J.; Wang, X.; Tang, Z., Boosting Hot Electrons in Hetero-Superstructures for Plasmon-Enhanced Catalysis. *Journal of the American Chemical Society* **2017**, *139*(49), 17964-17972.

336. Verma, P.; Kuwahara, Y.; Mori, K.; Yamashita, H., Pd/Ag and Pd/Au Bimetallic Nanocatalysts on Mesoporous Silica for Plasmon-Mediated Enhanced Catalytic Activity under Visible Light Irradiation. *Journal of Materials Chemistry A* **2016**, *4* (26), 10142-10150.

337. Trinh, T. T.; Sato, R.; Sakamoto, M.; Fujiyoshi, Y.; Haruta, M.; Kurata, H.; Teranishi, T., Visible to near-Infrared Plasmon-Enhanced Catalytic Activity of Pd Hexagonal Nanoplates for the Suzuki Coupling Reaction. *Nanoscale* **2015**, *7*(29), 12435-12444.

338. Sharma, K.; Kumar, M.; Bhalla, V., Aggregates of the Pentacenequinone Derivative as Reactors for the Preparation of Ag@Cu2o Core-Shell Nps: An Active Photocatalyst for Suzuki and Suzuki Type Coupling Reactions. *Chemical Communications* **2015**, *51* (63), 12529-12532.

339. Xiao, Q.; Sarina, S.; Bo, A.; Jia, J.; Liu, H.; Arnold, D. P.; Huang, Y.; Wu, H.; Zhu, H., Visible Light-Driven Cross-Coupling Reactions at Lower Temperatures Using a Photocatalyst of Palladium and Gold Alloy Nanoparticles. *ACS Catalysis* **2014**, *4*(6), 1725-1734.

340. Guo, X.-W.; Hao, C.-H.; Wang, C.-Y.; Sarina, S.; Guo, X.-N.; Guo, X.-Y., Visible Light-Driven Photocatalytic Heck Reaction over Carbon Nanocoil Supported Pd Nanoparticles. *Catalysis Science & Technology* **2016**, *6*(21), 7738-7743.

341. Lanterna, A. E.; Elhage, A.; Scaiano, J. C., Heterogeneous Photocatalytic C-C Coupling: Mechanism of Plasmon-Mediated Reductive Dimerization of Benzyl Bromides by Supported Gold Nanoparticles. *Catalysis Science & Technology* **2015**, *5*(9), 4336-4340.

342. Pineda, A.; Gomez, L.; Balu, A. M.; Sebastian, V.; Ojeda, M.; Arruebo, M.; Romero,
A. A.; Santamaria, J.; Luque, R., Laser-Driven Heterogeneous Catalysis: Efficient Amide
Formation Catalysed by Au/Sio2 Systems. *Green Chemistry* **2013**, *15*(8), 2043-2049.
343. Wei, C. M.; Li, C. J., A Highly Efficient Three-Component Coupling of Aldehyde,

Alkyne, and Amines Via C - H Activation Catalyzed by Gold in Water. *Journal of the American Chemical Society* **2003**, *125* (32), 9584-9585.

Transition

In the previous chapter we covered plasmon-mediated organic transformations. The following section focused on water splitting catalyzed by titanium dioxide and plasmonic metal hybrid nanostructures. Titania has been known for long to be an active photocatalyst, able to perform water splitting under light irradiation. However this activity is limited to the ultraviolet spectrum and suffers from too rapid charge carrier recombination. The addition of plasmonic nanostructures enables to push absorption properties to the visible region and prevent unwanted charge recombination. In this chapter, we explain the principles behind the activity of such nanohybrids towards visible light water splitting and detail the recent research developments relying on plasmonic metals, namely Au, Ag and Cu.

3 Chapter 3 - Water splitting catalyzed by titanium dioxide decorated plasmonic nanoparticles



This chapter is based upon one published article. IUPAC and De Gruyter granted permission to reprint the published article, as did all co-authors.

Alexandra Gellé and Audrey Moores, Water splitting catalyzed by titanium dioxide decorated with plasmonic nanoparticles, Pure and Applied Chemistry, 2017, 89, 12, 1917.

3.1 Introduction

The fast growing world population and the rapidly decreasing accessibility of fossil fuels call for new ways of supplying energy in order to fulfill worldwide demand, with reduced environmental impact. Therefore, alternative energy sources such as geothermal, wind and hydropower have been investigated, yet, none of them can be implemented at the required scale to solve the challenge.³⁴⁴ Harvesting energy from the sun offers a desirable approach towards the need for clean energy as sunlight is a free inexhaustible natural resource. Unfortunately, it is an intermittent source of energy due to its daily, seasonal and geographical variability.³⁴⁵ Hence providing a constant and stable energy flux is a challenge that has to be overcome to meet global energy consumption. Thus efficient conversion, storage and transport of energy harvested from the sun is required.³⁴⁶



Figure 3-1 Photosynthesis by green plants and photocatalytic water splitting as an artificial photosynthesis. Reproduced from Ref ⁵⁰ with permission of The Royal Society of Chemistry.

Photoelectrochemical (PEC) water splitting, also referred to as artificial photosynthesis, is a promising path towards clean generation of hydrogen by photocatalytic water splitting (Figure 3-1). In this reaction, the energy from light, ideally sun, is converted into chemical energy, *i.e.* "stored" in the form of dihydrogen.³⁴⁶ The water splitting reaction is an endothermic reaction featuring a Gibbs free energy of 237 kJ.mol⁻¹.⁹⁸ Such a photodriven conversion of water, an abundant raw material, to hydrogen gas is a headway towards the "Holy Grail": producing a clean and storable fuel.⁹⁸ Moreover, the overall water splitting

process is clean and renewable since sunlight and water are the only inputs required for the reaction to occur and no pollutant byproduct is formed during this process.⁵⁰ In the literature, this type of water splitting is indifferently defined as a PEC or photocatalytic process.⁹⁸

The ability for TiO₂ to act as a photocatalyst for water splitting has been known since it was first discovered by Fujishima and Honda in 1972.⁴⁹ Following this pioneer study, other photocatalytic materials such as TiO₂, GaP, WO₃, CdS and ZnO have gained wide attention³⁴⁷ as both light absorbers and energy converters. TiO₂ is an appealing material for this application considering its low-cost, good thermal stability, resistance to photocorrosion and superior photocatalytic properties. Moreover, it is a naturally occurring, non-toxic and earth abundant mineral.⁵¹ However, the wide use of this material has been hampered by the fast recombination of photogenerated electron-hole pairs (e-h) and its poor activation by visible light. Specifically, it features a large band gap, enabling only UV wavelength excitation, with thus a small portion of sunlight radiations being in use.²⁴ To address the limitations of bare TiO₂, efforts were made to broaden the adsorption capability of the system towards the visible spectrum relying on either the addition of sacrificial reagents or the modification of TiO₂ by metal deposition,³⁴⁸ anion doping,³⁴⁹ dye sensitization³⁵⁰ or other semiconductors³⁵¹ have been investigated to extend the activity spectrum to the visible range and enhance light-assisted catalytic hydrogen production catalyzed by TiO₂.^{24, 352} Recently, the integration of plasmonic nanoparticles (PNPs) as cocatalysts showed great potential for the design of more efficient photocatalysts.³⁵³ The surface plasmon resonance (SPR) is a property of metal nanoparticles (NPs) by which they strongly scatter light via resonance of their conductive electrons with incoming irradiation.^{70, 144, 354} Au, Ag and Cu are the most common metals studied for this property because of their excellent SPR property. It confers to colloidal suspensions of these metals with intense and tunable colors in the visible regions, but also opens opportunities to harvest solar radiation. In the context of energy conversion, such PNPs have emerged as highly appealing antennas, able to deliver visible-light-excited electrons to TiO₂, to enable

further reactivity. Since 2004, when the coupling of TiO₂ with Au NPs was first discovered to enhance water splitting, the use of PNPs as cocatalyst for this reaction has become a research field of its own.¹⁰³ Warren and Thimsen reviewed this research topic in 2012, with a strong emphasis on the physics aspects of the phenomenon.³⁵⁵ In the present chapter, we have focused on recent progresses made in visible-light driven water splitting catalyzed by PNPs supported onto TiO₂ (PNP@TiO₂). As explained below, water splitting involves two reactions occurring at two distinct sites: hydrogen evolution on one end and oxygen reduction on the other. Herein we have selected research towards PEC catalysts enabling both reactions, sometimes referred to as "overall water splitting". Below, the principles of semiconductor-catalyzed water splitting, and SPR in plasmonic NPs are briefly explained, before we highlight recent use of PNP@TiO₂ as photocatalyst for this reaction and survey research reports by metals. Synthesis of various PNPs-decorated TiO₂ catalysts are also briefly described. For a more complete overview over synthetic methods to access PNP@TiO₂, the reader to directed to the review by Mao *et al.*³⁵²

3.2 Semiconductor-catalyzed photoelectrochemical water-splitting

The photocatalytic properties of TiO_2 arise from the photogeneration of electron/hole pairs, also called charge carriers, following light irradiation. When incident light with energy greater than the band gap interacts with a photocatalyst, electrons are injected to the conduction band of the material while holes are left behind in the valence band (Figure 3-2). Photogenerated holes and electrons then diffuse in the valence band (VB) and conduction band (CB) respectively to surface active sites where the reactions take place. The generation of hydrogen and oxygen gas by water splitting is driven by the concomitance of 2 events: (1) molecular oxygen and protons are produced by the oxidation of H₂O and (2) the excited electrons reduce the aforementioned protons to form hydrogen. Therefore, the four-electron process for splitting water into H₂ and O₂ requires a material with a band gap equal to at least 1.2 eV which corresponds to difference in the two redox potential of the couples involved in water splitting. The efficiency of a photocatalyst lies in its ability to

absorb light in order to create charge carriers, by excitation of an electron form the VB to the CB.⁵⁹ In PEC cells, hydrogen and oxygen evolution take place on two electrodes, usually separate by a membrane as illustrated in Figure 3-2.³⁴⁶





Figure 3-2 - UV-driven water splitting with a semiconductor where oxygen and hydrogen evolution take place on the valence band and conduction band respectively. Reproduced from Ref ⁷⁶ with permission of De Gruyter (left) and diagram of the basic principles of water splitting for a photoelectrochemical cell with an n-type semiconductor photoanode where oxygen is evolved and a photocathode (Pt sheet) where hydrogen is evolved (right). Reproduced from Ref ³⁵⁶ with permission of The Royal Society of Chemistry.

Additionally to the band gap width, respective potential level of the semiconductor VB and CB also have their importance when designing a photocatalyst for water splitting: they have to match the potential of the redox couples involved in the photo-driven reaction. Thus the top level of VB is required to be above the redox potential of O_2/H_2O (+ 1.2 eV VS SHE) and the bottom level of CB has to be more negative than the redox potential of H^+/H_2 (0 eV). The width of the band gap as well as the potential of the CB and VB are characteristic of each semiconductor hence it has to be chosen adequately when designing photocatalysts. TiO₂ appears as a suitable photocatalyst since its band gap is large enough to split water (3.0 eV VS 1.2 eV for the formation of H₂ and O₂) and its band structure matches redox potentials of water splitting as shown in Figure 3-3.⁵⁰ Metal oxides semiconductors have indeed been found to be highly active for the splitting of water, however they require UV irradiation because of their large band gap and are thus not

suitable for visible-light-driven reactions.³⁵⁷ One avenue in the field of TiO_2 photocatalysis has focused on the reduction of this material to access black TiO_2 , a material able to absorb in the visible region.³⁵⁸



Figure 3-3 - Relationship between band structure of semiconductor and redox potentials of water splitting. Reprinted by permission from Macmillan Publishers Ltd: NATURE (reference ³⁵⁹, copyright 2001.)

Another critical obstacle limiting the efficiency of photocatalytic reactions on semiconductors is the high rate of electron-hole recombination occurring before charge carriers can reach the semiconductor surface and perform the desired chemical transformations. Although efforts have been made to optimize photosensitivity while minimizing charge-charrier recombination, semiconductors usually exhibit limited

efficiency. Their functionalization with PNPs as cocatalysts shows great promise for the design of more efficient sunlight driven water splitting catalysts, because it addresses the shortcomings of plain TiO₂.

3.3 Surface plasmon resonance in group XI metal nanoparticles

Cu, Ag and Au NPs feature characteristic strong absorption in the visible spectrum arising from SPR.⁷⁰ This phenomenon emerges from the collective resonance of the electrons when incident light matches their oscillation frequency against the restoring force of nuclei (Figure 3-4).³⁶⁰ The SPR leads to a number of unique properties featured by PNPs: 1) As electrons oscillate in resonance, strong absorption and scattering of incoming light takes place. This leads to the intense color of PNPs suspensions.¹⁴⁴ 2) SPR causes an enhanced electromagnetic field at vicinity of the NPs which is at the root of surface enhanced Raman spectroscopy (SERS) used for detection with molecular sensitivity. 3) Field enhancement also causes local heat generation and this has been used in the development of nanomedicines.³⁶¹ 4) Finally SPR allows for the generation of hot electrons at the surface of plasmonic NPs, a property exploited in catalysis.^{362, 363} Owing to their morphology-dependant optical properties, PNPs offer great deal of flexibility when engineering photocatalysts.³⁶⁴



Figure 3-4 - Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei. Reprinted with permission from ¹³⁹. Copyright 2003 American Chemical Society.

Upon excitation of PNPs, charge carriers relax within tens to femtoseconds either through scattering (radiative photon re-emission) or through absorption (non-radiative excitation of energetic charge carriers).¹¹⁴ Non-radiative pathways are necessary for the utilization of energetic charge carriers in chemical transformation but scattering by radiative photon re-emission is the dominant decay mode and prevent further use of e-h pairs. Solar-to-fuel catalyst efficiencies are currently limited by the kinetic discrepancy between the lifetimes of photogenerated charge carriers (picoseconds-microseconds) and the extended timescale necessary for photocatalytic reaction to occur at the semiconductor surface (milliseconds to seconds).

3.4 Plasmonic nanoparticle supported on titanium dioxide as photocatalyst for water splitting

In an effort to address the limitations of TiO_2 towards the photocatalysis of water splitting, researchers have explored the use of PNPs acting as a relay by trapping visible light in order activate TiO_2 . PNPs offer a number of advantages as cocatalyst in the context of water

splitting.⁵⁹ (1) The introduction of the PNPs at the surface of TiO₂ prevents recombination of the e-h pair by trapping them and promoting charge carrier separation. (2) The visible light absorption properties of PNPs allows more complete and efficient use of solar irradiation. (3) Because PNPs act as antennas for incoming light, less semiconductor material is needed to trap the same amount of energy, thus increasing efficiency. (4) Metal NPs at the surface of TiO₂ constitute sites, which are potentially catalytically active.³⁶⁵ (5) Finally the presence of metal NPs at the surface of TiO₂ plays a positive role in reducing the reflection losses taking place at the surface of the electrodes.

The PNP@TiO₂ hybrid system allows for the use of visible light to activate TiO₂. The mechanism of this reaction proceeds as follows. The PNP is able to absorb visible light and generate hot electrons.⁶⁶ These are subsequently transferred to the CB of TiO₂ (Figure 3-5.³⁶⁵ Xiong and coworkers determined the directions of charge transfer across the interface using charge kinetics models and evidenced the interplay relationships between the light harvesting material and the cocatalyst.³⁶⁶ Given the key contribution of cocatalysts to the photoactivity, synergetic engineering of its structure, its surface and the interface with the semiconductor is required to maximize performance. The PNP composition, exposed facets, phase and defects as well as the interface composition, location and facets play key roles in catalyst design. Another advantage of PNP is that, due to the interfacial upward energy band, called Schottky junction, electrons injected to the semiconductor cannot transfer back to the light harvesting metal.³⁶⁷ Therefore, e-h recombinations and back reactions are prevented by spatial separation of the charge carriers.



Figure 3-5 - Visible light-driven water splitting catalyzed by PNP@TiO2 via plasmonmediated electron transfer. Reproduced from Ref ⁷⁶ with permission of De Gruyter

Photoelectrochemical studies performed by Wei's group demonstrated that the addition of plasmonic cocatalysts generates long-lived charge carriers by plasmon-mediated electron transfer and could further enable visible-light-driven photocatalytic reactions.³⁶⁷ Electrons transferred at the Au/TiO₂ heterojunction displayed an excited-state lifetime 1 to 2 orders of magnitude longer than the one displayed by electrons photogenerated by UV irradiation on bare TiO₂. The prolonged hot electron dynamics was attributed to the Schottky barrier at the interface which reduces electron-hole recombination.³⁶⁷

3.4.1 Gold nanostructures on titanium dioxide

Because of the versatility of its synthesis and its chemical stability, Au NPs¹⁴⁹ have been by far the most used metal for this application.³⁵⁵ Because of the number of reports in this area, we present below seminal works, followed by the most recent developments, over the last 5 years. Pioneer studies by Tian and Tatsuma reported the first use of plasmonic Au NPs as sensitizers of TiO₂ films for plasmon-induced photoelectrochemistry.³⁶⁸ They later demonstrated that plasmonic Au NPs on TiO₂ can be used for the visible light induced

photocatalytic oxidation of methanol and ethanol as well as the reduction of oxygen.¹⁰³ This paved the way for the design of a new class of visible light sensitive photocatalysts for chemical transformation. Tian and Tatsuma suggested that upon excitation due to the SPR, charge separation is accomplished by transfer of photo-excited electrons from Au NPs to the TiO₂ conduction band and that such a charge separation was facilitated by the Schottky barrier formed by their interface.³⁶⁹ Following this early work, supported Au NPs were found to be applicable for various chemical transformations including of the oxidation of formaldehyde, alcohols, and amines to imines, C–C and amine–alkyne–aldehyde couplings, hydroamination of alkynes, oxidative degradation of phenol, oxidative aldehyde-amine condensation to amide, and hydroxylation of benzene, as well as the production of hydrogen or oxygen gas from organic molecules.^{209, 370, 371}

To effectively utilize the solar spectrum in catalytic water splitting, optical properties of the photocatalysts may be tuned by the careful design of both PNPs and their support. Photoanodes designed by Moskovits and coworkers harvest light through array of aligned Au nanorods partially capped with TiO₂. In the plasmonic electrochemical cell reported by the Moskovits group in 2012, a cobalt-based oxygen evolution catalyst (Co-OEC) is deposited on exposed regions of PNPs.³⁷² Au nanorods can be excited by visible light to form hot electrons which are then collected at the Schottky junction and transferred to a platinum counter-electrode, followed by hydrogen evolution at its surface. The holes thus formed on the Au NPs are filled in by electrons formed by oxidation of water catalyzed on the surface of the cobalt oxygen evolution catalyst. Devices with Co-OEC exhibit excellent photocurrents as the oxidation catalyst act as a charge carrier mediator at the interface of the PNPs and the solution, increasing the charge transfers through the device. The role of each component of the photoanodes were subsequently confirmed by studying another Pt/TiO₂/Co-OEC@Au photocatalyst developed by Moskovits et al. ⁴⁵ TiO₂ was found not to participate in the hydrogen production process but only act as an electron filter, photoexcited electrons transfer from the Au nanorods to the platinum NPs through TiO₂ without transformation. Similarities between the visible region of the device extinction spectrum, dominated by the SPR band of Au PNPs, and the photoelectrochemical action

spectrum were also observed, endorsing the mechanism initially proposed. Plasmonmediated hot electrons are created by excitation of Au NPs and then injected in TiO₂ and Pt components for hydrogen evolution while photogenerated holes are extracted by the cobalt-based oxidation catalyst. TiO₂@Au nanodumbbells were reported in 2016 by the same group as an alternative to TiO₂ semi-coated Au nanorods with Co-OEC.³⁷³ Moskovits's group controlled the orientation and anisotropic growth of TiO₂ onto Au nanorods using surface-capping agents as soft template and obtained TiO₂-tipped PNPs exhibiting enhanced hydrogen production compared to counterpart core-shell structures. Addition of a co-catalyst on Au@TiO₂ for light-driven water splitting has also been investigated by Tanaka's group.³⁷⁴ The Ni-modified Au@TiO₂ catalyst proposed absorbed light *via* Au NPs, hot electrons are then injected in TiO₂ CB and reduce protons to form hydrogen at the surface of NiOx NPs.

Engineering the morphology of TiO₂ supports can also enhance the efficiency of Audecorated TiO₂ nanostructures. TiO₂ nanotubes arrays decorated with Au NPs of various shapes were reported extensively. Au nanospheres and nanorods deposited by Li and coworkers on the surface of TiO₂ nanowire arrays improved the photocatalytic activity in the UV and visible regions respectively.³⁷⁵ Therefore by coating TiO₂ wires with a mixture of Au nanospheres and nanorods, increased water splitting photoactivity across the entire UV-visible region was observed. Misawa *et al.* investigated three-dimensional TiO₂ structures loaded with Au PNPs.³⁷⁶ Deposited Au NPs on the walls of TiO₂ nanotunnels exhibited enhanced photocurrent generation compared to conventional two-dimensional devices due to the large specific area and high electron mobility of the hollowed TiO₂ phase (Figure 3-6).



Figure 3-6 - Schematics of the Au-NP fabrication procedure via chemical reduction. Reproduced from Ref. ³⁷⁶with permission from The Royal Society of Chemistry.

The Wang group has also designed visible light responsive Au NPs coated TiO₂ nanotubes for catalytic water splitting.³⁷⁷ Attractive properties of tubular one-dimensional TiO₂ loaded with PNPs for photodriven reactions could be explained by optical confinement effects.³⁷⁸ Diffusion of the hot electrons being constrained in TiO₂ walls, charge carrier separation efficiency increases and life time of charge carrier is extended. Guo *et al.* proposed an Au/TiO₂/Au electrode formed by aligned TiO₂ nanosheets with Au NPs deposited on both sides.³⁷⁹ The device showed improved photocurrent in the visible region compared to core-shell structures due to the SPR coupling between Au NPs. The spatial arrangement and the interparticle spacing of the PNPs allows fine tuning of this coupling and optimize the photogeneration of e-h pairs. Interestingly, the Zheng group observed that Au NPs embedded in TiO₂ outperform electrodes formed by Au NPs deposited on TiO₂.³⁸⁰ Simulations showed that the local electric field in the semiconductor is more intense near PNPs for Au-in-TiO₂ compared to Au-on-TiO₂ devices. Therefore, higher light absorption

and enhancement of charge carrier generation are obtained with Au NPs embedded in semiconductor matrix, despite the absence of direct contact between PNPs and the liquid phase. Kang and coworkers proposed to use photonic crystals (PC) and slow photon effect to enlarge absorption spectrum of photocatalyst in the visible region by tuning the SPR response.³⁸¹ "Slow light" in photonic crystals and its attractiveness for photochemistry has been reported by several groups³⁸² and has been used in photocatalysis towards the generation of long-lived charge carriers.³⁸³ Slow photons are observed when light interacts with the periodic dielectric structure of TiO₂ PCs and photons propagate at reduced velocity through ordered PCs. Therefore when the SPR band of Au NPs deposited on TiO₂ bi-layer structure, made of nanorod arrays and PCs, overlaps the slow photon effect region light can be harvested by the TiO₂ photonic crystals, and not only the PNPs. By engineering the size of the PCs to match the frequency of the SPR, the number of hot electrons photogenerated and injected in the TiO₂ nanorods CB was steeply increased.

Tuning of the semiconductor energy levels has also been investigated to enhance photocatalytic activity. The Wang group reported that the addition of Cu_2O , a semiconductor featuring a small band gap, enhanced light-harvesting and improved charge carrier separation of Au@TiO₂ electrodes.³⁸⁴ Cu₂O is known for its appealing photocatalytic properties but suffers from decomposition by photocorrosion.³⁸⁵

Wang *et al.* designed a sandwich-like Au@TiO₂/Al₂O₃/Cu₂O electrode (Figure 3-7) where Cu₂O is protected by TiO₂ and promotes hydrogen evolution at its surface. The Al₂O₃ layer between Au@TiO₂ and Cu₂O increases the interfacial charge separation and the sensitivity of the device. Other methods such as nitrogen doping³⁸⁶ have been used to lower the band gap of TiO₂ by creating localized state lower in energy and thus promote charge carrier separation.³⁸⁷



Figure 3-7 - (left) Energy level diagram superimposed on a schematic of an individual unit of the plasmonic solar water splitter, showing the proposed processes occurring in its various parts and in energy space. CB, conduction band; VB, valence band; EF, Fermi energy. Reprinted by permission from Macmillan Publishers Ltd: NATURE NANOTECHNOLOGY (reference ³⁸⁸), copyright 2013. (right) Schematic diagram of excitation and separation of electrons and holes on TiO₂-1 wt% Au@TiO₂/Al₂O₃/Cu₂O heterostructure photoelectrodes in PEC system. Reproduced from Ref ³⁸⁴ with permission of The Royal Society of Chemistry.

3.4.2 Silver nanostructures on titanium dioxide

AgNPs@TiO₂ were first reported to be active photocatalysts using near UV light by the Awazu group in 2008.¹⁰⁴ They featured a seven-fold activity increase compared to bare TiO₂ for the degradation of methylene blue. Key to their design, was the protection of the Ag NP within an SiO₂ layer to prevent oxidation. Interestingly authors coined the term "plasmonic photocatalytic" in this report. Linic and coworkers synthesized various shaped Ag nanostructures deposited onto TiO₂ and applied them towards the decomposition of methylene blue using visible light.³⁸⁹ They observed a sharp increase of activity compared to bare TiO₂ and showed that rational control of shape and size, and thus change in SPR,

resulted in a modification of the wavelength at which photoactivation occurs. Ag NPs, both in supported and unsupported forms, have otherwise been used for organic transformations, including alkene epoxidation, and carbonyl hydrogenation.^{209, 362, 390} The same group applied this principle to the PEC water splitting, using Ag nanocubes onto nitrogen-doped TiO₂. They demonstrated that Ag nanocubes where able to favor the lightinduced formation of charge carriers at the nearby semiconductor surface and allowed a 10-fold increase in photocurrent.³⁹¹ Interestingly Au NPs in a similar setup showed only small activity enhancement. The mismatch between the Au NP SPR band and the semiconductor absorption was evoked to explain the small catalytic improvement while a large absorption spectrum overlap exits between Ag nanocubes and TiO₂, featuring a higher catalytic activity. Further to these discoveries, researchers explored the morphology of the semiconductor for this reaction and deposited Ag NPs onto TiO₂ nanotubes³⁹² and TiO₂ nanosheets³⁹³ to afford catalysis enhancement of 3.3 and 8.5 respectively, compared to the corresponding bare TiO₂ materials. Finally the group of Lai designed TiO₂ nanotube arrays, organized in a parallel fashion and vertically on a substrate, using an electrochemical anodization technique.³⁹⁴ They deposited Ag NPs on these structures using sonication and observed a 15 fold increase in the water splitting activity under visible light (Figure 3-8). Using a similar synthetic procedure, Li and coworkers developed photoelectrodes based on Ag quantum dots decorated TiO₂ nanotube arrays.³⁹⁵ The advantages of the nanotube array for PEC reside in a greatly enhanced specific surface and a faster charge transfer due to the coherent orientation of all the tubes.



Figure 3-8 - Synthetic procedure for accessing TiO2 nanotube vertical arrays, followed by the deposition of Ag NPs. Reproduced from Ref ³⁹⁴ with permission of The Royal Society of Chemistry.

3.4.3 Copper nanoparticles on titanium dioxide

The development of Cu PNPs for photocatalytic applications has been slower than for the other coinage metals.²³⁵ Indeed Cu NPs readily reacts with oxygen under atmospheric conditions to form an oxide layer preventing access to the active Cu(0) surface, and deeply affecting the optical properties.³⁹⁶ The group of Van Duyne studied the effect of Cu oxide layer on Cu(0) NPs and demonstrated that it causes shifting and damping of the plasmonic properties.⁷¹ Cu(0) however is of great interest in the context of photocatalytic device manufacturing as it possesses excellent optical properties at the nanoscale, it is an earth-abundant element, and it is already heavily used in electronics. In 2013, the group of Linic reported the first application of plasmonically active Cu(0) NPs in catalysis, for the reaction

of propylene epoxidation.²³⁵ Using *in situ* ultra violet extinction spectroscopy, they were able to prove that, under light irradiation at the NPs SPR wavelength, the oxide layer reduced and the particles were able to perform the selective formation of propylene oxide. Cu(0) NPs on TiO₂ was first reported to performed PEC water splitting in 2015. In this scheme, Cho and coworkers performed the reaction under inert conditions to ensure Cu would not oxidize. Cu(0) NPs of less than 5 nm, dispersed on TiO₂ were affording stable production of H₂ from water splitting, using glycerol as a hole scavenger.³⁹⁷

3.5 Conclusion

Photocatalytic water splitting is an attractive pathway for the generation of hydrogen and could contribute to the development of more sustainable energy sources by exploiting sunlight instead of producing H₂ from fossil resources. Semiconductors have proven to exhibit photocatalytic properties but they can be activated by UV irradiation only whereas a cost-effective efficient solar-to-hydrogen conversion system requires catalyst with visible light response. PNPs have shown to be efficient catalysts to drive versatile organic transformations under visible light. Recently, their use as cocatalysts appeared to be great potential for the design of more efficient visible-light-driven water splitting systems. Low energy photoactivation of PNPs originates their characteristic optical property, the SPR, which can channel electron to the semiconductor conduction band. A number of benefits result from the synergy of PNPs with TiO₂, the two important ones being the ability to use visible light for water splitting and the limitation of the fast recombination of photogenerated charge carriers. To conceive high-performance photocatalytic devices, careful design of each component and their interface is required to maximize efficiency. Despite the substantial progress achieved towards the design of solar-driven water splitting catalyst, more work is needed to achieve industrial use of photo-induced hydrogen by water splitting considering the high running cost as well as the gas storage and transport unsolved issues. In this chapter, we highlighted the most recent results in the dynamic research field of PNP-decorated TiO₂. We have made an effort to collect the performance

of the catalysts as they were reported, but research groups tend to use different parameters to evaluate their catalysts. It would be important in the future to establish standards in the fields to allow direct comparison between systems and ensure consistency.
3.6 References

24. Zhou, D.; Chen, Z.; Gao, T.; Niu, F.; Qin, L.; Huang, Y., Hydrogen Generation from Water Splitting on Tio2 Nanotube-Array-Based Photocatalysts. *Energy Technology* **2015**, *3*(9), 888-895.

49. Fujishima, A.; Honda, K., Electrochemical Photolysis of Water at a Semiconductor Electrode. *nature* **1972**, *238*(5358), 37-38.

50. Kudo, A.; Miseki, Y., Heterogeneous Photocatalyst Materials for Water Splitting. *Chemical Society Reviews* **2009**, *38*(1), 253-278.

51. Pelaez, M.; Nolan, N. T.; Pillai, S. C.; Seery, M. K.; Falaras, P.; Kontos, A. G.; Dunlop, P. S.; Hamilton, J. W.; Byrne, J. A.; O'shea, K., A Review on the Visible Light Active Titanium Dioxide Photocatalysts for Environmental Applications. *Applied Catalysis B: Environmental* **2012**, *125*, 331-349.

59. Tang, J.; Durrant, J. R.; Klug, D. R., Mechanism of Photocatalytic Water Splitting in Tio2. Reaction of Water with Photoholes, Importance of Charge Carrier Dynamics, and Evidence for Four-Hole Chemistry. *Journal of the American Chemical Society* **2008**, *130* (42), 13885-13891.

66. Clavero, C., Plasmon-Induced Hot-Electron Generation at Nanoparticle/Metal-Oxide Interfaces for Photovoltaic and Photocatalytic Devices. *Nature Photonics* **2014**, *8* (2), 95-103.

70. Moores, A.; Goettmann, F., The Plasmon Band in Noble Metal Nanoparticles: An Introduction to Theory and Applications. *New J. Chem.* **2006**, *30*(8), 1121-1132.

76. Gellé, A.; Moores, A., Water Splitting Catalyzed by Titanium Dioxide Decorated with Plasmonic Nanoparticles. *Pure and Applied Chemistry* **2017**, *89*(12), 1817-1827.

98. Hisatomi, T.; Kubota, J.; Domen, K., Recent Advances in Semiconductors for Photocatalytic and Photoelectrochemical Water Splitting. *Chemical Society Reviews* **2014**, *43*(22), 7520-7535.

103. Tian, Y.; Tatsuma, T., Mechanisms and Applications of Plasmon-Induced Charge Separation at Tio2 Films Loaded with Gold Nanoparticles. *Journal of the American Chemical Society* **2005**, *127*(20), 7632-7637.

104. Awazu, K.; Fujimaki, M.; Rockstuhl, C.; Tominaga, J.; Murakami, H.; Ohki, Y.; Yoshida, N.; Watanabe, T., A Plasmonic Photocatalyst Consisting of Silver Nanoparticles Embedded in Titanium Dioxide. *J. Am. Chem. Soc.* **2008**, *130*(5), 1676-1680.

114. Garnett, J. M., Colours in Metal Glasses and in Metallic Films. *Philos. Trans. R. Soc. London* **1904**, *203*, 359-371.

139. Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C., The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *The Journal of Physical Chemistry B* **2003**, *107*(3), 668-677.

nanoparticles

144. Liz-Marzan, L. M., Tailoring Surface Plasmons through the Morphology and Assembly of Metal Nanoparticles. Langmuir 2006, 22(1), 32-41.

149. Daniel, M.-C.; Astruc, D., Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology. Chemical reviews 2004, 104(1), 293-346.

209. Landry, M. J.; Gellé, A.; Meng, B. Y.; Barrett, C. J.; Moores, A., Surface-Plasmon-Mediated Hydrogenation of Carbonyls Catalyzed by Silver Nanocubes under Visible Light. ACS Catalysis 2017, 7(9), 6128-6133.

235. Marimuthu, A.; Zhang, J.; Linic, S., Tuning Selectivity in Propylene Epoxidation by Plasmon Mediated Photo-Switching of Cu Oxidation State. Science 2013, 339 (6127), 1590-1593.

344. Gu, J.; Yan, Y.; Krizan, J. W.; Gibson, Q. D.; Detweiler, Z. M.; Cava, R. J.; Bocarsly, A. B., P-Type Curho2 as a Self-Healing Photoelectrode for Water Reduction under Visible Light. Journal of the American Chemical Society 2014, 136(3), 830-833.

345. Cartlidge, E., Saving for a Rainy Day. American Association for the Advancement of Science: 2011.

346. Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S., Solar Water Splitting Cells. *Chemical reviews* **2010**, *110*(11), 6446-6473.

347. Fechete, I.; Wang, Y.; Védrine, J. C., The Past, Present and Future of Heterogeneous Catalysis. Catalysis Today 2012, 189(1), 2-27.

348. Dholam, R.; Patel, N.; Adami, M.; Miotello, A., Hydrogen Production by Photocatalytic Water-Splitting Using Cr-or Fe-Doped Tio2 Composite Thin Films Photocatalyst. International Journal of Hydrogen Energy 2009, 34(13), 5337-5346.

349. Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y., Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides. science 2001, 293 (5528), 269-271.

350. Youngblood, W. J.; Lee, S.-H. A.; Maeda, K.; Mallouk, T. E., Visible Light Water Splitting Using Dye-Sensitized Oxide Semiconductors. Accounts of chemical research **2009**, *42*(12), 1966-1973.

351. Momeni, M. M.; Ghayeb, Y., Photoelectrochemical Water Splitting on Chromium-Doped Titanium Dioxide Nanotube Photoanodes Prepared by Single-Step Anodizing. Journal of Alloys and Compounds 2015, 637, 393-400.

352. Chen, X.; Mao, S. S., Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chemical reviews* **2007**, *107*(7), 2891-2959.

353. Chen, J.-J.; Wu, J. C.; Wu, P. C.; Tsai, D. P., Plasmonic Photocatalyst for H2 Evolution in Photocatalytic Water Splitting. The Journal of Physical Chemistry C 2011, 115(1), 210-216.

354. Hartland, G. V., Optical Studies of Dynamics in Noble Metal Nanostructures. Chemical Reviews 2011, 111(6), 3858-3887.

355. Warren, S. C.; Thimsen, E., Plasmonic Solar Water Splitting. *Energy & Environmental Science* **2012**, *5*(1), 5133-5146.

356. Chen, H. M.; Chen, C. K.; Liu, R.-S.; Zhang, L.; Zhang, J.; Wilkinson, D. P., Nano-Architecture and Material Designs for Water Splitting Photoelectrodes. *Chemical Society Reviews* **2012**, *41*(17), 5654-5671.

nanoparticles

357. Baffou, G.; Quidant, R., Nanoplasmonics for Chemistry. *Chemical Society Reviews* **2014**, *43*(11), 3898-3907.

358. Chen, X.; Liu, L.; Huang, F., Black Titanium Dioxide (Tio2) Nanomaterials. *Chemical* Society Reviews 2015, 44(7), 1861-1885.

359. Gratzel, M., Photoelectrochemical Cells. *Nature* **2001**, *414*(6861), 338-345.

360. Linic, S.; Aslam, U.; Boerigter, C.; Morabito, M., Photochemical Transformations on Plasmonic Metal Nanoparticles. *Nature materials* **2015**, *14*(6), 567-576.

361. Jain, P. K.; Huang, X.; El-Sayed, I. H.; El-Sayed, M. A., Review of Some Interesting Surface Plasmon Resonance-Enhanced Properties of Noble Metal Nanoparticles and Their Applications to Biosystems. *Plasmonics* **2007**, *2*(3), 107-118.

362. Linic, S.; Christopher, P.; Ingram, D. B., Plasmonic-Metal Nanostructures for Efficient Conversion of Solar to Chemical Energy. *Nat. Mater.* **2011**, *10*(12), 911.

363. Long, R.; Li, Y.; Song, L.; Xiong, Y., Coupling Solar Energy into Reactions: Materials Design for Surface Plasmon-Mediated Catalysis. Small 2015, 11(32), 3873-3889.

364. Halas, N. J.; Lal, S.; Chang, W. S.; Link, S.; Nordlander, P., Plasmons in Strongly Coupled Metallic Nanostructures. Chemical Reviews 2011, 111(6), 3913-3961.

365. Bai, S.; Yin, W.; Wang, L.; Li, Z.; Xiong, Y., Surface and Interface Design in Cocatalysts for Photocatalytic Water Splitting and Co2 Reduction. RSC advances 2016, 6(62), 57446-57463.

Jiang, W.; Li, Z.; Xiong, Y., Surface and Interface Engineering in 366. Bai, S.; Photocatalysis. *ChemNanoMat* **2015**, *1*(4), 223-239.

367. DuChene, J. S.; Sweeny, B. C.; Johnston-Peck, A. C.; Su, D.; Stach, E. A.; Wei, W. D., Prolonged Hot Electron Dynamics in Plasmonic-Metal/Semiconductor Heterostructures with Implications for Solar Photocatalysis. Angewandte Chemie International Edition **2014**, *53*(30), 7887-7891.

368. Tian, Y.; Tatsuma, T., Plasmon-Induced Photoelectrochemistry at Metal Nanoparticles Supported on Nanoporous Tio 2. Chemical communications 2004, (16), 1810-1811.

369. Yu, K.; Tian, Y.; Tatsuma, T., Size Effects of Gold Nanaoparticles on Plasmon-Induced Photocurrents of Gold-Tio 2 Nanocomposites. Physical Chemistry Chemical Physics 2006, 8(46), 5417-5420.

370. Wang, C. L.; Astruc, D., Nanogold Plasmonic Photocatalysis for Organic Synthesis and Clean Energy Conversion. *Chemical Society Reviews* **2014**, *43*(20), 7188-7216.

371. Lang, X. J.; Chen, X. D.; Zhao, J. C., Heterogeneous Visible Light Photocatalysis for Selective Organic Transformations. *Chemical Society Reviews* **2014**, *43*(1), 473-486.

372. Lee, J.; Mubeen, S.; Ji, X. L.; Stucky, G. D.; Moskovits, M., Plasmonic Photoanodes for Solar Water Splitting with Visible Light. Nano Letters 2012, 12(9), 5014-5019.

373. Wu, B.; Liu, D.; Mubeen, S.; Chuong, T. T.; Moskovits, M.; Stucky, G. D., Anisotropic Growth of Tio2 onto Gold Nanorods for Plasmon-Enhanced Hydrogen Production from Water Reduction. Journal of the American Chemical Society 2016, 138(4), 1114-1117.

374. Tanaka, A.; Teramura, K.; Hosokawa, S.; Kominami, H.; Tanaka, T., Visible Light-Induced Water Splitting in an Aqueous Suspension of a Plasmonic Au/Tio 2 Photocatalyst with Metal Co-Catalysts. Chemical science 2017, 8(4), 2574-2580.

nanoparticles

375. Pu, Y.-C.; Wang, G.; Chang, K.-D.; Ling, Y.; Lin, Y.-K.; Fitzmorris, B. C.; Liu, C.-M.; Lu, X.; Tong, Y.; Zhang, J. Z., Au Nanostructure-Decorated Tio2 Nanowires Exhibiting Photoactivity across Entire Uv-Visible Region for Photoelectrochemical Water Splitting. *Nano letters* **2013**, *13*(8), 3817-3823.

376. Takakura, R.; Oshikiri, T.; Ueno, K.; Shi, X.; Kondo, T.; Masuda, H.; Misawa, H., Water Splitting Using a Three-Dimensional Plasmonic Photoanode with Titanium Dioxide Nano-Tunnels. Green Chemistry 2017, 19(10), 2398-2405.

377. Zhang, Z.; Zhang, L.; Hedhili, M. N.; Zhang, H.; Wang, P., Plasmonic Gold Nanocrystals Coupled with Photonic Crystal Seamlessly on Tio2 Nanotube Photoelectrodes for Efficient Visible Light Photoelectrochemical Water Splitting. Nano *Letters* **2013**, *13*(1), 14-20.

378. Roy, P.; Berger, S.; Schmuki, P., Tio2 Nanotubes: Synthesis and Applications. Angewandte Chemie International Edition 2011, 50(13), 2904-2939.

379. Wang, H.; You, T.; Shi, W.; Li, J.; Guo, L., Au/Tio2/Au as a Plasmonic Coupling Photocatalyst. The Journal of Physical Chemistry C2012, 116(10), 6490-6494.

380. Zhan, Z.; An, J.; Zhang, H.; Hansen, R. V.; Zheng, L., Three-Dimensional Plasmonic Photoanodes Based on Au-Embedded Tio2 Structures for Enhanced Visible-Light Water Splitting. ACS applied materials & interfaces 2014, 6(2), 1139-1144.

381. Zhang, X.; Liu, Y.; Lee, S.-T.; Yang, S.; Kang, Z., Coupling Surface Plasmon Resonance of Gold Nanoparticles with Slow-Photon-Effect of Tio 2 Photonic Crystals for Synergistically Enhanced Photoelectrochemical Water Splitting. Energy & Environmental Science 2014, 7(4), 1409-1419.

Baba, T., Slow Light in Photonic Crystals. *Nature photonics* **2008**, *2*(8), 465-473. 382.

383. Chen, J. I.; von Freymann, G.; Choi, S. Y.; Kitaev, V.; Ozin, G. A., Amplified Photochemistry with Slow Photons. Advanced Materials 2006, 18(14), 1915-1919.

Peerakiatkhajohn, P.; Butburee, T.; Yun, J.-H.; Chen, H.; Richards, R. M.; Wang, L., A 384. Hybrid Photoelectrode with Plasmonic Au@ Tio 2 Nanoparticles for Enhanced Photoelectrochemical Water Splitting. Journal of Materials Chemistry A 2015, 3 (40), 20127-20133.

385. Valdes, A.; Brillet, J.; Grätzel, M.; Gudmundsdottir, H.; Hansen, H. A.; Jonsson, H.; Klüpfel, P.; Kroes, G.-J.; Le Formal, F.; Man, I. C., Solar Hydrogen Production with Semiconductor Metal Oxides: New Directions in Experiment and Theory. Physical *Chemistry Chemical Physics* **2012**, *14*(1), 49-70.

386. Pany, S.; Naik, B.; Martha, S.; Parida, K., Plasmon Induced Nano Au Particle Decorated over S, N-Modified Tio2 for Exceptional Photocatalytic Hydrogen Evolution under Visible Light. ACS applied materials & interfaces **2014**, 6(2), 839-846.

387. Sathish, M.; Viswanathan, B.; Viswanath, R.; Gopinath, C. S., Synthesis, Characterization, Electronic Structure, and Photocatalytic Activity of Nitrogen-Doped Tio2 Nanocatalyst. Chemistry of materials 2005, 17(25), 6349-6353.

388. Mubeen, S.; Lee, J.; Singh, N.; Krämer, S.; Stucky, G. D.; Moskovits, M., An Autonomous Photosynthetic Device in Which All Charge Carriers Derive from Surface Plasmons. *Nature nanotechnology* **2013**, *8*(4), 247-251.

389. Christopher, P.; Ingram, D. B.; Linic, S., Enhancing Photochemical Activity of Semiconductor Nanoparticles with Optically Active Ag Nanostructures: Photochemistry

nanoparticles

Mediated by Ag Surface Plasmons. *The Journal of Physical Chemistry C* **2010**, *114* (19), 9173-9177.

390. Christopher, P.; Linic, S., Shape-and Size-Specific Chemistry of Ag Nanostructures in Catalytic Ethylene Epoxidation. *ChemCatChem* **2010**, *2*(1), 78-83.

391. Ingram, D. B.; Linic, S., Water Splitting on Composite Plasmonic-Metal/Semiconductor Photoelectrodes: Evidence for Selective Plasmon-Induced Formation of Charge Carriers near the Semiconductor Surface. *Journal of the American Chemical Society* **2011**, *133*(14), 5202-5205.

392. Wu, F.; Hu, X.; Fan, J.; Liu, E.; Sun, T.; Kang, L.; Hou, W.; Zhu, C.; Liu, H., Photocatalytic Activity of Ag/Tio 2 Nanotube Arrays Enhanced by Surface Plasmon Resonance and Application in Hydrogen Evolution by Water Splitting. *Plasmonics* **2013**, *8* (2), 501-508.

393. Liu, E.; Kang, L.; Yang, Y.; Sun, T.; Hu, X.; Zhu, C.; Liu, H.; Wang, Q.; Li, X.; Fan, J., Plasmonic Ag Deposited Tio2 Nano-Sheet Film for Enhanced Photocatalytic Hydrogen Production by Water Splitting. *Nanotechnology* **2014**, *25*(16), 165401.

394. Ge, M.-Z.; Cao, C.-Y.; Li, S.-H.; Tang, Y.-X.; Wang, L.-N.; Qi, N.; Huang, J.-Y.; Zhang, K.-Q.; Al-Deyab, S.; Lai, Y.-K., In Situ Plasmonic Ag Nanoparticle Anchored Tio 2 Nanotube Arrays as Visible-Light-Driven Photocatalysts for Enhanced Water Splitting. *Nanoscale* **2016**, *8*(9), 5226-5234.

395. Lian, Z.; Wang, W.; Xiao, S.; Li, X.; Cui, Y.; Zhang, D.; Li, G.; Li, H., Plasmonic Silver Quantum Dots Coupled with Hierarchical Tio 2 Nanotube Arrays Photoelectrodes for Efficient Visible-Light Photoelectrocatalytic Hydrogen Evolution. *Scientific reports* **2015**, *5*(1), 1-10.

396. Chan, G. H.; Zhao, J.; Hicks, E. M.; Schatz, G. C.; Van Duyne, R. P., Plasmonic Properties of Copper Nanoparticles Fabricated by Nanosphere Lithography. *Nano letters* **2007**, *7*(7), 1947-1952.

397. Kum, J. M.; Park, Y. J.; Kim, H. J.; Cho, S. O., Plasmon-Enhanced Photocatalytic Hydrogen Production over Visible-Light Responsive Cu/Tio2. *Nanotechnology* **2015**, *26* (12), 125402.

Transition

Plasmon mediated nanocatalysis is an emerging field and reports of free-standing plasmonic nanocatalysts for organic transformations are still rare. Herein we report the first plasmon-driven oxidation and hydrogenation of carbonyls. This chapter describes how Ag NC catalysts were synthesized, their characterization and use for the oxidation and hydrogenation of carbonyls in both batch and flow.



This chapter is based upon two published articles and unpublished data. The American Chemical Society and Elsevier granted permission to reprint the published article, as did all co-authors.

Michael J. Landry, Alexandra Gellé, Beryl Y. Meng, Christopher J. Barrett, and Audrey Moores, Surface-Plasmon-Mediated Hydrogenation of Carbonyls catalyzed by Silver Nanocubes under Visible Light, ACS Catalysis, 2017, 7, 9, 6128-6133.

Nicolas Brodusch, Hendrix Demers, Alexandra Gellé, Audrey Moores, and Raynald Gauvin, Electron energy-loss spectroscopy (EELS) with a wold-field emission scanning electron microscope at low accelerating voltage in transmission mode, Ultramicroscopy, 2019, 203, 21-36.

4.1 Introduction

The potential of Ag as an oxidation catalyst has been first demonstrated more than a century ago and since, numerous applications of Ag complexes or NPs for oxidation chemistry have been reported.³⁹⁸⁻⁴⁰⁰ Ag-based nanocatalysts often require high temperatures and long reaction times under thermal conditions.³⁹⁸⁻⁴⁰⁰ Ag is nowadays commonly employed for two major industrial applications, namely the formation of ethylene oxide and the one of formaldehyde. Ag also proved to be a key hydrogenation catalyst for the fragrance, flavor and pharmaceutical industries, owing to its ability to selectively reduce unsaturated carbonyls, even though C=C reduction is more thermodynamically favorable than the one of C=0.⁴⁰¹ However harsh conditions, up to 30 atm and high temperatures, were reported.^{402, 403} While stochiometric compounds like NaBH₄ and LiAlH₄ have been used efficiently to reduce carbonyls, catalytic alternatives that generates less waste and hazards are more desirable.

For this work, Ag NCs were selected for their enhanced SPR properties arising from their sharp vertices.⁴⁰⁴⁻⁴⁰⁶ These features are well-known to create "hot spots" where SPR is greatly enhanced.^{360, 363} Yet, only a few experimental studies have drawn attention on the morphology-dependent activity of plasmon-mediated catalysts.⁴⁰⁷ Linic and coworkers studied reaction selectivity as a function of the morphology of Ag PNPs. Using ethylene epoxidation as a model, they reported an enhanced selectivity toward ethylene oxide using NCs dominated by (100) facets compared to nanospheres featuring (111) facets.⁴⁰⁶ A study by the Camargo group on the shape-dependence reactivity of Ag PNPs towards the oxidation of *p*-aminothiophenol to *p*,*p*/-dimercaptoazobenzene by O₂ revealed a contradicting trend. In their case, the plasmon-mediated activity increased with the number of (111) facets,⁴⁰⁸ i.e. triangular prisms and quasi-spheres exhibiting (111) facets. They rationalized this trend by suggesting that the weaker interaction of O₂ with (111) facets, as compared to the (100) ones (i.e. cubes and wires), favored its easier desorption following excitation *via* transfer of hot electrons and thus drove the reaction forward. Zhang and

Wang investigated the intrinsic facet-dependent catalytic activities of Au NPs and shed light on the key contribution of undercoordinated surface atoms in high-index facets for the hydrogenation of 4-nitrothiophenol using sodium borohydride.⁴⁰⁹

4.2 Synthesis of the nanocatalysts

Synthesis of Ag NPs is traditionally achieved *via* polyol process, by reducing precursor Ag nitrate salt (AgNO₃) with hot ethylene glycol which is also used as the solvent.¹⁷³ The active reductant species was found to be glycoaldehyde, formed *via in situ* oxidation of ethylene glycol.¹⁷³ Small molecules or polymers such as polyvinylpyrrolidone (PVP) are usually employed as capping agents to stabilize the NPs obtained.⁴¹⁰ Quasi-spherical NPs are usually formed under such conditions. To obtain the desired Ag NCs or other non-spherical morphologies, an additive and modifications to the protocol are required.¹⁷⁸ Several authors reported the use of various kinds of additives to form NCs but their role in the NPs synthesis remained unclear and overlooked for years.⁴¹¹⁻⁴¹³ Because, the reducing agent and capping agent are distinct species, the polyol method allows more control over reaction parameters. This is in contrast to early citrate-based methods for which citrate is used as both reducing and capping agent. There, the reaction happens faster and leads to less control over the morphology. Specifically highly faceted morphologies cannot be accessed.

For this study, Ag NCs were by the polyol method formed upon addition of HCl and using PVP as a ligand. HCl is the most commonly employed and easiest additive for the formation of Ag NCs. Various hypothesis about the role of HCl and PVP in directing the formation of cubes have been proposed^{175, 176, 411, 414-416} but it is only recently that the Rioux group conducted a joint theoretical-experimental studies and analyzed the influence of PVP, Cl⁻ and H⁺ during NPs growth in an effort to elucidate the role of the different reagents and the mechanism leading to the formation of sharp and monodisperse Ag NCs with (100) facets.^{179,417}

One of the main challenges when investigating the formation of NPs is the access to

technology permitting to do *in situ* and in real time measurements. Despite the formation of NCs occurring over long hours, several key steps happen within minutes in the early stages of the reactions, based on several color changes observed.

Pioneer studies predominantly attributed control over the morphology of Ag NCs to PVP preferential binding to Ag (100) facets rather than to Ag (111). Observations made by several groups when varying the concentration of PVP and its molecular weight and DFT calculations, suggested that the growth of the cubes was driven by (100) facet blocking, due to PVP binding more strongly to Ag(100) than Ag(111). Pioneer studies suggested that preferential binding of PVP on (100) facets happened *via* the 2-pyrrolidone ring and led to thermodynamically-controlled synthesis of anisotropic Ag PNPs.^{175, 176}

Yet, more recent studies showed that the binding preference is not substantial enough to fully explain how the presence of PVP alone favors the formation of cubes.^{175, 176, 415, 417} It therefore became clearer that the additive, HCl, was playing a pivotal role in the formation of Ag NCs even though it had been rarely mentioned in the previously reported mechanisms.

XRD and EDX *in situ* experiments conducted by the Peng and Sangaru groups coworkers allowed to identify the presence of AgCl cubes during the formation of Ag NCs.^{418,419} Many questions remained about the formation of Ag(0) NPs in presence of HCl and PVP, and how AgCl was formed then dismantled until a study by the Rioux and coworkers.

SEM and EDS elemental mapping of Ag and Cl of the solids formed at different time points (from a few minutes up to 28h) showed a rapid formation of large AgCl NCs. Subsequently, Ag NCs are formed by reduction by ethylne glycol of free Ag⁺ and ions released from the AgCl NCs. Their findings suggest that HNO₃ is formed *in situ* and etches the Ag seeds formed with in the first minutes of the reaction.(Figure 4-1) The kinetics of the reduction of Ag+ would also be controlled by the presence of H⁺. The authors reported that HNO₃ slows down the reduction and therefore promotes the formation of well-defined Ag NCs. It is

worth highlighting that both H⁺ and Cl⁻ therefore play a role in the synthesis of AgNCs, as experiments by the Rioux group revealed that the presence of only one of these ions lead to a mix of shapes, and PVP ensures the stability of the structure obtained. ¹⁷⁹



Figure 4-1 - Mechanism for the formation of Ag NCs via AgCl NCs proposed by Rioux and coworkers. Schematic of 28 h growth process of Ag nanocubes with four identified stages: (i) initial formation of AgCl nanocubes; (ii) reduction of AgNO₃ to Ag seeds and their subsequent etching by in situ formed HNO₃; (iii) dissolution of AgCl along with AgNO₃ reduction; and (iv) the continued growth of Ag nanocubes along with AgCl disappearance. From ref ¹⁷⁹

Some studies also observed that the morphology and aspect ratio of the NPs obtained depended on the amount and nature of halides ions employed as additives and the relative quantities of reagents used. For example, varying the initial concentration of Ag precursor, while keeping the ratio Ag/PVP the same, led to the formation of Ag nanowires instead of NCs.¹⁷⁷ Yet using NaBr instead of HCl led to the growth of right bipyramids.¹⁷⁰ Moreover, for a bromide ion concentration twice higher, nanobars were obtained.¹⁷¹

While protocols to obtain Ag NCs were already reported, the synthesis of PNPs is extremely sensitive to the environmental conditions and the purity of the reagents used. Initial trials performed in our laboratory using protocols reported by the Xia and Linic groups failed to provide the desired NPs, and either seeds or micrometer particles were

usually obtained. Informal exchange with the Rioux group confirmed that such protocols typically needed reoptimisation in a specific lab context.

Several modifications to the protocol were made in order to develop a procedure that leads to the formation of Ag NPs with the designed characteristics in our laboratory set up. First, PVP with different molecular weight were used but none led to the formation of cubic morphologies. While ethylene glycol had been mostly reported for the formation of Ag NCs, 1,5-pentanediol was suggested as a potential solvent and reducing agent featuring a different reduction rate.¹⁷² Our first trials with ethylene glycol had revealed that the reaction may be happening too fast considering the color changes observed within the first minutes following the addition of all the reagents.

1,5-pentanediol was used to replace ethylene glycol as a solvent while keeping the quantities of reagents similar to the protocols reported by the Xia and Linic groups. The color changes observed during the initial phase of the reaction were similar to the one reported by the Xia group and then aliquots of the solution at different time points were analyzed by SEM to follow the formation of NPs over time and determine the reaction time that would lead to the formation of Ag NCs. As expected, the reaction happened quite slowly as even after 24h, only small quasi-spherical NPs were produced, while Xia and Linic coworkers reported the formation of hundred-nanometer size NCs after 24 h. When letting the reaction run longer in 1,5-pentanediol, long nanowires with (111) facets were obtained in a mixture with large quasi-spherical NPs (27 h). Longer and larger NPs were observed after 30 h.(Figure 4-2) 1,5-pentanediol therefore seemed to slow down the kinetics of the reaction but the formation of NPs with predominantly (111) facets was not observed in our case.



Figure 4-2 – SEM images of NPs samples when using 1,5-pentanediol as a reducing agent at different time points (19, 21, 24, 27 et 30 h) after being centrifuged in ethanol

A similar protocol was then employed using ethylene glycol as a solvent instead of 1,5pentanediol. First, we noticed that different bottle of extra pure ethylene glycol (anhydrous, 99.8%) led to variations in the observations made when making the stock solutions and within the first minutes of the reactions. Indeed, some AgNO₃ in ethylene glycol stock solution turned slightly pink after 5-20 min while the vial was covered in foil at room temperature in the shaker waiting for the salt to dissolved, indicating that reduction was taking place already. The speed and intensity at which the reduction happened varied depending on the ethylene glycol bottle used. The bottles for which the stock solution of AgNO₃ turned pink were not used for the other experiments. We hypothesized that Cl ions could be present in the solvent from trace amounts of FeCl₃ used as a catalyst for the formation of ethylene glycol. For other bottles of ethylene glycol, unusual amounts of vapors were observed, suggesting that despite being recently opened bottles with a septum in good condition and handled with care, the water content in these bottles was higher than expected. Further NMR analysis confirmed the presence of water in some extra pure ethylene glycol bottles.

Upon careful selection of the ethylene glycol, slight modifications to the protocols reported by the Xia and Linic groups were made: the reagents were let to dissolved longer before being combined and the temperature of the oil bath was increased. Unlike our initial trials, the color changes observed shortly after the addition of all the reagents were similar to the ones previously published, despite our slight modification to the protocol. Similarly to the experiments performed with 1,5-pentanediol, aliquots of the solution at different time points were analyzed by SEM.(Figure 4-3) As early as 19 h, the SEM images revealed the formation of cubic nanoparticles. After 21h, sharp and monodisperse cubes of approximately a hundred nanometer, with a few occasional rods, were observed. When the reaction was let for longer, the rounding of the NCs corners started and the number of rods increased too. After 27 et 30 hours, the morphologies observed by SEM were mostly rods and quasi-spherical with some cubic edges NPs.

This study showed that by slightly increasing the temperature of the oil bath and delaying the addition of the reagents, NCs could be obtained. Yet the reaction happened faster than previously reported (21 h compared to 24 h reported by Linic and Xia's coworkers). Moreover, the NCs seemed to outgrow themselves into more spherical and rods-like NPs, highlighting the metastability of these (100) faceted particles.



Figure 4-3 - SEM images of NPs sampled at different time point (19, 21, 24, 27 et 30 h) after being centrifuged in ethanol when using ethylene glycol as a reducing agent

We then reproduced the reaction under the same conditions but with a rapid quench followed by centrifugation and washing in ethanol after 21 h. The NPs obtained following this protocol were cubic and monodisperse as detailed in the next section, and imaging weeks later revealed that cubes suspended in ethanol after washing were still stable up to four months after the synthesis.

Our results may be used as a cautionary tale on how each laboratory environment, purity of the reagents and length of the synthesis can alter the outcomes of such demanding (111) faceted NPs.

4.3 Characterization of nanocatalysts

4.3.1 Morphology and nature of the Ag NCs

First, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and bright-field scanning transmission electron microscopy (BFSTEM) showed that most of the synthesized NPs featured a cubic morphology, with occasionally a few rod- or prism-shaped particles observed. (Figure 4-4A-C) These cubes were monodispersed with an average

length of 126 ± 12 nm, counted over 120 cubes in a TEM image. The presence of a halo was observed in several images and was attributed to the organic capping layer made of PVP.



Figure 4-4 – Images of the Ag NCs by TEM (A), SEM (B) and BFSTEM (C)

Further analysis by EDS linescans using STEM, XPS and XRD provided more information about the distribution and coordination of these elements within the nanostructure. EDS measurements on the NPs imaged by STEM confirmed the nature of the material. (Figure 4-5A-B) Ag NCs were found to contain only Ag, Cl, C and O. Importantly, no other noble metals, such as Pt, Pd, or Ru, which could also lead to the expected reduction chemistry, were detected. EDS linescans performed across the NP showed that Ag is the dominant element and is evenly present across the cube. C and O were prominently found along the edges of the cubes, thus confirming the presence of the capping layer of PVP. A small quantity of CI was also revealed by EDS. CI and Ag were found to overlap. XPS showed Ag, Cl, C, O, and N were present in the sample. (Figure 4-5C) Cl content was quantified against Ag, and CI accounts for 8 % of the subsurface inorganic material. Also, the 3d5/2 band of Ag, centered at 368.3 eV is consistent with Ag(0). Moreover, XRD diffractogram featured (111) and (200) peaks distinctive of pure Ag(0).(Figure 4-5D) Therefore, despite the presence of Cl, no evidence of AgCl was found using multiple techniques. The catalytic activity of the NCs can hence be attributed to the plasmonic behavior of Ag(0) and not the photocatalytic properties of AgCl.⁴²⁰⁻⁴²²



Figure 4-5 – BFSTEM image of the Ag NCs (A) with the corresponding EDS linescan (B), XPR spectrum (C) and XRD diffractogram (D).

The presence of CI revealed by EDS and XPS, and its nature, is consistent with the observations from the Rioux group and the role played by CI ions to direct the selective facet growth of the cubes. At the end of the reaction, they detected only Ag(0) by XRD, whereas during the course of the synthesis both AgCl and Ag(0) peak were identified.¹⁷⁹ It suggests that while AgCl is present in intermediate structures, the final NPs are made of Ag(0) with some CI ions adsorbed on the surface although in small proportion, while both XPS and XRD confirmed Ag (0) is the dominant species, with no AgCl phase observed. Our TEM-EDS measurements confirmed the presence of CI on the Ag NCs surface. This is in agreement with a study by Sangaru *et al.*,⁴¹⁸ who estimated the amount of CI to be equal to a half monolayer.

4.3.2 Optical properties of the Ag NCs

The optical properties of the plasmonic Ag NCs were characterized using UV-Vis and EELS. The measured plasmonic band is centered at 410 nm and is coherent with previously reported Ag NCs (Figure 4-6).



Figure 4-6 - UV-Vis spectrum of the Ag NCs in ethanol

In order to gain a better insight into the local effect of the of the LSPR on a specific nanoparticle, the technique of choice is EELS in a STEM. Essentially, in a STEM experiment a sample is scanned by a focused electron beam. EELS allows to analyze the energy spectrum of any such electron collected after interaction with the sample. Typically, two main types of data are available: for a given point, an energy spectrum can be provided,

while for a STEM image, one can overlay a map of EELS intensity at a given energy onto the STEM image, using a color code.¹⁴⁵ EELS allows for visualization at sub-angstrom resolution of spatial symmetries controlling the excitation of plasmonic modes at the surface of the object under scrutiny.¹⁴⁵ EELS also allows for the filtering of the signal in terms of energy, thus providing a unique view on the different symmetries of plasmonic modes as a function of the energy, with excellent energy resolution as well. What is particularly interesting for NPs with highly faceted morphologies, is the possibility to use EELS to discern the different plasmonic modes. Unlike UV-Vis spectroscopy, EELS data can be acquired by filtering by energy and therefore isolate the several modes highly faceted NPs have, and also localized the region of the NP from which plasmonic mode arises. This technique has become fairly mainstream now and many catalysis application articles nowadays feature LSPR characterization by this method.¹⁴⁶

A plasmon band centered at 410 nm (3.02 eV) was identified by UV-Vis which includes all the modes that exist for the Ag NCs. Using EELS, the edge and the corner modes of the NCs were measured separately (Figure 4-7A-B) at 3.53 and 2.95 eV respectively, which correspond to 351and 420 nm.(Figure 4-7C)



Figure 4-7 - Localized surface plasmon (LSP) energy-filtered STEM images of a 50 nm NC extracted from a spectrum image acquired with spectrometer dispersion was 0.055 eV/channel with an energy width of $\Delta E = 0.21$ eV. (a) Edge LSP with $E_f = 3.53$ eV, (b) corner LSP with $E_f = 2.95$ eV, (c) overlapped spectra extracted from the corner and edge LSPs. LSP energies determined by Gaussian fit are 3.32 and 3.53 eV for the corner and edges spectra respectively. Reproduced with permission from reference ¹⁴⁶. Copyrights 2020 Elsevier.

The values obtained by EELS for the corner and the edge modes are similar to previously reported studies by Nicoletti et al.⁴²³ They have measured LSP energies of 3.3 eV for modes localized at the edges while they reported 2.8 eV for modes located at the corner. Ding and coworkers have identified edge and corner modes of Ag NCs at 3.3 and 3.5 eV respectively.⁴²⁴

The discrepancies between the EELS values reported by various groups can be explained by the various sizes of the NPs, and the shift between the UV-Vis and EELS data is due to the different medium.⁷⁰ While NPs are deposited on a grid and surrounded by vacuum once in the STEM-EELS, the Ag NCs were suspended in a solvent for UV-Vis measurements.

4.4 Photo-nanocatalysis in batch

4.4.1 Oxydation of aldehydes (work done by Michael Landry)

 O_2 dissociation at the surface of Ag PNPs induced by indirect hot electron transfer was reported by Linic and coworkers to drive epoxidation reactions of ethylene and propylene with Ag and Cu PNPs respectively.^{234, 235}

Using similar Ag NCs, various aldehydes were oxidized into carboxylic acids in 18 h at 80 °C under a 405 nm laser irradiation in an open-air flask.(

Scheme 4-1) The corresponding carboxylic acids were obtained in moderate to high yields under these conditions.(Figure 4-8) More sterically hindered molecules featured the lowest yields. Oxidation of the corresponding alcohols to the carboxylic acids was also achieved using Ag NCs but the yields obtained were considerably lower, which can be explained by the complexity of forming the carboxylic acid from the alcohol compared to starting from the aldehyde which requires less steps.







Figure 4-8 - Scope of products obtained from SPR-enhanced oxidation of aldehydes with Ag NCs using the conditions detailed in Scheme 4-1. Reproduced with permission from reference ⁴²⁵. Copyright 2007 American Chemical Society

4.4.2 Hydrogenation of carbonyls (work done by Michael Landry)

The Halas group proved the potential of plasmon-generated hot electrons to drive hydrogenations when they demonstrated the dissociation of H₂ and D₂ at the surface of Au NPs upon irradiation at room temperature and under atmospheric pressure. As discussed previously, Ag is known for being an attractive metal to catalyze hydrogenation of carbonyls under thermal and harsh conditions.²⁷⁴ Ag NCs were therefore promising candidate for light-activated hydrogenation under mild conditions.

Using the Ag NCs under atmospheric pressure at 80 °C and with 405 nm laser irradiation showed that Ag is efficient for plasmon-driven hydrogenations under mild conditions.(Scheme 4-2) With only 1 atm of molecular hydrogen, alcohols were accessed with complete chemoselectivity for C=O over C=C reduction. Twelve carbonyls were reduced under these conditions and afforded the corresponding alcohols in moderate and high yields.(Figure 4-9) Irradiation outside of the plasmonic band did not lead to reduction of the carbonyls.

$$R_1 = R_1$$

$$R_1 = R_1$$

$$R_1 = R_1$$

$$R_1 = R_1$$

$$R_2 = H, Ar, alkyl, or alkene$$

$$H_2 (1 atm), 80^{\circ}C, 5 mol% Ag NCs OH Ad S R_1$$

$$R_1 = R_1$$

$$R_2 = H, Ar, alkyl, or alkene$$

Scheme 4-2 - Reaction conditions for the hydrogenation of carbonyls using Ag NCs



Figure 4-9 - Scope of products obtained from SPR-enhanced hydrogenation of ketones with Ag NCs using the conditions detailed in Scheme 4-2. Reproduced with permission from reference ⁴²⁵. Copyright 2007 American Chemical Society

4.5 Going with the flow

4.5.1 Introduction to continuous flow chemistry

The round-bottom flask is iconic and indispensable in research laboratories, yet it is not suited for large scale production and is being replaced by large reaction vessels and pipes in industrial settings. A recently developed technology called continuous flow has emerged as a powerful tool for organic chemists, and has the opportunity to benefit chemists working in both small-scale laboratories and larger industrial settings. Continuous flow reactors feature several advantages for large scale production and for scaling up reactions, but is also of great interest in the development of greener and safer processes.⁴²⁶⁻⁴²⁸ Despite being a recent technology for academic research, continuous flow chemistry has already received widespread attention and showed promising benefits for both research and industrial settings. The reactors, combined with long small diameter tubes and pumps, provide chemists with unique control over the reaction parameters, therefore offering more reproductible, scalable, safe and efficient options. Better mixing, energy transfer and adaptability are among the most commonly reported benefits of flow processes. Flow processes can also enhance reactivity, enable new reactions and provide access to greener reaction conditions. The potential of flow chemistry to be transformative in the field of organic chemistry goes beyond scaling up reactions. Continuous flow processes have enabled to perform reactions under conditions that were unobtainable in batch. Flow reactors offer a precise control over the reaction parameters, owing to an enhanced mass and heat transfer, which increases the efficiency and safety of the processes.⁴²⁹ Having a better control over the reaction conditions therefore enabling to use higher temperatures and concentrations, which has led to a decrease in solvent use and more sustainable processes.⁴²⁶ Many common organic transformations, which are key in field of medicinal, synthetic and photo-chemistry, have been successfully adapted to continuous flow conditions in the recent years.⁴³⁰⁻⁴³³ Batch reactors still remain the main production process in the fine-chemical and pharmaceutical industries but continuous flow is being implemented for the synthesis of commercially relevant products.434-437

Contrary to reactions done in batch, in continuous flow processes, there is a constant incoming and outcoming flow of the reaction medium, including the solvent, the reagents and the products. Such set up entails steadily addition of reagents *via* tubes and pumping, which leads to an enhanced control over the reaction conditions. Using small diameter tubes to add the reagents allows to precisely control the concentration of the reagents, their mixing, the heat transfer and the reproducibility of the conditions. It then becomes fairly easy to scale up continuous flow processes while maintaining efficiency as the local concentration and reaction conditions remain constant. Owing to the appealing characteristics previously listed, continuous flow chemistry has been recognized as a viable and sustainable alternative to batch chemistry that offers increased safety and efficiency.^{426,438}

In certain cases, such as photochemical transformations and reactions with hazardous compounds, continuous flow technology offers singular advantages that no flasks or vessels can feature. This technology provides options for handling of toxic, explosive and highly reactive, and has hence increased the range of reactions conditions chemists can exploit.^{427, 428} Also, flow processes alleviate the risks associated with unstable intermediates as they are generated in-line and immediately consumed. The smaller reaction volumes allow for more regulated control of exothermic processes, gas handling, and efficient thermal management which reduces safety hazard and side reactions.

4.5.2 How to access greener reaction conditions with flow processes

The reduced volumes handled in the small diameter tubes are of great interest for both liquid-gas reactions and photochemical transformations.

First, continuous flow reactors provide a powerful alternative to photo-transformations conducted in batch that suffer from poor irradiation efficiency. Photons have long been

recognized as a valuable tool to perform green organic transformations, but challenges associated with light penetration have hindered the efficiency of photochemical processes. According to the Beer-Lambert law, light transmittance decreases exponentially with distance. In order to overcome light penetration issues, catalyst loadings are often increased as a trade of to ensure high conversion and rates when using batch reactors.^{429, 439, 440} Performing reactions in small diameter transparent polymer tubes allows to ensure good and consistent irradiation as the path through which light has to travel is considerably reduced in flow chemistry set-ups compared to conventional reaction vessels. Using flow reactors also reduces the amount of solvent and other chemicals that may absorb light within a given volume, making the irradiation of the photoactive species present more efficient. Flow technology therefore affords more efficient and uniform irradiation than in batch owing to the high surface-area-to-volume ratio.

Moreover, due to the morphology of the batch reaction vessels, the irradiation efficiency could be hindered by the positioning and direction of the light source. Using flow chemistry tubes and LEDs ribbons enables close proximity and multidirectional irradiation of the reaction medium. Typical flow set up for photochemical processes include transparent tubes coiled around a light source, or surrounded by it, to ensure strong and uniform irradiation. This explain why flow photochemical processes were found to be order of magnitude faster than the corresponding batch reactions.⁴²⁹

Most of the early studies by Seeberger, Gagné, Stephenson and Jamison focused on homogeneous photo-transformation, such as cycloadditions, rearrangements, cyclizations, redox, oxidations with photogenerated ¹O₂, often using UV irradiation.⁴²⁹ Flow chemistry has since been increasingly applied to visible light-driven transformations, and also reactions catalyzed by organometallic complexes.⁴²⁹

Continuous flow reactors have proved to be of interest for multiphasic reactions and enabled reaction conditions that cannot be reproduced in batch vessels. Flow processes enable higher safety due to the small volumes handled and improve the efficiency of the

reaction due to better mixing. It can also give the opportunity to use high temperatures, concentration and pressures while remaining safe. This is particularly advantageous for multiphasic systems for which the interfacial area plays an important role in phase transfer, which is often rate limiting. For this reason, flow processes outperform their batch counterparts.^{440,441}

The use of gas as environmentally friendly reagents is appealing for organic transformation as they are widely available, renewable, and atom economical reagents. Yet, they are often associated with safety concerns, and the efficiency of gas-liquid reactions is hindered by the morphology of the reaction vessels. Large excess of gaseous reagents are required to account for the unfavorable reaction conditions provided by traditional reaction vessels.

Using traditional research glassware results in filling the headspace of a batch reactor with a gas in unpressurized systems and serious mass transfer limitations. Pressurized systems present serious safety concerns in case of toxic or reactive gases, and/or require to use autoclaves vessels that prevent light irradiation and photochemical reactions.⁴²⁹ While vigorous stirring can provide sufficient interfacial area in small round-bottom flasks to ensure good mass transfer, continuous flow conditions are more advantageous. Due to the high surface area per reactor volume, flow technology provides tools to address mass transfer limitations, and safety concerns related to the use of gas under high temperature and pressures. Flow reactors are safe even at high pressures and transparent tubing offers a venue to perform photocatalytic transformations at pressure greater than 1 atm,⁴³⁹ which is usually prevented when using round-bottom flask or autoclave vessels.

Continuous flow technology has a lot of offer to unravel the potential of multiphasic photochemistry transformations owing to the enhanced mass and heat transfer, while accessing more sustainable processes by optimizing the use of resources. Flow chemistry provides highly efficient tools to conduct gas-liquid transformations and irradiate reagents. As technology evolves and more tools are being developed, continuous flow reactors become more accessible, cheaper and more efficient, which benefits both research and

industrial implementations. So far mostly homogeneous photocatalytic transformations have been reported using flow technology and extensive studies showed that continuous flow reactors hold great promises for photocatalytic transformations with gaseous reagents.

4.5.3 From batch to flow conditions

Tubes made of perfluoroalkoxy alkane (PFA) were used to transport the reaction medium because they are flexible, chemically resistant, and transmit light. The whole set up was powered by a pump that dictates the flow rate, hence the time spent by the reaction in the reactors and the overall reaction time. Two modules were implemented to this basic set up to perform gas-liquid photoreactions: first a tube-in-tube to saturate the solvent in gas then a coil with a LED tower for irradiation. (Figure 4-10)



Figure 4-10 - Set up featuring the injection sites, the pumps, the tube-in-tube, the irradiated coil and the product collection

Tube-in-tubes, designed by Ley and coworkers, use gas-permeable polymer to achieve homogeneous solutions of reactive gases in flow *via* efficient gas-liquid contact. (Figure 4-11) Pressurized gas permeates trough an inner Teflon tubing and is incorporated in the solvent that flows within a second tube. The tube-in-tube was selected because it enables controlled delivery of a gas and uniform dissolution within the liquid phase. Such continuous flow approach proved to be a suitable for multistep methods, unlike other liquid-gas reactors. This kind of reactor has been used primarily for thermal reactions, or a method to pre-saturate a solution with gas prior to a photochemical reaction.



Figure 4-11 - Close up tube-in-tube. Reproduced with permission from Ref ⁴²⁹. Copyright 2017 American Chemical Society.

Solutions of our substrate (4-bromobenzaldehyde) and the catalyst (Ag NCs) were prepared in dioxane and loaded in syringes to be injected into the flow set up described previously.(Figure 4-10)



Figure 4-12- Continuous-flow reactor set-up used for the purple light-mediated oxidation of 4-bromobenzaldehyde catalyzed by Ag NCs (5 mol%) including a VapourTec module connected to a tube-in-tube module and a PFA coil (1mm I.D.) around a LED tower.

The quantities used were adapted from the batch procedure in respect with the residence time established, while conserving the concentration of substrate and molecular loading. A blank reaction was also performed without catalyst.



Scheme 4-3 - Conversion of 4-bromobenzaldehyde aldehyde into 4-bromobenzoic acid in presence of Ag NCs in the continuous flow photoreactor

With a residence time of 2 h in the tube-in-tube and 2 h irradiation (total retention time 5 h), a 67 % yield was obtained for the conversion of 4-bromobenzaldehyde aldehyde into 4-bromobenzoic acid in presence of Ag NCs.(Scheme 4-3) Only traces of the product were measured without catalyst. Performing the reaction in batch offered a slightly higher yield (79 %) but required a much longer reaction time of 18 h.(Table 4-1)

Table 4-1 - Comparison of the yields obtained for the oxidation of 4-bromobenzaldehyde aldehyde to 4-bromobenzoic acid under flow and batch conditions, and with and without catalysts.

Reactor	Reaction time	Temperature	O ₂ pressure	Catalyst	Yield
	(h)	(° C)	(atm)		(%)
Flow	5	50	5	None	Traces
Flow	5	50	5	Ag NCs 10 mol%	67
Batch	18	80	1	None	Traces
Batch	18	80	1	Ag NCs 10 mol%	79

Even though the yield obtained using a continuous flow reactor is slightly inferior to the one in batch using a similar loading, this result highlights the potential of flow chemistry for photo-catalytic multiphasic reactions using nanocatalysts. The substantial reduction of the reaction time made possible using a flow set up with a tube-in-tube and LED tower shows that continuous flow chemistry has the potential to be influential for the development of greener processes for photochemical reactions using gaseous reagents as such systems allow to improve gas transfer and irradiation, therefore maximizing the use of resources.

Parameters of the flow reactor, such as the residence time, the solvent chosen, the temperature and the pressure of gas used could be further optimized to increase the efficacy of this set up and potentially afford higher yields than in batch, still using greener reaction conditions and substantially shorter reaction time.

4.6 Conclusion

The formation of sharp and monodispersed Ag NCs is demanding and may need to be adapted for each laboratory environment due to the different reaction paths. Yet, once obtained the Ag NCs were stabled and proved to be efficient photocatalysts.

SPR can be harnessed to activate silver toward hydrogenation and oxidation of carbonyls using Ag NCs. Hot-electron-mediated silver-catalyzed hydrogenation proceeded at 1 atm of H₂ and 80 °C, conditions much milder than what is known for purely thermal silvercatalyzed processes. The reaction is the first example of SPR-activated reductive catalysis performed using pure, unmodified plasmonic nanoparticles. This catalyst has been shown to tolerate a wide variety of substrates with moderate to high yields, with complete selectivity for C=0 over C=C bond reduction. Moderate to high yield were obtained in batch for a variety of substrates under both oxidation and reduction conditions. This work expends the scope of reactions catalyzed by free-standing plasmonic particles and casts light on H₂ photo-activation by silver surfaces, in addition to being a proof-of-concept of the use of plasmon-active nanocatalysts for important organic transformations. We also

showed that continuous flow reactors are an appealing venue to further improve the performances of such heterogenous photocatalysts.

4.7 References

70. Moores, A.; Goettmann, F., The Plasmon Band in Noble Metal Nanoparticles: An Introduction to Theory and Applications. *New J. Chem.* **2006**, *30*(8), 1121-1132.

145. Wu, Y. Y.; Li, G. L.; Camden, J. P., Probing Nanoparticle Plasmons with Electron Energy Loss Spectroscopy. *Chemical Reviews* **2018**, *118*(6), 2994-3031.

146. Brodusch, N.; Demers, H.; Gellé, A.; Moores, A.; Gauvin, R., Electron Energy-Loss Spectroscopy (Eels) with a Cold-Field Emission Scanning Electron Microscope at Low Accelerating Voltage in Transmission Mode. *Ultramicroscopy* **2018**, *203*, 21-36.

170. Wiley, B. J.; Xiong, Y.; Li, Z.-Y.; Yin, Y.; Xia, Y., Right Bipyramids of Silver: A New Shape Derived from Single Twinned Seeds. *Nano letters* **2006**, *6*(4), 765-768.

171. Wiley, B. J.; Chen, Y.; McLellan, J. M.; Xiong, Y.; Li, Z.-Y.; Ginger, D.; Xia, Y., Synthesis and Optical Properties of Silver Nanobars and Nanorice. *Nano letters* **2007**, *7*(4), 1032-1036.

172. Wiley, B.; Sun, Y.; Xia, Y., Synthesis of Silver Nanostructures with Controlled Shapes and Properties. *Accounts of chemical research* **2007**, *40*(10), 1067-1076.

173. Skrabalak, S. E.; Wiley, B. J.; Kim, M.; Formo, E. V.; Xia, Y., On the Polyol Synthesis of Silver Nanostructures: Glycolaldehyde as a Reducing Agent. *Nano letters* **2008**, *8*(7), 2077-2081.

175. Al-Saidi, W. A.; Feng, H. J.; Fichthorn, K. A., Adsorption of Polyvinylpyrrolidone on Ag Surfaces: Insight into a Structure-Directing Agent. *Nano Letters* **2012**, *12*(2), 997-1001. 176. Saidi, W. A.; Feng, H. J.; Fichthorn, K. A., Binding of Polyvinylpyrrolidone to Ag Surfaces: Insight into a Structure-Directing Agent from Dispersion-Corrected Density Functional Theory. *Journal of Physical Chemistry C***2013**, *117*(2), 1163-1171.

177. Sun, Y.; Yin, Y.; Mayers, B. T.; Herricks, T.; Xia, Y., Uniform Silver Nanowires Synthesis by Reducing Agno3 with Ethylene Glycol in the Presence of Seeds and Poly(Vinyl Pyrrolidone). *Chemistry of Materials* **2002**, *14*(11), 4736-4745.

178. Ghosh, S.; Manna, L., The Many "Facets" of Halide Ions in the Chemistry of Colloidal Inorganic Nanocrystals. *Chemical reviews* **2018**, *118*(16), 7804-7864.

179. Chen, Z.; Balankura, T.; Fichthorn, K. A.; Rioux, R. M., Revisiting the Polyol Synthesis of Silver Nanostructures: Role of Chloride in Nanocube Formation. *ACS Nano* **2019**, *13*(2), 1849-1860.

234. Christopher, P.; Xin, H.; Linic, S., Visible-Light-Enhanced Catalytic Oxidation Reactions on Plasmonic Silver Nanostructures. *Nature chemistry* **2011**, *3*(6), 467-472.

235. Marimuthu, A.; Zhang, J.; Linic, S., Tuning Selectivity in Propylene Epoxidation by Plasmon Mediated Photo-Switching of Cu Oxidation State. *Science* **2013**, *339* (6127), 1590-1593.

274. Li, A. Y.; Gellé, A.; Segalla, A.; Moores, A., Silver Nanoparticles in Organic Transformations. In *Silver Catalysis in Organic Synthesis*, Li, C. J., Bi, Xihe., Ed. Wiley: 2019.
360. Linic, S.; Aslam, U.; Boerigter, C.; Morabito, M., Photochemical Transformations on Plasmonic Metal Nanoparticles. *Nature materials* **2015**, *14*(6), 567-576.

363. Long, R.; Li, Y.; Song, L.; Xiong, Y., Coupling Solar Energy into Reactions: Materials Design for Surface Plasmon-Mediated Catalysis. *Small* **2015**, *11* (32), 3873-3889.

398. McClellan, P., Manufacture and Uses of Ethylene Oxide and Ethylene Glycol. *Industrial & Engineering Chemistry* **1950**, *42*(12), 2402-2407.

399. Hader, R. N.; Wallace, R.; McKinney, R., Formaldehyde from Methanol. *Industrial & Engineering Chemistry* **1952**, *44*(7), 1508-1518.

400. Wachs, I. E.; Madix, R. J., The Oxidation of Methanol on a Silver (110) Catalyst. *Surface Science* **1978**, *76*(2), 531-558.

401. Medlin, J. W., Understanding and Controlling Reactivity of Unsaturated Oxygenates and Polyols on Metal Catalysts. *Acs Catalysis* **2011**, *1*(10), 1284-1297.

402. Claus, P., Selective Hydrogenation of A, B-Unsaturated Aldehydes and Other C= O and C= C Bonds Containing Compounds. *Topics in Catalysis* **1998**, *5*(1), 51-62.

403. Li, A. Y.; Kaushik, M.; Li, C.-J.; Moores, A., Microwave-Assisted Synthesis of Magnetic Carboxymethyl Cellulose-Embedded Ag–Fe3o4 Nanocatalysts for Selective Carbonyl Hydrogenation. *ACS Sustainable Chemistry & Engineering* **2016**, *4*(3), 965-973.

404. Lacheb, H.; Puzenat, E.; Houas, A.; Ksibi, M.; Elaloui, E.; Guillard, C.; Hermann, J., Photocatalytic Degradation of Various Types of Dyes (Alizarin S, Grocein Orange G, Methyl Red, Congo Red, Methylene Blue) in Water by Uv-Irradiated Titania. *Appl. Catal. B: Environ* **2002**, *39*, 75-90.

405. Wiley, B. J.; Im, S. H.; Li, Z.-Y.; McLellan, J.; Siekkinen, A.; Xia, Y., Maneuvering the Surface Plasmon Resonance of Silver Nanostructures through Shape-Controlled Synthesis. ACS Publications: 2006.

406. Linic, S.; Christopher, P., Overcoming Limitation in the Design of Selective Solid Catalysts by Manipulating Shape and Size of Catalytic Particles: Epoxidation Reactions on Silver. *ChemCatChem* **2010**, *2*(9), 1061-1063.

407. Zhang, X.; Ke, X.; Yao, J., Recent Development of Plasmon-Mediated Photocatalysts and Their Potential in Selectivity Regulation. *Journal of Materials Chemistry A* **2018**, *6*(5), 1941-1966.

408. da Silva, A. G.; Rodrigues, T. S.; Wang, J.; Yamada, L. K.; Alves, T. V.; Ornellas, F. R.; Ando, R. m. A.; Camargo, P. H., The Fault in Their Shapes: Investigating the Surface-Plasmon-Resonance-Mediated Catalytic Activities of Silver Quasi-Spheres, Cubes, Triangular Prisms, and Wires. *Langmuir* **2015**, *31*(37), 10272-10278.

409. Zhang, Q.; Wang, H., Facet-Dependent Catalytic Activities of Au Nanoparticles Enclosed by High-Index Facets. *ACS Catalysis* **2014**, *4*(11), 4027-4033.

410. Heuer-Jungemann, A.; Feliu, N.; Bakaimi, I.; Hamaly, M.; Alkilany, A.; Chakraborty, I.; Masood, A.; Casula, M. F.; Kostopoulou, A.; Oh, E., The Role of Ligands in the Chemical Synthesis and Applications of Inorganic Nanoparticles. *Chemical reviews* **2019**, *119* (8), 4819-4880.

411. Im, S. H.; Lee, Y. T.; Wiley, B.; Xia, Y., Large-Scale Synthesis of Silver Nanocubes: The Role of Hcl in Promoting Cube Perfection and Monodispersity. *Angewandte Chemie International Edition* **2005**, *44*(14), 2154-2157.

412. Kirner, F.; Potapov, P.; Schultz, J.; Geppert, J.; Müller, M.; González-Rubio, G.; Sturm, S.; Lubk, A.; Sturm, E., Additive-Controlled Synthesis of Monodisperse Single Crystalline Gold Nanoparticles: Interplay of Shape and Surface Plasmon Resonance. *Journal of Materials Chemistry C***2020**, *8*(31), 10844-10851.

413. Murphy, C. J.; Sau, T. K.; Gole, A. M.; Orendorff, C. J.; Gao, J.; Gou, L.; Hunyadi, S. E.; Li, T., Anisotropic Metal Nanoparticles: Synthesis, Assembly, and Optical Applications. *The Journal of Physical Chemistry B***2005**, *109*(29), 13857-13870.

414. Sun, Y.; Mayers, B.; Herricks, T.; Xia, Y., Polyol Synthesis of Uniform Silver Nanowires: A Plausible Growth Mechanism and the Supporting Evidence. *Nano letters* **2003**, *3*(7), 955-960.

415. Xia, X.; Zeng, J.; Oetjen, L. K.; Li, Q.; Xia, Y., Quantitative Analysis of the Role Played by Poly (Vinylpyrrolidone) in Seed-Mediated Growth of Ag Nanocrystals. *Journal of the American Chemical Society* **2012**, *134*(3), 1793-1801.

416. Qi, X.; Balankura, T.; Zhou, Y.; Fichthorn, K. A., How Structure-Directing Agents Control Nanocrystal Shape: Polyvinylpyrrolidone-Mediated Growth of Ag Nanocubes. *Nano letters* **2015**, *15*(11), 7711-7717.

417. Chen, Z.; Chang, J. W.; Balasanthiran, C.; Milner, S. T.; Rioux, R. M., Anisotropic Growth of Silver Nanoparticles Is Kinetically Controlled by Polyvinylpyrrolidone Binding. *Journal of the American Chemical Society* **2019**, *141*(10), 4328-4337.

418. Sangaru, S. S.; Zhu, H.; Rosenfeld, D. C.; Samal, A. K.; Anjum, D.; Basset, J.-M., Surface Composition of Silver Nanocubes and Their Influence on Morphological Stabilization and Catalytic Performance in Ethylene Epoxidation. *ACS applied materials & interfaces* **2015**, *7* (51), 28576-28584.

419. Peng, S.; Okasinski, J. S.; Almer, J. D.; Ren, Y.; Wang, L.; Yang, W.; Sun, Y., Real-Time Probing of the Synthesis of Colloidal Silver Nanocubes with Time-Resolved High-Energy Synchrotron X-Ray Diffraction. *The Journal of Physical Chemistry* **C2012**, *116*(21), 11842-11847.

420. Han, L.; Wang, P.; Zhu, C.; Zhai, Y.; Dong, S., Facile Solvothermal Synthesis of Cube-Like Ag@ Agcl: A Highly Efficient Visible Light Photocatalyst. *Nanoscale* **2011**, *3*(7), 2931-2935.

421. Wang, P.; Huang, B.; Qin, X.; Zhang, X.; Dai, Y.; Wei, J.; Whangbo, M. H., Ag@ Agcl: A Highly Efficient and Stable Photocatalyst Active under Visible Light. *Angewandte Chemie International Edition* **2008**, *47*(41), 7931-7933.

422. Yang, Y.; Zhao, Y.; Yan, Y.; Wang, Y.; Guo, C.; Zhang, J., Preparation of Agcl Nanocubes and Their Application as Efficient Photoinitiators in the Polymerization of N-Isopropylacrylamide. *The Journal of Physical Chemistry* **B2015**, *119*(46), 14807-14813.

423. Nicoletti, O.; de La Peña, F.; Leary, R. K.; Holland, D. J.; Ducati, C.; Midgley, P. A., Three-Dimensional Imaging of Localized Surface Plasmon Resonances of Metal Nanoparticles. *Nature* **2013**, *502* (7469), 80-84.

424. Zhang, K.; Da, B.; Ding, Z., Effect of Asymmetric Morphology on Coupling Surface Plasmon Modes and Generalized Plasmon Ruler. *Ultramicroscopy* **2018**, *185*, 55-64.

425. Landry, M. J.; Gelle, A.; Meng, B. Y.; Barrett, C. J.; Moores, A., Surface-Plasmon-Mediated Hydrogenation of Carbonyls Catalyzed by Silver Nanocubes under Visible Light. *Acs Catalysis* **2017**, *7*(9), 6128-6133.

426. Ley, S. V., On Being Green: Can Flow Chemistry Help? *The Chemical Record* **2012**, *12*(4), 378-390.

427. Deadman, B. J.; Collins, S. G.; Maguire, A. R., Taming Hazardous Chemistry in Flow: The Continuous Processing of Diazo and Diazonium Compounds. *Chemistry–A European Journal* **2015**, *21*(6), 2298-2308. 428. Movsisyan, M.; Delbeke, E.; Berton, J.; Battilocchio, C.; Ley, S.; Stevens, C., Taming Hazardous Chemistry by Continuous Flow Technology. *Chemical Society Reviews* **2016**, *45* (18), 4892-4928.

429. Plutschack, M. B.; Pieber, B. u.; Gilmore, K.; Seeberger, P. H., The Hitchhiker's Guide to Flow Chemistry. *Chemical reviews* **2017**, *117*(18), 11796-11893.

430. Wegner, J.; Ceylan, S.; Kirschning, A., Flow Chemistry-a Key Enabling Technology for (Multistep) Organic Synthesis. *Advanced Synthesis & Catalysis* **2012**, *354*(1), 17-57.

431. Gérardy, R.; Emmanuel, N.; Toupy, T.; Kassin, V. E.; Tshibalonza, N. N.; Schmitz, M.; Monbaliu, J. C. M., Continuous Flow Organic Chemistry: Successes and Pitfalls at the Interface with Current Societal Challenges. *European Journal of Organic Chemistry* **2018**, *2018*(20-21), 2301-2351.

432. Rehm, T. H., Flow Photochemistry as a Tool in Organic Synthesis. *Chemistry (Weinheim an der Bergstrasse, Germany)* **2020**, *26*(71), 16952.

433. Baxendale, I. R., The Integration of Flow Reactors into Synthetic Organic Chemistry. *Journal of Chemical Technology & Biotechnology* **2013**, *88*(4), 519-552.

434. Porta, R.; Benaglia, M.; Puglisi, A., Flow Chemistry: Recent Developments in the Synthesis of Pharmaceutical Products. *Organic Process Research & Development* **2016**, *20* (1), 2-25.

435. Pastre, J. C.; Browne, D. L.; Ley, S. V., Flow Chemistry Syntheses of Natural Products. *Chemical Society Reviews* **2013**, *42*(23), 8849-8869.

436. Bogdan, A. R.; Dombrowski, A. W., Emerging Trends in Flow Chemistry and Applications to the Pharmaceutical Industry. *Journal of medicinal chemistry* **2019**, *62*(14), 6422-6468.

437. Kockmann, N.; Gottsponer, M.; Zimmermann, B.; Roberge, D. M., Enabling Continuous-Flow Chemistry in Microstructured Devices for Pharmaceutical and Fine-Chemical Production. *Chemistry–A European Journal* **2008**, *14*(25), 7470-7477.

438. Vaccaro, L.; Lanari, D.; Marrocchi, A.; Strappaveccia, G., Flow Approaches Towards Sustainability. *Green Chemistry* **2014**, *16*(8), 3680-3704.

439. Sambiagio, C.; Noël, T., Flow Photochemistry: Shine Some Light on Those Tubes! *Trends in Chemistry* **2020**, *2*(2), 92-106.

440. Newman, S. G.; Jensen, K. F., The Role of Flow in Green Chemistry and Engineering. *Green chemistry* **2013**, *15*(6), 1456-1472.

441. Brzozowski, M.; O'Brien, M.; Ley, S. V.; Polyzos, A., Flow Chemistry: Intelligent Processing of Gas-Liquid Transformations Using a Tube-in-Tube Reactor. *Accounts of chemical research* **2015**, *48*(2), 349-362.

Transition

While naked Ag NCs proved to be efficient catalysts under oxidative and reductive conditions, the surface chemistry of such nanoparticles limits the number of reactions that can be performed using SPR-induced hot electrons to mediate transformations. Design of antenna-reactor based on hybrid structures constitute appealing nanostructures to explore other photocatalytic activity of plasmon-based nanostructures. This chapter shows how Ag NPs served as plasmonically active supports for tris(bipyridine)ruthenium(II), [Ru(bpy)₃]²⁺, and boost the catalytic performance of this homogeneous photocatalyst due to the field enhancement in the vicinity of plasmonic structures.
5 Chapter 5 – Enhancing singlet oxygen photocatalysis with plasmonic nanoparticles



This chapter is based upon one article submitted for publication. All co-authors granted permission to include this manuscript in the thesis.

Alexandra Gellé, Gareth Price, Frédéric Voisard, Nicolas Brodusch, Raynald Gauvin, Zacharias Amara, and Audrey Moores. Enhancing Singlet Oxygen Photocatalysis With Plasmonic Nanoparticles, ACS Applied Materials and Interfaces. 2021. In press.

5.1 Introduction

Visible light photocatalysis is currently at the heart of intense research developments,⁴⁴² in particular in the fields of energy,^{443, 444} pollution remediation⁴⁴⁵ and organic transformations.⁴⁴⁶ Photocatalysis is often praised as a method enabling high energyefficiency and chemical selectivity, complying with the principles of green chemistry.^{442, 447} Many visible light photocatalysts have been developed, based on nanomaterials,⁴⁴⁸ 2D structures,^{449, 450} metal organic frameworks,⁴⁵¹ organometallic complexes⁴⁵² or organic molecules.^{26, 453} Among the most popular molecular photocatalysts used in organic synthesis, tris(bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, stands out for a number of reasons. It has the ability to catalyse a large variety of organic ^{20, 35, 454-456} and inorganic^{457, 458} reactions, and it absorbs in the visible range. It has shown superior performances compared to other organometallic and organic photocatalysts in a variety of organic transformations.^{459,460, 461} $[Ru(bpy)_3]^{2+}$ also features excellent phosphorescence properties, thanks to its ability to facilitate intersystem crossing in the excited state, which is key to enable energy transfer reactions.⁴⁶² Finally [Ru(bpy)₃]²⁺ features good resistance to photobleaching and is thus stable under catalytic conditions, especially as compared to organo-photocatalysts.462,463

Photocatalysts have been particularly efficient when they are harnessed towards the generation of singlet oxygen (¹O₂), a powerful manifold for oxidative chemistry.^{16,464} In this context, the Schenck Ene reaction, which allows for the selective conversion of alkenes into allylic hydroperoxides, has found important industrial applications. It constitutes a key step in the commercial production of rose oxide, a marketed fragrance, and artemisinin, a major antimalarial drug.¹⁶ More generally, such photooxidations are extremely valuable as they combine green and sustainable attributes, ^{16,47,107,454,465-467} such as relying on cheap and available resources, i.e. molecular oxygen from air and visible light, while enabling highly selective oxidations, even on complex substrates.¹⁶ Yet, as a member of the platinum series, Ru remains expensive and fairly toxic.⁴⁶⁸ There is therefore a need to develop new

methodologies to enhance the performance of such molecular photocatalysts, so as to limit the quantity used in the process.^{463, 469}

Plasmonic nanoparticles (PNPs) strongly interact with light via a phenomenon called localized surface plasmon resonance (LSPR), and have found applications⁶¹ in spectroscopy,⁴⁷⁰ nanomedicine,^{160, 471} optoelectronics, energy conversion^{362, 472} and catalysis.^{136, 473-477} PNPs are, among other effects, able to act as antennae modulating and concentrating light in their immediate vicinity.⁴⁷⁸⁻⁴⁸² This property is at the heart of surface enhanced Raman spectroscopy (SERS) and surface plasmon resonance (SPR) spectroscopy techniques.⁴⁸³⁻⁴⁸⁸ The antenna effect enabled by PNPs has been exploited to tweak the selectivity and activity of metal based catalysts.^{75, 267, 489, 490} As early as 1968, Drexhage and coworkers foresaw the potential of associating PNPs to fluorophores, when witnessing the altered optical properties of a Eu complex in the proximity of a plasmonic Ag film.⁴⁹¹ This first observation of metal enhanced luminescence (MEL) led to numerous applications in biology, including extensive studies by the Geddes and Lakowicz groups.^{473, 483, 492-495} The Heyne group has recently studied silica covered Au and Ag PNPs decorated with Rose Bengal (RB) towards the generation of ¹O₂ for antibacterial activity.⁷⁷ They have studied in depth the role of the PNP metal by comparing Ag and Au performances,^{77,496} as well as the influence of the PNP shape on photocatalysis enhancement.⁴⁹⁷ Moreover, they noticed that in all systems, there was an optimal shell thickness at which the LSPR effect was maximal. Interestingly, the thickness at which the maximum RB luminescence was measured slightly differed from the one at which ¹O₂ production peaked. Mendoza *et al.* have further studied similar silica covered Au PNPs and analyzed ¹O₂ generation by three independent methods to conclude that the SPR promoted the absorption and triplet state generation in the RB photosynthesizer.⁴⁹⁸ Other groups studied similar systems with [Ru(bpy)₃]²⁺ or fluorescein isothiocyanate.⁴⁹⁹⁻⁵⁰¹ Non rigid spacers such as human serum albumin⁵⁰², phospholipid membrane⁵⁰³ and DNA⁵⁰⁴ were also used to immobilized dyes at the surface of PNPs. Despite these developments, the application of this strategy for catalysis has been scarce. Mori et al. reported in 2010 the use of Ag@SiO₂ NPs decorated with [Ru(bpy)₃]²⁺ for the oxidation of styrene.²³⁷ More recently, Reinhard and coworkers used a phospholipid

membrane-covered Ag NP to deposit [Ru(bpy)₃]²⁺ and demonstrated its efficiency for lightenhanced urea degradation.⁵⁰³ Yet, considering the importance of ¹O₂ methodologies in the pharmaceutical industry, more work is needed into establishing a structure/activity relationship, and studying the mechanism of this enhancement in the specific context of these organic transformations. ¹⁶ As highlighted in a recent review by Linic and coworkers, such hybrid plasmonic materials relying on a plasmonic antenna to boost catalysts are a promising venue for the development of new plasmon-mediated catalysts.⁵⁰⁵

We thus synthesized silica coated Ag PNPs decorated with [Ru(bpy)₃]²⁺, and studied their luminescence and catalytic activity towards citronellol oxidation, a key step in the manufacturing of the commercial fragrance rose oxide performed on a 100 T/year⁴⁵³ scale. In particular, we carefully tuned the silica layer thickness as a mean to control the distance between the supporting PNP and the catalytically active species. Here, immobilisation was performed by simple absorption onto the silica surface, following a strategy developed in our group (Amara) ^{466, 506} and simplifying past approaches relying on covalent bonding.²³⁷ Photocatalysis for this reaction under optimized conditions was enhanced by the presence of plasmonic core, affording an almost 3-fold enhancement in reaction yield. The shell thickness affording the maximum for luminescence emission for [Ru(bpy)₃]²⁺ was found to be 33 nm while the maximum catalytic enhancement was observed at 28 nm. In order to shed light onto the mechanism of plasmonic enhancement, we conducted a thorough LSPR mapping study using scanning transmission electron microscopy - electron energy loss spectroscopy (STEM-EELS).

5.2 Synthesis and characterization of plasmon-active supports for photocatalysis



5.2.1 Synthesis of Ag@SiO $_2$ and Ag@SiO $_2$ -[Ru] NPs

Figure 5-1 - A) Synthesis of the silver plasmonic nanoparticles core with a silica shell and immobilization of the photocatalyst $[Ru(bpy)_3]^{2+}$ B-E) TEM images of Ag NPs (1B) and Ag@SiO₂ NPs with various thicknesses 1C-E (7 nm, 30 nm and 37 nm) F) High-angle annular dark-field image (HAADF), overlaid with EDS mapping for Ag (blue), Si (pink), and O (green) of an individual Ag@SiO₂ NP with a 28 nm shell thickness; G-I) EDS mapping of the same particle for Ag, Si and O; J) Intensity for HAADF and EDS of Ag, O and Si across the linescan shown in G. Scale bars for F), G), H), and I) is 50 nm.

For this study, we designed Ag NPs covered with a silica layer, Ag@SiO₂ NPs, to serve as supports for photocatalyst $[Ru(bpy)_3]^{2+}$ thus affording Ag@SiO₂-[Ru] (Figure 5-1A). Briefly, Ag NPs were first synthesized using AgNO₃ as a precursor and polyvinylpyrrolidone (PVP) as a capping agent following previously reported methods (see Annex for details).⁵⁰⁷ The Ag NPs were then coated with SiO₂ *via* the Stöber process, which consists of repeated addition and hydrolysis of tetraethyl orthosilicate (TEOS) until reaching the desired silica

shell thickness.⁵⁰⁸ Following this step, Ag@SiO₂ were decorated with $[Ru(bpy)_3]^{2+}$ taking advantage of electrostatic interactions, and provided access to Ag@SiO₂-[Ru].^{466, 509, 510}

In this design, Ag was selected as the plasmonic metal, since it had been shown to exhibit better luminescence enhancement performances than Au.^{511, 512} We initially optimized the Ag core diameter and the thickness of the silica shell to ensure that the SPR signal effectively overlapped with [Ru(bpy)₃]²⁺, which has a maximum absorption at 450 nm.⁵¹³ Indeed, recent studies suggested that MEL was strongly favored by a good overlap between the SPR band and the excitation band of the photocatalyst.^{494, 504, 514-517} In particular, we made sure that this overlap remained good across a range of silica shell thicknesses. This initial study allowed to identify an Ag core of 80 nm in diameter, with a shell of 25-35 nm, as a good fit. Afterwards, we optimized the amount of photocatalyst immobilized on the surface to maximise the luminescence of the photosynthesizer (See complete discussion in Annex).

5.2.2 Characterization of Ag@SiO₂ and Ag@SiO₂-[Ru] NPs

Transmission electron microscopy (TEM) analysis of the resulting Ag@SiO₂ NPs confirmed the formation of Ag cores with diameters of 80.4 \pm 8.1 nm (Figure 1B). Their silica shells featured thicknesses of 7 (Figure 1C), 10, 15, 19, 25, 28, 30 (Figure 1D), 33, 37 (Figure 1E), 40 or 45 nm, a parameter we could control *via* the number of TEOS additions. In all cases, the particles core and shells were very uniform across samples, with no core-free particles or irregular shells observed. High-angle annular dark-field image (HAADF) (Figure 1G) and mapping by Energy Dispersive X-Ray Spectroscopy (EDS) (Figures 1H-J) confirmed the presence of the silver core surrounded by a shell made of Si and O of approximatively 28 nm as measured on the TEM images. We then evaluated the specific surface of Ag@SiO₂ NPs by Brunauer–Emmett–Teller (BET) measurements. It ranged from 4 m²/g to 21 m²/g for shells of 7 nm to 45 nm, respectively (Table S1 ESI). While the variation in specific surface area was small, it did increase as the particle size grow, which is counter intuitive. We attributed it to surface roughening as layers of silica were added, as we found in an earlier report.⁵¹⁸ During subsequent [Ru(bpy)₃]²⁺ immobilization, care was taken to control their density per surface unit, as a way to maintain two consecutive photocatalysts at a similar distance, on average. Upon optimization (see ESI section 2), the value of 6.5 10^{-5} mmol of [Ru(bpy)₃]²⁺/m² of support was kept constant for all Ag@SiO₂ NP samples. Indeed, it is well known that photoactive molecules may undergo self-quenching when they are in close proximity, thus this parameter was considered the most important one to lock for comparison purposes.⁵¹⁸ The subsequent immobilization of [Ru(bpy)₃]²⁺ onto the silica shell was evaluated by ζ -potential measurements (Table 8-5). The naked Ag@SiO₂ NP surface featured a negatively charged surface of -29.0 mV, a value which dropped to -17.2 mV upon functionalization with [Ru(bpy)₃]²⁺. The amount of photocatalyst immobilized at the surface of Ag@SiO₂ NPs was determined by UV-Vis absorption spectroscopy, by subtracting the concentrations of [Ru(bpy)₃]²⁺ before and after exposure to the support. Optimal immobilization was achieved when collected supernatants were colorless.



Figure 5-2- Normalized extinction spectra of studied photoactive systems in ethanol. Black line: Ag NPs; blue line: Ag@SiO₂; red line: homogeneous [Ru(bpy)₃]Cl₂; orange gradient Ag@SiO₂-[Ru].

Prior to silica coating, the core Ag NPs featured a plasmonic band centered at 420 nm Figure 5-2-black). Upon silica layer growth, the plasmon band of Ag@SiO₂ NPs redshifted (Figure 8-8 and Figure 8-9) and broadened (Figure 5-2-blue) as an effect of dielectric medium change at the vicinity of the Ag core.⁵¹⁹⁻⁵²¹ As the photocatalyst was immobilized at the surface of Ag@SiO₂ NPs, the extinction profile of the ensemble enveloped both the SPR band and the absorption of $[Ru(bpy)_3]^{2+}$ (Figure 5-2- red and orange). The immobilization of $[Ru(bpy)_3]^{2+}$ hardly affected the position of the SPR band of the PNPs, yet it caused a small broadening, as reported before.^{93, 522, 523}

In order to evaluate the ability of the synthesized plasmon-active nanosupports to enhance the optical properties of $[Ru(bpy)_3]^{2+}$, we turned to fluorescence measurements. First, we irradiated Ag@SiO₂-[Ru] samples, at the excitation wavelength of $[Ru(bpy)_3]^{2+}$, namely 450 nm, and the intensity of the luminescence was measured at its emission wavelength, 615 nm. The photoluminescence properties were studied for silica layers ranging from 7 to 45 nm with an identical concentration of photocatalysts immobilized on commercial SiO₂ NPs (Figure 8-11). For all samples with medium and large silica shell, we observed an emission peak, which confirms the presence of $[Ru(bpy)_3]^{2+}$ onto the Ag@SiO₂ NPs and the preservation of its luminescence (Figure 8-11).

For a given $[Ru(bpy)_3]^{2+}$ loading, its emission intensity was strongly dependant on the thickness of the silica shell. In order to establish a clear comparison framework, we calculated an enhancement factor for each support. It is defined as the ratio between the intensity measured for each system and the one for commercial 80 nm SiO₂ NPs, without metallic core, decorated with the photocatalyst (SiO₂-[Ru]).

The trend in emission intensity observed when varying the shell thickness (Figure 5-3 orange dotted line) is in agreement with previous studies by the Heyne group, on the effect of plasmonic enhancement on the emission of Rose Bengal immobilized on Ag@SiO₂ NPs.^{77, 497} For very thin SiO₂ layers, the photocatalyst experienced a significant non radiative decay⁴⁸⁴ and the emission was strongly quenched, presumably due to charge transfer between the photocatalyst and the metal. As we increased the shell thickness, the emission

intensity started to increase significantly, until reaching a maximum for NPs decorated with $[Ru(bpy)_3]Cl_2$ with a layer of a 33 nm. Under these conditions, the catalysts were no longer quenched by the metal surface, thus allowing radiative pathways to take place. The increase in emission intensity was attributed to the enhanced electric field caused by the plasmonic Ag core, which boosts the excitation of the fluorophore and its emission. The maximum luminescence enhancement corresponded to a 4-fold increase, as compared to $[Ru(bpy)_3]^{2+}$ immobilized on commercial SiO₂. For thicker shells, the emission intensity lowered and reached a plateau which correlates to the emission intensity of plasmonic free system (SiO₂-[Ru]), suggesting that the influence of the plasmonic core becomes negligible.

5.3 Photocatalytic studies

We then proceeded to the study of the photocatalytic activity of Ag@SiO₂-[Ru] NPs for the Schenck Ene reaction, specifically, the photooxidation of citronellol to the corresponding allylic hydroperoxydes (Scheme 5-1).



Scheme 5-1- Reaction scheme for the oxidation of citronellol using Ag@SiO₂-[Ru] NPs. Standard reaction conditions: 0.33 mmol citronellol, CH₃CN, 3 h, O₂ balloon, 3.4 mmol% in $[Ru(bpy)_3]^{2+}$ for Ag@SiO₂-[Ru], white LED illumination.

The oxidation of citronellol was performed in a photoreactor illuminated with white LEDs using Ag@SiO₂-[Ru] with shell thicknesses ranging from 7 to 45 nm, under aerobic conditions in acetonitrile for 3 hours (Figure 5-3 blue and green and Table 8-6). The formation of the desired alcohol regioisomers was monitored using GC-MS and ¹H NMR, following quenching of the peroxides by triphenylphosphine. The molar catalytic loading was selected to be 3.4 mmol% in [Ru(bpy)₃]²⁺ in all cases discussed onwards, while

maintaining the surface coverage equal for the $Ag@SiO_2$ -[Ru] series. A full reaction mechanism is provided in Figure 8-13.



Figure 5-3 - Conversion of citronellol as determined by GC-MS (green) and NMR (blue) after 3h of reaction in comparison with the intensity of the luminescence measured for Ag@SiO₂-[Ru] NPs (orange), plotted as a function of SiO₂ shell thickness. Conversion by NMR for [Ru(bpy)₃]Cl₂ homogeneous (*) and [Ru(bpy)₃]Cl₂ immobilized on commercial SiO₂ NPs (\blacklozenge). The molar catalytic loading was identical in all reactions (3.4 mmol%).

In the following section, we used NMR yield values to compare the catalytic systems. When the reaction was carried out with homogeneous $[Ru(bpy)_3]Cl_2$ under the same molar catalytic loading as with the supported systems, it afforded a yield of 41%. When $[Ru(bpy)_3]Cl_2$ was immobilized on commercial SiO₂ NPs (SiO₂-[Ru] NPs), the yield dropped to 25% (Table 8-6). Such a drop is commonly observed for immobilized homogeneous catalysts.⁵²⁴ We then turned to the reaction catalyzed by the Ag@SiO₂-[Ru] series. With thin SiO₂ shells, of 7 and 10 nm, conversions of 17 and 18 % were observed. They were lower than the conversion observed with SiO₂-[Ru] NPs. As mentioned above, this result can be rationalized by the presence of the nearby Ag core which can quench the catalyst and negatively impact its activity. A similar drop in activity was observed when adding Ag NPs to a reaction solution containing homogenous [Ru(bpy)₃]Cl₂. In this case the conversion dropped from 41 % to 12 % (Table 8-6). We hypothesized that this could be due to either electronic quenching or competitive absorption of light by the material, as observed by our group with an Fe(0) support.⁵¹⁸ As the shell thickness increased in the Ag@SiO₂-[Ru] series, conversion went up steadily, until a maximum conversion of 68 % was obtained for a SiO₂ thickness of 28 nm. This value is higher than the one observed with both homogeneous [Ru(bpy)₃]Cl₂ and SiO₂-[Ru] NPs. Specifically, this means that, at the maximum of plasmonic enhancement, the yield is improved by a factor of 2.6, as compared to the supporting on the simple SiO₂ NPs. Above a shell thickness of 28 nm the yields dropped rapidly and, beyond 35 nm, conversion plateaued at around 30 %, a value close to the performance of the simple SiO₂-[Ru] system. Control experiments show that almost no conversion occur under light irradiation in the absence of catalyst, or with Ag@SiO₂-[Ru] NPs without light irradiation Table 8-6). When naked Ag NPs were used alone as catalyst, the conversion remained negligible. Previous study showed that Ag PNPs could directly catalyze the formation of ${}^{1}O_{2}$, ${}^{525-527}$ but in our hands, this did not prove to be efficient for the Schenck Ene process.

Interestingly, the most intense luminescence of Ag@SiO₂-[Ru] was measured for a shell of 33 nm, while 28 nm of SiO₂ performed the best for the photocatalytic oxidation of citronellol. A similar discrepancy in optimal shell thickness was observed by Heyne and coworkers when comparing the enhancement of the emission of a PNP enhanced photocatalyst (Rose Bengal) with its ability to produce ¹O₂. While a 20 nm SiO₂ layer offered the highest luminescence for Ag@SiO₂-RB NPs, the maximum ¹O₂ production was observed for a 11 nm silica shell.⁷⁷ We note that similarly to our system, the maximum for catalysis occurs for thinner shells than the maximum of the luminescence enhancement. Also, similar to this system, Heyne and coworkers reported that, at the peak of ¹O₂ emission enhancement, the amount of ¹O₂ available in solution is enhanced by a 3-fold factor. This values are in agreement with the 2.6 enhancement factor we observed. Other antennaphotocatalyst systems employing a variety of metallic core, molecular dyes and spacing component have been developed. The characteristic of each system and the optimal spacing between the plasmon-active surface and the photocatalyst are detailed in the

Chapter 5 - Enhancing singlet oxygen photocatalysis with plasmonic nanoparticles

Annex. A number of systems were developed with silica shells and they feature similar thicknesses for the maximum effect (most emission) in the range of 20-30 nm distances, similar to what we are reporting. A couple of systems do report much shorter distances, in the order of a few nm, one with silica²³⁷ and one of a phospholipid layer.⁵⁰³ At such short distances though, we did observe significant quenching, incompatible with high enhancement. The quenching of dye fluorescence close to PNPs has been extensively studied and confirms that with shell thicknesses of the order of 10 nm and lower significant quenching should take place.⁵²⁸ This effect should be maximized when there is overlap between the LSPR and the dye excitation wavelength, which is the case here.⁵²⁸ Beyond these values, plasmonic enhancement has been shown before to remain strong even into the long distances, all the way to 200 nm.⁵¹⁷ Our system is the sole one presenting such an optimization of the shell thickness in the context of catalysis (Table 8-7).¹²⁰

Finally, it is well known that dyes coupled with PNPs excited at their LSPR wavelength do feature a reduction in their lifetime. This effect is associated as well with the broadening of the LSPR observed upon deposition of $[Ru(bpy)_3]^{2+}$ onto Ag@SiO₂.⁵²⁸ We did not observe that this had any significant effect on catalytic results.

Based on the results on catalytic tests, we turned to electron energy loss spectroscopy (EELS) in order to better rationalise the optimal enhancement effect observed for a certain shell thickness.

5.4 Electron Energy Loss Spectroscopy

5.4.1 Experimental data from scanning transmission electron microscopy

Electron energy loss spectroscopy (EELS), used in conjunction with scanning transmission electron microscopy (STEM), is a powerful technique to map both bulk or surface plasmons intensity and energy. One of the advantages of STEM-EELS is to simultaneously provide both geospatial and energetic information of the surface plasmons.^{529, 530} Using STEM-EELS, the surface plasmon energy of the naked Ag cores was measured to be 3.4 eV (365 nm), at the surface of the NPs.⁷⁰ This value is different from the SPR value obtained for the same systems by UV-Vis spectroscopy, because the STEM-EELS experiment takes place in ultra-high vacuum, and not in solution. This value is similar to results from previous studies on other Ag NPs, such as citrate-coated spheres, PVP-cubes, prisms, triangles, fractals, and wires.⁵³¹⁻⁵³⁴

Coating Ag NPs with silica affected the surface plasmons, as it altered the dielectric medium around the PNP. Indeed, the energy of the surface plasmon measured at the surface of the NP decreased as a function of silica shell thickness.⁷⁰ For naked AgNPs, and Ag@SiO₂ with 7, 19 and 28 nm shells, we studied the intensity of the surface plasmon as a function of the distance to the Ag core (Figure 5-4). As expected, the intensity of the surface plasmon decreased exponentially in all cases. For no shell or a thin shell (7 nm), intensity was high and the decrease constant (Figure 4 grey and blue). For thicker shells (19 and 26 nm), there was a threshold effect, whereby almost no surface plasmon intensity was observed within the shell, while at the surface of the silica, intensity was restored and the signal decayed as a function of the distance like the naked system (Figure 5-4 green and orange). Interestingly in the latter systems, the intensity at the SiO₂/vacuum interface was greater than at a similar distance from the plasmonic core for naked NPs and with a thin shell of 7 nm. Moreover, the LSPR peak shifted in energy as the silica shell became thicker,

from 3.4 eV for naked Ag NPs down to 3.0 eV for a shell of 28 nm, which parallels the shift in the maximum of UV-Vis absorption shown in Figure 5-2. As STEM-EELS analysis are performed on individual particle, we selected NPs characteristic of the samples they belonged to. Analysis of shells larger than 30 nm could not be performed because the specimen was then too thick, preventing electrons from reaching the detector.⁵³¹



Figure 5-4- Intensity of the LSPR peak measured by STEM-EELS at 3,4, 3.2, 3.0 and 3.0 eV, for naked Ag, Ag@SiO₂_7nm, Ag@SiO₂_19nm and Ag@SiO₂_28nm NP respectively, measured as a function of the distance from the Ag surface.

5.4.2 Simulations using boundary element method

We then performed boundary element method (BEM) calculations with Matlab for metallic nanoparticles using MNPBEM toolbox^{535, 536} on 80 nm Ag spheres with various thicknesses of SiO₂ shells, in order to simulate electron energy loss spectra and study the influence of the solvent on the surface plasmon energy position.

The energies determined by the simulations using a dielectric medium equals to 0 are similar to the ones obtained in the STEM experiment (I.e. under vacuum). Both simulation in vacuum and experimental data showed a peak centered at 3.4 eV for naked Ag NPs and a decreasing energy as a function of SiO₂ shell thickness (Figure 5-5A). By changing the value of the dielectric medium around the core shell NPs to mimic materials in a solvent, the general trend obtained is similar but the energies are altered by the environment surrounding the material. When switching from vacuum to CH₃CN, the trend is similar but there is a small shift in energy associated to the change in the dielectric environment (Figure 5-5B). In both media, when the thickness of the shell increases, the energy and the intensity decrease. Yet for thin silica layers, between 0 and 15 nm, a peak with a lower energy but more intense than for naked NPs is observed, similarly to data collected using STEM-EELS.



Figure 5-5 - Simulations of the intensity of the LSPR peaks at energies ranging between 2.25 and 3.75 eV for Ag@SiO₂ with shell ranging from 0 to 45 nm obtained with Matlab MNPBEM toolbox in vacuum (A) and in CH₃CN (B)

Despite some discrepancies in the energy values obtained by STEM-EELS, MNPBEM toolbox and UV-Vis spectroscopy, which can be attributed to the polydispersity of the NPs and the different dielectric media, similar trends in the energy decrease with increasing silica thickness were observed for the three methods. Even though, the intensity is dumped when going away from the metallic core, the plasmonic NP still has a significant impact in its surrounding environment as far as 40 nm away from its surface (Figure 5-6). Moreover, the intensity at the surface of the silica shell is particularly compelling for thicker coating. Thus, higher conversions were observed for Ag@SiO₂-[Ru] NPs for which the separation between the photocatalyst and the plasmonic core was enough to avoid surface quenching but still offers an appealing enhanced electromagnetic field.



Figure 5-6– Intensity of the LSPR peak calculated with Matlab MNPBEM toolbox in CH_3CN as a function of the distance from the Ag surface for naked Ag NPs and Ag@SiO₂ with 7, 19 and 28 nm shells

These results suggest that each component in the catalyst design is essential to efficient plasmonic enhancement. First, the Ag core allows the needed electro-magnetic field enhancement by SPR. Second, $[Ru(bpy)_3]^{2+}$ acted as the catalyst for the reaction. Third, both the core and fluorophores needed to be properly sheltered from one another by a thick enough silica shell, while the shell could not be too thick, otherwise the plasmon effect was too weak. Fourth, light was needed to activate both the SPR and the fluorophore itself. If any of these conditions was not met, catalysis was sub optimal. Like for the fluorescence study, we observed a maximum in catalysis activity for a medium shell thickness, namely at 28 nm. Thinner shells are less efficient, likely because of quenching. For larger ones, the SPR of the core is likely to be less effective.

5.5 Conclusion

In conclusion, we have synthesized a series of plasmonic nanoparticles coated with silica at various thicknesses and decorated with a photocatalyst (Ag@SiO₂-[Ru] NPs). This system allowed for the first time a systematic study of the phosphorescence and the photocatalytic activity of these materials. The light-induced field enhancement in the vicinity of the plasmonic Ag NPs is responsible for the increased production of ¹O₂ thus the catalytic activity of the [Ru(bpy)₃]Cl₂ towards the oxidation of alkenes. We have demonstrated an up to 4-fold activity increased compared to [Ru(bpy)₃]Cl₂ immobilized on SiO₂ NPs for nanomaterials with a 28 nm silica shell. Careful engineering of the photocatalyst was observed for thinner silica shells, while the photocatalyst was not affected by the LSPR for materials with thicker shells. Interestingly, EELS measurements and Matlab MNPBEM toolbox simulations revealed that even though there is an isolating layer, the intensity of the surface plasmons is strong at the interface between the silica layer and the photocatalyst, thus separation between the photocatalyst and the plasmonic core avoid surface quenching but still offers an appealing enhanced electromagnetic field in the

photocatalyst's environment. The LSPR-induced field enhancement is the strongest at the surface of naked Ag NPs yet photocatalysts undergo quenching and for our Ag@SiO₂-[Ru] NPs, maximum luminescence emission and catalytic activity were observed for thicker silica coatings, for which the intensity of the surface plasmon is still significant.

5.6 References

16. Ghogare, A. A.; Greer, A., Using Singlet Oxygen to Synthesize Natural Products and Drugs. *Chem. Rev.* **2016**, *116*(17), 9994-10034.

20. Yoon, T. P.; Ischay, M. A.; Du, J., Visible Light Photocatalysis as a Greener Approach to Photochemical Synthesis. *Nat. Chem.* **2010**, *2*(7), 527-532.

26. Sharma, S.; Sharma, A., Recent Advances in Photocatalytic Manipulations of Rose Bengal in Organic Synthesis. *Org. Biomol. Chem.* **2019**, *17*(18), 4384-4405.

35. Teegardin, K.; Day, J. I.; Chan, J.; Weaver, J., Advances in Photocatalysis: A Microreview of Visible Light Mediated Ruthenium and Iridium Catalyzed Organic Transformations. *Org. Proc. Res. Dev.* **2016**, *20*(7), 1156-1163.

47. Amara, Z.; Bellamy, J. F.; Horvath, R.; Miller, S. J.; Beeby, A.; Burgard, A.; Rossen, K.; Poliakoff, M.; George, M. W., Applying Green Chemistry to the Photochemical Route to Artemisinin. *Nat. Chem.* **2015**, *7*(6), 489-495.

61. de Aberasturi, D. J.; Serrano-Montes, A. B.; Liz-Marzán, L. M., Modern Applications of Plasmonic Nanoparticles: From Energy to Health. *Adv. Opt. Mater.* **2015**, *3*(5), 602-617.

70. Moores, A.; Goettmann, F., The Plasmon Band in Noble Metal Nanoparticles: An Introduction to Theory and Applications. *New J. Chem.* **2006**, *30*(8), 1121-1132.

75. Swearer, D. F.; Zhao, H.; Zhou, L.; Zhang, C.; Robatjazi, H.; Martirez, J. M. P.; Krauter, C. M.; Yazdi, S.; McClain, M. J.; Ringe, E., Heterometallic Antenna– Reactor Complexes for Photocatalysis. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113*(32), 8916-8920.

77. Planas, O.; Macia, N.; Agut, M.; Nonell, S.; Heyne, B., Distance-Dependent Plasmon-Enhanced Singlet Oxygen Production and Emission for Bacterial Inactivation. *J. Am. Chem. Soc.* **2016**, *138*(8), 2762-2768.

93. Chavez, S.; Aslam, U.; Linic, S., Design Principles for Directing Energy and Energetic Charge Flow in Multicomponent Plasmonic Nanostructures. *ACS Energy Lett.* **2018**, *3*(7), 1590-1596.

107. Polshettiwar, V.; Varma, R. S., Green Chemistry by Nano-Catalysis. *Green Chem.* **2010**, *12*(5), 743-754.

120. Maier, S. A., *Plasmonics: Fundamentals and Applications*. Springer Science & Business Media: 2007.

136. Xiao, M.; Jiang, R.; Wang, F.; Fang, C.; Wang, J.; Jimmy, C. Y., Plasmon-Enhanced Chemical Reactions. *J. Mater. Chem. A* **2013**, *1*(19), 5790-5805.

160. Mayer, K. M.; Hafner, J. H., Localized Surface Plasmon Resonance Sensors. *Chemical Reviews* **2011**, *111*(6), 3828-3857.

237. Mori, K.; Kawashima, M.; Che, M.; Yamashita, H., Enhancement of the Photoinduced Oxidation Activity of a Ruthenium(Ii) Complex Anchored on Silica-Coated Silver Nanoparticles by Localized Surface Plasmon Resonance. *Angew. Chem.* **2010**, *122* (46), 8780-8783.

267. Zhang, C.; Zhao, H.; Zhou, L.; Schlather, A. E.; Dong, L.; McClain, M. J.; Swearer, D. F.; Nordlander, P.; Halas, N. J., Al-Pd Nanodisk Heterodimers as Antenna-Reactor Photocatalysts. *Nano Lett.* **2016**, *16*(10), 6677-6682.

362. Linic, S.; Christopher, P.; Ingram, D. B., Plasmonic-Metal Nanostructures for Efficient Conversion of Solar to Chemical Energy. *Nat. Mater.* **2011**, *10*(12), 911.

442. Ravelli, D.; Dondi, D.; Fagnoni, M.; Albini, A., Photocatalysis. A Multi-Faceted Concept for Green Chemistry. *Chem. Soc. Rev.* **2009**, *38*(7), 1999-2011.

443. Luo, J.; Zhang, S.; Sun, M.; Yang, L.; Luo, S.; Crittenden, J. C., A Critical Review on Energy Conversion and Environmental Remediation of Photocatalysts with Remodeling Crystal Lattice, Surface, and Interface. *ACS Nano* **2019**, *13*(9), 9811-9840.

444. Li, J.; Wu, N., Semiconductor-Based Photocatalysts and Photoelectrochemical Cells for Solar Fuel Generation: A Review. *Catal. Sci. Technol.* **2015**, *5*(3), 1360-1384.

445. McCullagh, C.; Skillen, N.; Adams, M.; Robertson, P. K., Photocatalytic Reactors for Environmental Remediation: A Review. *J. Chem. Technol. Biotechnol.* **2011**, *86* (8), 1002-1017.

446. König, B., Photocatalysis in Organic Synthesis–Past, Present, and Future. *Eur. J. Org. Chem.* **2017**, *2017*(15), 1979-1981.

447. Michelin, C.; Hoffmann, N., Photocatalysis Applied to Organic Synthesis–a Green Chemistry Approach. *Curr. Opin. Green Sustain. Chem.* **2018**, *10*, 40-45.

448. Ong, C. B.; Ng, L. Y.; Mohammad, A. W., A Review of Zno Nanoparticles as Solar Photocatalysts: Synthesis, Mechanisms and Applications. *Renew. Sust. Energy Rev.* **2018**, *81*, 536-551.

449. Wang, X.; Blechert, S.; Antonietti, M., Polymeric Graphitic Carbon Nitride for Heterogeneous Photocatalysis. *ACS Catal.* **2012**, *2*(8), 1596-1606.

450. Cao, S.; Low, J.; Yu, J.; Jaroniec, M., Polymeric Photocatalysts Based on Graphitic Carbon Nitride. *Adv. Mater.* **2015**, *27*(13), 2150-2176.

451. Wang, J.-L.; Wang, C.; Lin, W., Metal–Organic Frameworks for Light Harvesting and Photocatalysis. *ACS Catal.* **2012**, *2*(12), 2630-2640.

452. Wang, J.-L.; Wang, C.; deKrafft, K. E.; Lin, W., Cross-Linked Polymers with Exceptionally High Ru (Bipy) 32+ Loadings for Efficient Heterogeneous Photocatalysis. *ACS Catal.* **2012**, *2*(3), 417-424.

453. Ravelli, D.; Protti, S.; Neri, P.; Fagnoni, M.; Albini, A., Photochemical Technologies Assessed: The Case of Rose Oxide. *Green Chem.* **2011**, *13*(7), 1876-1884.

454. Prier, C. K.; Rankic, D. A.; MacMillan, D. W., Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113*(7), 5322-5363.

455. Twilton, J.; Zhang, P.; Shaw, M. H.; Evans, R. W.; MacMillan, D. W., The Merger of Transition Metal and Photocatalysis. *Nat. Rev. Chem.* **2017**, *1*(7), 1-19.

456. Kuramochi, Y.; Ishitani, O.; Ishida, H., Reaction Mechanisms of Catalytic Photochemical Co2 Reduction Using Re (I) and Ru (Ii) Complexes. *Coord. Chem. Rev.* **2018**, *373*, 333-356.

457. Deponti, E.; Natali, M., Photocatalytic Hydrogen Evolution with Ruthenium Polypyridine Sensitizers: Unveiling the Key Factors to Improve Efficiencies. *Dalton Trans.* **2016**, *45*(22), 9136-9147.

458. Lehn, J.-M.; Ziessel, R., Photochemical Reduction of Carbon Dioxide to Formate Catalyzed by 2, 2ť-Bipyridine-or 1, 10-Phenanthroline-Ruthenium (Ii) Complexes. *J. Organomet. Chem.* **1990**, *382*(1-2), 157-173.

459. Luo, Q.; Mao, R.; Zhu, Y.; Wang, Y., Photoredox-Catalyzed Generation of Sulfamyl Radicals: Sulfonamidation of Enol Silyl Ether with Chlorosulfonamide. *J. Org. Chem.* **2019**, *84*(21), 13897-13907.

460. Sumino, S.; Uno, M.; Fukuyama, T.; Ryu, I.; Matsuura, M.; Yamamoto, A.; Kishikawa, Y., Photoredox-Catalyzed Hydrodifluoroalkylation of Alkenes Using Difluorohaloalkyl Compounds and a Hantzsch Ester. *J. Org. Chem.* **2017**, *82*(10), 5469-5474.

461. Chandrasekhar, D.; Borra, S.; Nanubolu, J. B.; Maurya, R. A., Visible Light Driven Photocascade Catalysis: Ru (Bpy) 3 (Pf6) 2/Tbhp-Mediated Synthesis of Fused B-Carbolines in Batch and Flow Microreactors. *Org. Lett.* **2016**, *18*(12), 2974-2977.

462. Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P. I.; von Zelewsky, A. v., Ru (Ii) Polypyridine Complexes: Photophysics, Photochemistry, Eletrochemistry, and Chemiluminescence. *Coord. Chem. Rev.* **1988**, *84*, 85-277.

463. Cerfontaine, S.; Wehlin, S. A.; Elias, B.; Troian-Gautier, L., Photostable Polynuclear Ruthenium (Ii) Photosensitizers Competent for Dehalogenation Photoredox Catalysis at 590 Nm. *J. Am. Chem. Soc.* **2020**, *142*(12), 5549-5555.

464. Montagnon, T.; Tofi, M.; Vassilikogiannakis, G., Using Singlet Oxygen to Synthesize Polyoxygenated Natural Products from Furans. *Accounts of chemical research* **2008**, *41*(8), 1001-1011.

465. Astruc, D.; Lu, F.; Aranzaes, J. R., Nanoparticles as Recyclable Catalysts: The Frontier between Homogeneous and Heterogeneous Catalysis. *Angew. Chem. Int. Ed.* **2005**, *44*(48), 7852-7872.

466. Tambosco, B.; Segura, K.; Seyrig, C.; Cabrera, D.; Port, M.; Ferroud, C.; Amara, Z., Outer-Sphere Effects in Visible-Light Photochemical Oxidations with Immobilized and Recyclable Ruthenium Bipyridyl Salts. *ACS Catal.* **2018**, *8*(5), 4383-4389.

467. Fabry, D. C.; Ronge, M. A.; Rueping, M., Immobilization and Continuous Recycling of Photoredox Catalysts in Ionic Liquids for Applications in Batch Reactions and Flow Systems: Catalytic Alkene Isomerization by Using Visible Light. *Chemistry – A European Journal* **2015**, *21*(14), 5350-5354.

468. Sheehan, F. Element Scarcity – Euchems Periodic Table. <u>https://www.euchems.eu/euchems-periodic-table/</u> (accessed Feb. 5 2021).

469. Teixeira, R. I.; de Lucas, N. C.; Garden, S. J.; Lanterna, A. E.; Scaiano, J. C., Glass Wool Supported Ruthenium Complexes: Versatile, Recyclable Heterogeneous Photoredox Catalysts. *Catal. Sci. Technol.* **2020**, *10*(5), 1273-1280.

470. Li, J.-F.; Li, C.-Y.; Aroca, R. F., Plasmon-Enhanced Fluorescence Spectroscopy. *Chem. Soc. Rev.* **2017**, *46*(13), 3962-3979.

471. Turner, A. P., Biosensors: Sense and Sensibility. *Chem. Soc. Rev.* **2013**, *42* (8), 3184-3196.

472. Ueno, K.; Oshikiri, T.; Sun, Q.; Shi, X.; Misawa, H., Solid-State Plasmonic Solar Cells. *Chem. Rev.* **2017**, *118*(6), 2955-2993.

473. Li, N.; Zhao, P.; Astruc, D., Anisotropic Gold Nanoparticles: Synthesis, Properties, Applications, and Toxicity. *Angew. Chem. Int. Ed.* **2014**, *53*(7), 1756-1789.

474. Lang, X.; Chen, X.; Zhao, J., Heterogeneous Visible Light Photocatalysis for Selective Organic Transformations. *Chem. Soc. Rev.* **2014**, *43*(1), 473-486.

475. Gellé, A.; Moores, A., Plasmonic Nanoparticles: Photocatalysts with a Bright Future. *Current Opinion in Green and Sustainable Chemistry* **2018**.

476. Gellé, A.; Jin, T.; de la Garza, L.; Price, G. D.; Besteiro, L. V.; Moores, A., Applications of Plasmon-Enhanced Nanocatalysis to Organic Transformations. *Chemical Reviews* **2019**.

477. Scaiano, J. C.; Stamplecoskie, K., Can Surface Plasmon Fields Provide a New Way to Photosensitize Organic Photoreactions? From Designer Nanoparticles to Custom Applications. *J. Phys. Chem. Let.* **2013**, *4*(7), 1177-1187.

478. Giannini, V.; Fernández-Domínguez, A. I.; Heck, S. C.; Maier, S. A., Plasmonic Nanoantennas: Fundamentals and Their Use in Controlling the Radiative Properties of Nanoemitters. *Chem. Rev.* **2011**, *111*(6), 3888-3912.

479. Schuller, J. A.; Barnard, E. S.; Cai, W.; Jun, Y. C.; White, J. S.; Brongersma, M. L., Plasmonics for Extreme Light Concentration and Manipulation. *Nat. Mater.* **2010**, *9*, 193.

480. Barnes, W. L.; Dereux, A.; Ebbesen, T. W., Surface Plasmon Subwavelength Optics. *Nature* **2003**, *424*(6950), 824-830.

481. Kinkhabwala, A.; Yu, Z.; Fan, S.; Avlasevich, Y.; Müllen, K.; Moerner, W., Large Single-Molecule Fluorescence Enhancements Produced by a Bowtie Nanoantenna. *Nat. Photonics* **2009**, *3*(11), 654-657.

482. Wertz, E.; Isaacoff, B. P.; Flynn, J. D.; Biteen, J. S., Single-Molecule Super-Resolution Microscopy Reveals How Light Couples to a Plasmonic Nanoantenna on the Nanometer Scale. *Nano Lett.* **2015**, *15*(4), 2662-2670.

483. Darvill, D.; Centeno, A.; Xie, F., Plasmonic Fluorescence Enhancement by Metal Nanostructures: Shaping the Future of Bionanotechnology. *Phys. Chem. Chem. Phys* **2013**, *15*(38), 15709-15726.

484. Deng, W.; Goldys, E. M., Plasmonic Approach to Enhanced Fluorescence for Applications in Biotechnology and the Life Sciences. *Langmuir* **2012**, *28*(27), 10152-10163. 485. Deng, W.; Xie, F.; Baltar, H. T.; Goldys, E. M., Metal-Enhanced Fluorescence in the Life Sciences: Here, Now and Beyond. *Phys. Chem. Chem. Phys* **2013**, *15* (38), 15695-15708.

486. Anker, J.; Hall, P.; Lyandres, O.; Shah, N.; Zhao, J.; Van Duyne, R., Biosensing with Plasmonic Nanosensors. *Nat. Mater.* **2008**, *7*, 442-453.

487. Willets, K. A.; Van Duyne, R. P., Localized Surface Plasmon Resonance Spectroscopy and Sensing. *Annu. Rev. Phys. Chem.* **2007**, *58*, 267-297.

488. Banholzer, M. J.; Millstone, J. E.; Qin, L.; Mirkin, C. A., Rationally Designed Nanostructures for Surface-Enhanced Raman Spectroscopy. *Chem. Soc. Rev.* **2008**, *37*(5), 885-897.

489. Robatjazi, H.; Zhao, H.; Swearer, D. F.; Hogan, N. J.; Zhou, L.; Alabastri, A.; McClain, M. J.; Nordlander, P.; Halas, N. J., Plasmon-Induced Selective Carbon Dioxide Conversion on Earth-Abundant Aluminum-Cuprous Oxide Antenna-Reactor Nanoparticles. *Nat Commun* **2017**, *8*(1), 27.

490. Li, K.; Hogan, N. J.; Kale, M. J.; Halas, N. J.; Nordlander, P.; Christopher, P., Balancing near-Field Enhancement, Absorption, and Scattering for Effective Antenna-Reactor Plasmonic Photocatalysis. *Nano Lett.* **2017**, *17*(6), 3710-3717.

491. Drexhage, K. H.; Kuhn, H.; Schäfer, F. P., Variation of the Fluorescence Decay Time of a Molecule in Front of a Mirror. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*(2), 329-329.

492. Aslan, K.; Gryczynski, I.; Malicka, J.; Matveeva, E.; Lakowicz, J. R.; Geddes, C. D., Metal-Enhanced Fluorescence: An Emerging Tool in Biotechnology. *Curr. Opin. Biotechnol.* **2005**, *16*(1), 55-62.

493. Lakowicz, J. R., Radiative Decay Engineering: Biophysical and Biomedical Applications. *Anal. Biochem.* **2001**, *298*(1), 1-24.

494. Lakowicz, J. R.; Ray, K.; Chowdhury, M.; Szmacinski, H.; Fu, Y.; Zhang, J.; Nowaczyk, K., Plasmon-Controlled Fluorescence: A New Paradigm in Fluorescence Spectroscopy. *Analyst* **2008**, *133*(10), 1308-1346.

495. Zhang, J.; Fu, Y.; Chowdhury, M. H.; Lakowicz, J. R., Single-Molecule Studies on Fluorescently Labeled Silver Particles: Effects of Particle Size. *J. Phys. Chem. C* **2008**, *112* (1), 18-26.

496. Macia, N.; Kabanov, V.; Heyne, B., Rationalizing the Plasmonic Contributions to the Enhancement of Singlet Oxygen Production. *J. Phys. Chem.* C**2020**, *124*(6), 3768-3777.

497. Macia, N.; Bresoli-Obach, R.; Nonell, S.; Heyne, B., Hybrid Silver Nanocubes for Improved Plasmon-Enhanced Singlet Oxygen Production and Inactivation of Bacteria. *J. Am. Chem. Soc.* **2018**, *141*(1), 684-692.

498. Mendoza, C.; Désert, A.; Chateau, D.; Monnereau, C.; Khrouz, L.; Lerouge, F.; Andraud, C.; Monbaliu, J.-C. M.; Parola, S.; Heinrichs, B., Au Nanobipyramids@ Msio 2 Core-Shell Nanoparticles for Plasmon-Enhanced Singlet Oxygen Photooxygenations in Segmented Flow Microreactors. *Nanoscale Advances* **2020**, *2*(11), 5280-5287.

499. Yin, N.; Liu, Y.; Liu, L.; Lei, J.; Jiang, T.; Wang, H.; Zhu, L.; Xu, X., Fluorescence Enhancement of Ru(Bpy)32+ by Core–Shell Ag@Sio2 Nanocomposites. *J. Alloys Compd.* **2013**, *581*, 6-10.

500. Tovmachenko, O. G.; Graf, C.; van den Heuvel, D. J.; van Blaaderen, A.; Gerritsen, H. C., Fluorescence Enhancement by Metal-Core/Silica-Shell Nanoparticles. *Adv. Mater.* **2006**, *18*(1), 91-95.

501. Cheng, D.; Xu, Q.-H., Separation Distance Dependent Fluorescence Enhancement of Fluorescein Isothiocyanate by Silver Nanoparticles. *Chem. Commun.* **2007**, (3), 248-250.

502. Bardhan, R.; Grady, N. K.; Cole, J. R.; Joshi, A.; Halas, N. J., Fluorescence Enhancement by Au Nanostructures: Nanoshells and Nanorods. *ACS Nano* **2009**, *3* (3), 744-752.

503. An, X.; Stelter, D.; Keyes, T.; Reinhard, B. M., Plasmonic Photocatalysis of Urea Oxidation and Visible-Light Fuel Cells. *Chem* **2019**, *5*(8), 2228-2242.

504. Chen, Y.; Munechika, K.; Ginger, D. S., Dependence of Fluorescence Intensity on the Spectral Overlap between Fluorophores and Plasmon Resonant Single Silver Nanoparticles. *Nano Lett.* **2007**, *7*(3), 690-696.

505. Linic, S.; Chavez, S.; Elias, R., Flow and Extraction of Energy and Charge Carriers in Hybrid Plasmonic Nanostructures. *Nat. Mater.* **2021**, 1-9.

506. Blanchard, V.; Asbai, Z.; Cottet, K.; Boissonnat, G.; Port, M.; Amara, Z., Continuous Flow Photo-Oxidations Using Supported Photocatalysts on Silica. *Org. Proc. Res. Dev.* **2020**, *24*(5), 822-826.

507. Wu, C.; Mosher, B. P.; Lyons, K.; Zeng, T., Reducing Ability and Mechanism for Polyvinylpyrrolidone (Pvp) in Silver Nanoparticles Synthesis. *J. Nanosci. Nanotechnol.* **2010**, *10*(4), 2342-2347.

508. Kobayashi, Y.; Katakami, H.; Mine, E.; Nagao, D.; Konno, M.; Liz-Marzán, L. M., Silica Coating of Silver Nanoparticles Using a Modified Stöber Method. *J. Colloid Interface Sci.* **2005**, *283*(2), 392-396.

509. Matsui, K.; Momose, F., Luminescence Properties of Tris (2, 2 '-Bipyridine) Ruthenium (Ii) in Sol- Gel Systems of Sio2. *Chem. Mater.* **1997**, *9*(11), 2588-2591.

510. Innocenzi, P.; Kozuka, H.; Yoko, T., Fluorescence Properties of the Ru (Bpy) 32+ Complex Incorporated in Sol– Gel-Derived Silica Coating Films. *J. Phys. Chem. B* **1997**, *101* (13), 2285-2291.

511. Macia, N.; Kabanov, V.; Côté-Cyr, M.; Heyne, B., Roles of near and Far Fields in Plasmon-Enhanced Singlet Oxygen Production. *J. Phys. Chem. Let.* **2019**, *10* (13), 3654-3660.

512. Szmacinski, H.; Lakowicz, J. R.; Catchmark, J. M.; Eid, K.; Anderson, J. P.; Middendorf, L., Correlation between Scattering Properties of Silver Particle Arrays and Fluorescence Enhancement. *Appl. Spectrosc.* **2008**, *62*(7), 733-738.

513. Liz-Marzán, L. M., Tailoring Surface Plasmons through the Morphology and Assembly of Metal Nanoparticles. *Langmuir* **2006**, *22*(1), 32-41.

514. Wertz, E. A.; Isaacoff, B. P.; Biteen, J. S., Wavelength-Dependent Super-Resolution Images of Dye Molecules Coupled to Plasmonic Nanotriangles. *ACS Photonics* **2016**, *3*(10), 1733-1740.

515. Abadeer, N. S.; Brennan, M. R.; Wilson, W. L.; Murphy, C. J., Distance and Plasmon Wavelength Dependent Fluorescence of Molecules Bound to Silica-Coated Gold Nanorods. *ACS Nano* **2014**, *8*(8), 8392-8406.

516. Hu, B.; Cao, X.; Nahan, K.; Caruso, J.; Tang, H.; Zhang, P., Surface Plasmon-Photosensitizer Resonance Coupling: An Enhanced Singlet Oxygen Production Platform for Broad-Spectrum Photodynamic Inactivation of Bacteria. *J. Mater. Chem. B***2014**, *2*(40), 7073-7081.

517. Kedem, O.; Wohlleben, W.; Rubinstein, I., Distance-Dependent Fluorescence of Tris (Bipyridine) Ruthenium (Ii) on Supported Plasmonic Gold Nanoparticle Ensembles. *Nanoscale* **2014**, *6* (24), 15134-15143.

518. Terra, J. C.; Desgranges, A.; Monnereau, C.; Sanchez, E. H.; De Toro, J. A.; Amara, Z.; Moores, A., Photocatalysis Meets Magnetism: Designing Magnetically Recoverable Supports for Visible-Light Photocatalysis. *ACS Appl. Mater. Inter.* **2020**, *12* (22), 24895-24904.

519. Banholzer, M. J.; Harris, N.; Millstone, J. E.; Schatz, G. C.; Mirkin, C. A., Abnormally Large Plasmonic Shifts in Silica-Protected Gold Triangular Nanoprisms. *J. Phys. Chem. C* **2010**, *114*(16), 7521-7526.

520. Rodríguez-Fernández, J.; Pastoriza-Santos, I.; Perez-Juste, J.; García de Abajo, F. J.; Liz-Marzan, L. M., The Effect of Silica Coating on the Optical Response of Sub-Micrometer Gold Spheres. *J. Phys. Chem.* C**2007**, *111*(36), 13361-13366.

521. Pastoriza-Santos, I.; Gomez, D.; Pérez-Juste, J.; Liz-Marzán, L. M.; Mulvaney, P., Optical Properties of Metal Nanoparticle Coated Silica Spheres: A Simple Effective Medium Approach. *Phys. Chem. Chem. Phys* **2004**, *6* (21), 5056-5060.

522. Aslam, U.; Chavez, S.; Linic, S., Controlling Energy Flow in Multimetallic Nanostructures for Plasmonic Catalysis. *Nat. Nanotechnol.* **2017**, *12*(10), 1000-1005.

523. Chavez, S.; Rao, V. G.; Linic, S., Unearthing the Factors Governing Site Specific Rates of Electronic Excitations in Multicomponent Plasmonic Systems and Catalysts. *Faraday Discuss.* **2019**, *214*, 441-453.

524. Cole-Hamilton, D. J.; Tooze, R. P., *Catalyst Separation, Recovery and Recycling: Chemistry and Process Design*. Springer Science & Business Media: 2006; Vol. 30.

525. Vankayala, R.; Sagadevan, A.; Vijayaraghavan, P.; Kuo, C.-L.; Hwang, K. C., Metal Nanoparticles Sensitize the Formation of Singlet Oxygen. *Angew. Chem. Int. Ed.* **2011**, *50* (45), 10640-10644.

526. Toftegaard, R.; Arnbjerg, J.; Daasbjerg, K.; Ogilby, P. R.; Dmitriev, A.; Sutherland, D. S.; Poulsen, L., Metal-Enhanced 1270 Nm Singlet Oxygen Phosphorescence. *Angew. Chem. Int. Ed.* **2008**, *47*(32), 6025-6027.

527. Huang, Y. F.; Zhang, M.; Zhao, L. B.; Feng, J. M.; Wu, D. Y.; Ren, B.; Tian, Z. Q., Activation of Oxygen on Gold and Silver Nanoparticles Assisted by Surface Plasmon Resonances. *Angew. Chem. Int. Ed.* **2014**, *53*(9), 2353-2357.

528. Reineck, P.; Gómez, D.; Ng, S. H.; Karg, M.; Bell, T.; Mulvaney, P.; Bach, U., Distance and Wavelength Dependent Quenching of Molecular Fluorescence by Au@ Sio2 Core-Shell Nanoparticles. *ACS Nano* **2013**, *7*(8), 6636-6648.

529. Wu, Y.; Li, G.; Camden, J. P., Probing Nanoparticle Plasmons with Electron Energy Loss Spectroscopy. *Chem. Rev.* **2017**, *118*(6), 2994-3031.

530. Kociak, M.; Stéphan, O., Mapping Plasmons at the Nanometer Scale in an Electron Microscope. *Chem. Soc. Rev.* **2014**, *43*(11), 3865-3883.

531. Brodusch, N.; Demers, H.; Gellé, A.; Moores, A.; Gauvin, R., Electron Energy-Loss Spectroscopy (Eels) with a Cold-Field Emission Scanning Electron Microscope at Low Accelerating Voltage in Transmission Mode. *Ultramicroscopy* **2019**, *203*, 21-36.

532. Bicket, I. C.; Bellido, E. P.; McRae, D. M.; Lagugné-Labarthet, F.; Botton, G. A., Carving Plasmon Modes in Silver Sierpinski Fractals. *ACS Photonics* **2019**, *6*(11), 2974-2984.

533. Wang, W.; Yang, Q.; Fan, F.; Xu, H.; Wang, Z. L., Light Propagation in Curved Silver Nanowire Plasmonic Waveguides. *Nano letters* **2011**, *11*(4), 1603-1608.

534. Koh, A. L.; Bao, K.; Khan, I.; Smith, W. E.; Kothleitner, G.; Nordlander, P.; Maier, S. A.; McComb, D. W., Electron Energy-Loss Spectroscopy (Eels) of Surface Plasmons in Single Silver Nanoparticles and Dimers: Influence of Beam Damage and Mapping of Dark Modes. *ACS Nano* **2009**, *3*(10), 3015-3022.

535. Hohenester, U., Simulating Electron Energy Loss Spectroscopy with the Mnpbem Toolbox. *Comput. Phys. Commun.* **2014**, *185*(3), 1177-1187.

536. De Abajo, F. G.; Howie, A., Retarded Field Calculation of Electron Energy Loss in Inhomogeneous Dielectrics. *Physical Review B* **2002**, *65* (11), 115418.

Transition

The Ag@SiO₂-[Ru] system presented in the previous chapter demonstrated that for a given photocatalyst, namely [Ru(bpy)₃]²⁺an optimal separation distance between the plasmonic surface and the photocatalyst gave the highest emission and catalytic performances. According to previous observations and hypotheses, spectral overlap between the PNP and the photocatalysts, and the quantum yield of the free species could also influence the enhancement of the luminescence. The following study focussed on evaluating the impact of these two parameters on the photocatalysts, and also to see if the optimal thickness of silica would be identical for different photocatalysts.

6 Chapter 6 - Rational for antenna-reactor design using Ag PNPs to boost photocatalysis



This chapter is based upon a manuscript in preparation. All co-authors granted permission to include this manuscript in the thesis.

Alexandra Gellé, Graham Beaton, Kevin Stamplecoskie, Zacharias Amara, and Audrey Moores. In preparation.

6.1 Introduction

Harvesting energy from light for photocatalysis has been at the center of attention for years, and promising results have been reported. Homogeneous visible light-mediated catalysts, such as Ru- and Ir-based complexes and organic fluorophores, have been exploited a large range of oxidation and coupling reactions.²⁰ Heterogenous catalysis is also at the heart of intense research developments owing to their robustness and easiness of separation. Anchoring of homogeneous catalysts on nanosupports allows to take advantage of the high activity of soluble species, as well as the heterogeneity of the support. In most cases, the support does not participate in the catalytic process. However, our previous work with Ag plasmonic nanoparticles and tris(bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, showed that the support could influence the catalytic activity. Our group showed that plasmonic nanoparticles (PNPs) can be used as both an anchor to immobilize homogeneous visible light-active species and to boost their activity owing to the plasmonic nanoparticles (PNPs) can be used as both an anchor to immobilize homogeneous visible light and enhanced the activity of $[Ru(bpy)_3]^{2+}$ immobilized on its surface the catalytic component of the bimetallic material.

The nanoantenna behavior of group XI nanoparticles arises from a strong interaction with light *via* a phenomenon called localized surface plasmon resonance (LSPR). PNPs are, among other effects, able to act as antennae modulating and concentrating light in their immediate vicinity.^{69, 478-482} This unique capacity has been most remarkably exploited for surface enhanced Raman spectroscopy (SERS) and surface plasmon resonance (SPR) spectroscopy techniques.^{483-485, 487, 488, 537} It is also well known that emission of luminescent species can be enhanced in the vicinity of plasmonic metals. More recently, metal-enhanced luminescence (MEL) has been extensively used to boost the photoactivity of Rose Bengal and the production of singlet oxygen ($^{1}O_{2}$) for bacteria degradation.^{77, 497} Only a few studies focusing on organic transformation reported the use of [Ru(bpy)₃]²⁺, and Ag NPs for the oxidation of styrene and urea degradation using $^{1}O_{2}$.^{237, 503}

In our previous work, we showed that $[Ru(bpy)_3]^{2+}$ catalytic activity could be boosted by a silica-coated Ag NP and that the separation distance between the photocatalysts and the plasmonic core played a pivotal role. We showed that tuning the thickness of silica influenced the photoactivity of Ag@SiO_2-[Ru] towards the Schenck Ene oxidation of citronellol using singlet oxygen as a green oxidant. A 4-fold enhancement of the catalytic performance was observed at the optimal thickness of 28 nm afforded the best catalytic results, while $[Ru(bpy)_3]^{2+}$ was quenched with thinner layers and the plasmonic core had limited impact on the photoactivity of the complex if the silica layer was too thick.

Herein, we report an analysis of the plasmonic boosting effect on three photocatalysts immobilized on Ag NPs. We synthesized a series of Ag@SiO₂ NPs with various shell thicknesses to immobilize [Ru(bpy)₃]²⁺, Methylene Blue (MB) and Rose Bengal (RB). All these photocatalyst are well-known for being able to form ${}^{1}O_{2}$ species, and therefore trigger oxidations of organic substrates, and feature various QY and excitation wavelengths (λ_{ex}). These three series of Ag@SiO₂-[photocatalyst] were used to study the impact of immobilization method, the QY of the photocatalyst and the spectral overlap between the photocatalyst and the Ag NPs on the luminescence and photocatalytic properties of the antenna-reactor nanomaterials.

The luminescence emission and photocatalytic activity of the nanomaterials were determined to evaluate the enhancement factor in each case and examine the impact of the different parameters. We found that the emission and catalytic activity for both MB and RB were significantly less enhanced than $[Ru(bpy)_3]^{2+}$, which we respectively attributed to the lack of spectral overlap and the already high QY. These results showed that careful design of nanoantenna-reactor with high enhancement factor is necessary to observe a high enhancement factor. Time-resolved spectroscopy measurements confirmed that the presence of the plasmonic core altered the photoactive properties of $[Ru(bpy)_3]^{2+}$ immobilized on Ag@SiO₂ NPs, and that the lifetime of the triplet excited state depends on the distance between the plasmonic surface and the photocatalyst.

6.2 Synthesis of plasmon-active supports for photocatalysis

For this study, we choose to synthesize silica-coated Ag NPs decorated with three common inorganic and organic photocatalysts, namely $[Ru(bpy)_3]^{2+}$, RB and MB. We studied how their luminescence and catalytic activity are influenced by the presence of the plasmonic core and the thickness of the separating layer. These photocatalysts were selected because they absorb at different wavelengths and feature various QY. The excitation wavelengths of $[Ru(bpy)_3]^{2+}$ ($\lambda_{ex} = 450$ nm) and RB ($\lambda_{ex} = 559$ nm) overlap with the SPR band, unlike the absorption of MB ($\lambda_{ex} = 690$ nm) which is redshifted compared to the other chosen photocatalysts and the SPR band.(Figure 1A) Moreover the three photocatalysts have different QY equal to 0.04, 0.14 and 0.52 respectively for $[Ru(bpy)_3]^{2+}$, RB and MB.

First, Ag NPs were obtained *via* polyol process ⁵⁰⁷ then the silica layer growth was done using the Stöber method. The thickness of the coating was adjusted by varying the amount of tetraethyl orthosilicate (TEOS) added.⁵⁰⁸ Both steps were conducted using previously reported methods and are detailed in the ESI.

The immobilization of the photocatalysts $[Ru(bpy)_3]^{2+}$ and MB was achieved readily by taking advantage of electrostatic interactions.^{466, 509, 510} Simple mixing of the positively charged photocatalysts with Ag@SiO₂ NPs afforded Ag@SiO₂-[Ru], Ag@SiO₂-MB NPs. (Figure 1B) The immobilization of RB required to first functionalize the silica surface with amino groups which was performed using (3-Aminopropyl)triethoxysilane (APTES). RB was activated with 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) prior to be mixing with functionalized Ag@SiO₂ NPs. Covalent bonding of RB was achieved by coupling and gave Ag@SiO₂-RB.(Figure 1B) the thus obtained series of decorated Ag@SiO₂ NPs also allowed us to investigate if the immobilization method had a significant impact on the photophysical properties of the antenna-reactor material. The three photosensitizers were immobilized on the same Ag@SiO₂ NPs with an identic surface coverage to ensure reproducibility and allow comparison of the photophysical properties.



Figure 6-1- A) Uv-Vis spectra of $Ag@SiO_2$ NPs and the three photocatalysts used, $[Ru(bpy)_3]^{2+}$, MB and RB, and B) B) synthesis of the silver plasmonic nanoparticles core with a silica shell and immobilization of the photocatalysts.

6.3 Characterization of Ag@SiO₂ and Ag@SiO₂-[photocatalyst] NPs

The Ag@SiO₂ NPs used for this study with RB and MB were identical to the ones used for our previous study. Their extensive characterization of Ag@SiO₂ is reported in details in Chapter 5.

Briefly, 80.4 ± 8.1 nm Ag NPs were observed by TEM and Ag@SiO₂ NPs with silica shell of 7, 15, 19, 25 28, 30, 33, 37, 40 and 45 nm were obtained depending on the amount of TEOS added. We determined the specific surface of Ag@SiO₂ NPs using Brunauer–Emmett–Teller (BET) measurements and immobilization of the photocatlysts was done ensuring the surface coverage on the NPs was identical for each thickness and

photocatalyst. ζ -potential measurements were used to confirm that functionalization of the SiO₂ with APTES was successful. The naked Ag@SiO₂ NP surface featured a negatively charged surface of -29.0 mV, a value which increased to -12.47 mV upon functionalization with APTES and finally reached -19.06 mV once RB was immobilized to form Ag@SiO₂-RB NPs. The amount of photocatalyst immobilized at the surface of Ag@SiO₂ NPs was determined by UV-Vis absorption spectroscopy, by computing the difference in the concentration of [Ru(bpy)₃]²⁺ in the initial solution and in the supernatant after exposure to the support. Optimal immobilization was achieved when collected supernatants were colorless.

Prior to the growth of the silica layer, the core Ag NPs featured a plasmonic band centered at 420 nm and the plasmon band of Ag@SiO₂ NPs redshifted and broadened as an effect of dielectric medium change at the vicinity of the Ag core.⁵¹⁹⁻⁵²¹ As the photocatalysts were immobilized at the surface of Ag@SiO₂ NPs, the extinction profile of the ensemble enveloped both the support SPR band and the absorption of the photocatalyst. This shows that immobilization of the photocatalysts hardly affected the absorption properties of the PNPs.

6.4

6.5 Evaluation of the bosting of the emission and catalytic activity of the photocatalysts

6.5.1 Influence of the plasmonic core on the luminescence properties

We then investigated the luminescence properties of the plasmonic materials synthesized. For each series, we irradiated at the excitation wavelength of its photocatalyst, 450, 559 and 660 nm for $[Ru(bpy)_3]^{2+}$, RB and MB respectively. The intensity of the luminescence was measured at their emission wavelength, 615, 571 and 690 nm respectively. Similarly to our previous study with $[Ru(bpy)_3]^{2+}$, the emission of the decorated PNPs was measured

and compared to commercial SiO_2 NPs with immobilized photocatalysts to evaluate the ability of the synthesized plasmon-active nanosupports to enhance the optical properties of RB and MB in presence of a plasmonic surface. The enhancement factor (EF), determined as the ratio of the intensity measured for each system and the one for the photocatalyst-decorated commercial 80 nm SiO₂ NPs without metallic core, was used to compare the nanomaterials.

The intensity of the emission measured was strongly correlated with the thickness of the shell for the three materials and each series followed a similar trend.

Figure 6-2 light doted lines) Thinner shells led to quenching and the intensity measured was less than the one of the plasmonic free system (SiO₂-[photocatatalyst]). As the shell thickened, the intensity of the emission measured increased until reaching a maximum for a 33 nm SiO₂ coating. For such materials, the photocatalysts were no longer quenched by the metallic core and radiative emissions were favored by the plasmon-enhanced field, hence boosting the emission of the photocatalysts. The greatest enhancement factor measured for $[Ru(bpy)_3]^{2+}$ immobilized on Ag@SiO₂_33nm NPs was equal to 4.1, RB and MB decorated NPs exhibited an enhancement factor equal to 2.3 and 1.6 respectively. Past this maximum, the intensity measured lowered with increasing shell thickness, and finally reached a plateau with an EF around 1, implying that the plasmonic core had a negligible influence for the materials with the thickest shells. Such a trend has been observed by other groups for various photoactive species immobilized on plasmonic nanoparticles.77, 497, 503 The Heyne group investigated the distance dependent emission of Rose Bengal, and ${}^{1}O_{2}$ produced by the photocatalyst. They also observed a maximum of emission of RB for an optimal SiO₂ layer, which was different than the thickness at which the production of ${}^{1}O_{2}$ was maximum.



Chapter 6 - Rational for antenna-reactor design using Ag PNPs to boost photocatalysis

Figure 6-2- Emission and catalytic enhancement factors measured for the three photocatalyst

6.5.2 Photocatalytic studies

The photooxidation of citronellol by singlet oxygen was then performed using the three Ag@SiO₂-[photocatalyst] series. The formation of allylic peroxydes by Schenck Ene reaction from citronellol was conducted in a photoreactor illuminated with white LEDs under aerobic conditions for 3 hours using the photocatalysts immobilized on Ag@SiO₂ with shell thicknesses ranging from 7 to 45 nm.(Scheme 6-1) Upon quenching with triphenylphosphine, the formation of the desired alcohol regioisomers was monitored using ¹H NMR (

Figure 6-2 dark lines) and GC-MS (Annex). The surface coverage was kept constant for the photooxidations with all the Ag@SiO₂-[photocatalyst] series for each species and the molar catalytic loading was selected so each SiO₂ commercial NPs decorated with a photocatalyst afforded a similar conversion around 60% in order to be able to compare each series.



Scheme 6-1 - Reaction scheme for the oxidation of citronellol using Ag@SiO₂-[photocatalyst] NPs. Standard reaction conditions: 3 h and O₂ balloon. For Ag@SiO₂-[Ru] : 0.33 mmol of citronellol and 0.0034 mol% in [Ru(bpy)₃]²⁺ in acetonitrile. For Ag@SiO₂-MB 0.42 mmol of citronellol and 0.0011 mol% in MB in isopropanol. For Ag@SiO₂-RB, 0.42 mmol of citronellol and 0.0009 mol% in RB in isopropanol.

It is worth noting that photocatalysts immobilized on SiO₂ were less efficient than their free counterparts, as it is often observed for immobilized homogeneous catalysts.⁵²⁴ Control experiments show that almost no conversion occured under light irradiation in the absence of catalyst, or with our Ag@SiO₂-[Ru] NPs without light irradiation (ESI). When naked Ag NPs were used alone as catalysts, the conversion remained negligible. Previous study showed that naked Ag PNPs could directly catalyze the formation of ${}^{1}O_{2}$, ${}^{64, 525, 526}$ but these did not prove to be efficient for the Schenck Ene process during our studies.

We used enhancement factor values, calculated as the ratios of the conversion measured for the plasmonic samples and the one of the decorated commercial SiO_2 NPs, to compare the catalytic systems within the series and with different photocatalysts. A similar trend was observed for all photocatalysts immobilized on Ag@SiO2 NPs.(

Figure 6-2 dark lines) The trends observed for the photocatalytic activity and the emission intensity were identical: enhancement factors were lower than 1 for the thinnest shells, then the enhancement factor increased with thicker SiO₂ layers and reached a maximum,

and finally a plateau was reached for the thickest shells. Similarly to our previous results with $[Ru(bpy)_3]^{2+}$, the thickness of SiO₂ for which RB and MB decorated PNPs gave the highest conversion was different than the optimal thickness at which the emission was the greatest. For the three catalysts, the Ag@SiO₂_28nm proved to be the support with the higher photocatalytic conversion and the enhancement factor observed were equal to 2.7, 1.9, and 1.4 for $[Ru(bpy)_3]^{2+}$, RB and MB respectively.

Table 6-1 summarizes the greatest enhancement factors observed for the emission and photocatalytic activity, the wavelength difference between the excitation wavelength and the center of the SPR band, (i.e. spectral overlap, $\Delta\lambda$), Φ_{lum} of the free species and Φ_{ISC} . Out of the three photocatalysts selected, $[Ru(bpy)_3]^{2+}$ was the one whose catalytic performance and emission intensity were the most boosted by the plasmon-triggered antenna effect of the Ag core. Shell thicknesses which gave the most intense emission and highest conversion were identical for all three photocatalysts. This interesting comparison is, to the best of our knowledge, reported for the first time. Hence the enhanced field and the quenching are the same for all the series, and the separation distance that gives the most favorable conditions are identical for the three photocatalysts. The differences in the amplitude of the enhancement factor can be rationalized by the spectra overlap, Φ_{lum} of the free species and Φ_{ISC} .

Table 6-1 – Summary of the emission and photoactivity enhancement factors observed for Ag@SiO2-(photocatalyst) with 33 and 28 nm shells respectively, the spectral overlap for the free photocatalyst and their QY

Photocatalyst	[Ru(bpy) ₃] ²⁺	MB	RB
EF _(em)	4.1	1.6	2.3
EF _(cat)	2.7	1.4	1.9
Δ λ (nm)	- 50	+ 160	+ 50

Chapter 6 - Rational for antenna-reactor design using Ag PNPs to boost photocatalysis

Φ _{lum}	0.04ª	0.52 ^c	0.14 ^b	
500 / 500 510				

Φ values in EtOH,^a: Ref⁵³⁸,^b: Ref⁵³⁹,^c: Ref⁵⁴⁰

Several groups before us have studied the impact of shell thickness on both luminescence and catalysis and found as well that an optimal thickness observed for both phenomena, although not the same.^{77, 497, 503, 515} The Heyne group investigated the distance dependent emission of Rose Bengal, and ${}^{1}O_{2}$ it produced. They also observed a maximum emission of RB for an optimal SiO₂ layer, which was different from the thickness leading to the maximum ¹O₂ production. Similarly, Yaraki et al. also witnessed that the optimal distance between the plasmonic core and the photoctalyst to achieve the greatest ¹O₂ generation was shorter than the one required for the highest MEL.⁵⁴¹ Yet, there was no precedent for the study of multiple photocatalysts over a plasmonic support with varying shell thicknesses. The results presented herein are the first to showcase that the optimal shell thickness for both luminescence and catalysis are not affected by the photocatalysts. This means that the optimal distance was not affected by the level of overlap, since MB which featured a poor overlap was enhanced at the same distance as Rupby and RB which experienced a better overlap. It was not affected either by Φ_{lum} or their respective mechanistic pathways, as they different for all photocatalysts. The Murphy's group observed a 10-fold enhancement when the SPR band of the nanostructure overlapped with the absorption of the dye, while smaller or no enhancement was observed when the SPR and absorption spectra were shifted, or the shell thickness was thicker or larger. Our results as well suggest a lower effect when overlap is low (catalysis enhancement of 1.4 for MB vs 2.7 for Ru), but yet all the dyes experienced some enhancement.

According to previous observations and hypothesis about metal-enhanced luminescence, greater MEL is observed for high overlap between the excitation wavelength of the luminescent species and the SPR band. Thus the emission and the catalytic activity of Rubpy and RB were more enhanced than the one of MB because the absorption of Ag overlays the absorption profile of the formers (Figure 6-1A) whereas MB absorption is shifted
compared to the SPR band. Despite having similar spectral overlap, $[Ru(bpy)_3]^{2+}$ featured a greater enhancement factor than RB. Based on previous observations, the enhancement of luminescence is greater for the species with a lower quantum yield.⁵⁴² Specifically free $[Ru(bpy)_3]^{2+}$ QY has the lowest QY of all, with a value of 0.04. RB has a much larger QY in the free form of 0.14. In this context, the SPR offers less opportunity for improvement on an already more efficient system. There $[Ru(bpy)_3]^{2+}$ had an enhancement equal to 4.1 while RB was only 2.3, when their spectral overlap was similar. Combining the influences of the spectral overlap and the QY therefore justifies that [Ru(bpy)₃]²⁺ featured the greatest enhancement factor for both photoactivities, followed by RB which also overlaps with Ag extinction spectrum but has a high QY, and finally MB luminescence and catalytic activity was also enhanced but to a smaller extend due to featuring the highest QY of all (0.52) and its poor spectral overlap. The immobilization method, electrostatic or covalent, did not seem to have a strong influence on the luminescence or catalytic performances. It is worth noting that the QY does not include all the steps and pathways needed to exhibit phosphorescence and be active in catalysis. Indeed, once excited the photocatalysts chosen for this study go through an intersystem crossing to reach their triplet state, and can then relax viaphosphorescence, excite O2 or follow other non-radiative pathways. Therefore the efficiency of the triplet state formation and the energy transfer with O₂ have an influence on the overall enhancement factor we calculated. Because these values have not been determined for each photocatalyst in the solvent of interest, they could not be taken into account when comparing the luminescence and catalytic activities.

6.6 Time-resolved spectroscopy study

Based on the results on catalytic tests, we turned to time-resolved spectroscopy to evaluate the effect of the plasmonic core on the photophysical properties of the photocatalysts and rationalize the fluctuations of the enhancement effect observed for different shell thicknesses. Time-resolved spectroscopy allows to determine the lifetime of an excited species by measuring the absorption of an excited species over time. Timeresolved emission at 610 nm of $[Ru(bpy)_3]^{2+}$ immobilized on commercial SiO₂ and Ag@SiO₂ NPs has been measured using a photoluminescence spectrometer with a pulse laser excitation source, and thus allowed to study the influence of the silver core on the phosphorescence lifetime of [Ru(bpy)₃]²⁺. Ag@SiO₂-[Ru] with 19, 28, 33 and 45 nm coating layer have been analyzed. Ag@SiO₂-[Ru] NPs with thinner shells and the Ag@SiO₂-RB and Ag@SiO₂-MB series could not be measured due to the resolution of the instrument. Subsequent fitting of the data revealed that the emission of Ag@SiO₂-[Ru] NPs over 4000 ns can be divided in two regimes: a fast component taking place within the first hundred ns, called T₁, which is followed by a longer one (T₂). On the contrary, [Ru(bpy)₃]²⁺ immobilized on commercial SiO₂ NPs exhibited only one component, namely T₂. The presence of the plasmonic metal therefore induced a fast relaxation taking place within a hundred ns. Fitting of the time-resolved emission data also provided the respective amplitude of the T₁ and T₂ components and we thus calculated the average lifetime T_{av} for each sample (equation and table with $T_1, T_2, B_1, B_2, T_{av}$ in ESI).

Figure 6-3 represents the lifetime of $[Ru(bpy)_3]^{2+}$ immobilized on commercial SiO₂ NPs (Tav, brown curve) and the lifetimes determined for $[Ru(bpy)_3]^{2+}$ immobilized on Ag@SiO₂ NPs with different thicknesses (T_{av}, T₁ and T₂ in yellow, blue and green curves respectively). Similarly to the phosphorescence enhancement factor (grey curve), each curve for the plasmonic materials featured an inflection point around the 28 nm mark and the maximum was reached for 33 nm. All samples with a Ag core had a lifetime T_{av} shorter than the ones on commercial SiO₂ NPs, because both quenching (short distances) and the presence of the

LSPR enhanced the decay rate. Indeed, for $[Ru(bpy)_3]^{2+}$ immobilized on Ag@SiO_{2_}33nm, the T_{av} was equal to 476 ns with T₁ and T₂ equal to 88 and 551 ns respectively, whereas the average lifetime measured for $[Ru(bpy)_3]^{2+}$ on commercial SiO₂ was 596 nm. These measurements are consistent with the steady state emission and catalytic results as samples with a SiO₂ layer of 33 and 28 nm respectively featured the greatest enhancement factor. The Murphy group also observed a fast and a slow component when measuring the emission of an infrared dye on Au nanorods using time-resolved photoluminescence. The overall lifetime, as well as the contribution of the fast and slow components, was dependant on the shell thickness. Interestingly, in their case too, the strongest fluorescence lifetime reduction did not correspond to a maximum in fluorescence intensity observed, thus highlighting the complexity of plasmon-triggered enhancement as a decrease in the lifetime alone, due to an increase in k_{rad}, cannot explain the enhancement observed as often hypothesized in previous studies.



Figure 6-3 - Lifetimes T_{av} for SiO₂-[Ru⁺] (brown curve), T_{av} (yellow curve), T_1 (blue curve), T_2 (green curve) determined for [Ru(bpy)₃]²⁺ immobilized on Ag@SiO₂ NPs with different thicknesses, and phosphorescence enhancement factor (grey curve) measured for the same samples.

The radiative and non-radiative decay rates, K_{rad} and K_{non-rad}, of each sample were calculated using the QY of [Ru(bpy)₃]²⁺ and the phosphorescence enhancement factor (equations and table in ESI) and are shown in Figure 6-4. The samples with a plasmonic core, except for the thinnest with a layer of 7 nm, exhibited a higher radiative decay rate compared to the one with commercial SiO_2 NPs (Figure 6-4 - light and dark green curves). These results reflect the observations made in steady state conditions for which the phosphorescence enhancement factor (Figure 6-4 - grey curve) increased with the SiO₂ thickness until reaching a maximum for 33 nm. When calculating the K_{non-rad} from T_{av} and K_{rad}, the variation over the range of SiO₂ thicknesses was more important than for K_{rad}. The calculated non-radiative decay rate followed an opposite trend: Knon-rad for [Ru(bpy)3]²⁺ immobilized of Ag@SiO₂ 33 nm is the minimum of the curve and all the samples with a plasmonic core featured a greater K_{non-rad} than for commercial SiO₂ NPs decorated with $[Ru(bpy)_3]^{2+}$. Moreover, for each sample, the K_{non-rad} is one or two orders of magnitude higher than the K_{rad} for a given thickness. While the K_{rad} for Ag@SiO_{2_}33 is double compared to the one for a 19 nm SiO₂ layer, for the same sample K_{non-rad} only decreased by half. Yet the variation in K_{non-rad} is more significant and explains the large increase in T_{av} and phosphorescence EF observed for Ag@SiO₂ 33 NPs.





Figure 6-4 - Decay rates ($K_{non-rad}$ et K_{rad}) determined for [Ru(bpy)₃]²⁺ immobilized on commercial SiO₂ NPs and Ag@SiO₂ NPs with different thicknesses, and emission enhancement factor measured for the same samples

6.7 Conclusion

In conclusion, we have synthesized three series of plasmonic nanoparticles coated with silica at various thicknesses and decorated with a photocatalyst (Ag@SiO₂-[Ru], Ag@SiO₂-MB and Ag@SiO₂-RB NPs). The influence of the light-induced field enhancement in the vicinity of the plasmonic Ag NPs on the catalytic activity towards the oxidation of alkenes *via* ¹O₂, and the emission intensity of these materials was evaluated. We used the enhancement factor to determine that for an optimal thickness of SiO₂, the catalytic activity of Ag@SiO₂-[Ru] was more boosted than the RB and MB counterparts. [Ru(bpy)₃]²⁺ demonstrated an enhancement of the catalytic activity up to 4-fold with a shell of 28 nm, whereas the enhancement factors for Ag@SiO₂-[RB] and Ag@SiO₂-[MB] with identical SiO2 layer were equal to 2.3 and 1.6. We showed that the distancing between the plasmonic surface and the photoactive species was key to favor radiative pathways and

production of ${}^{1}O_{2}$. We also demonstrated that the excitation spectral overlaps and QY of the free species had an influence on the overall efficiency of the antenna-reactor systems. This constitutes the first observation of the thickness dependence of ${}^{1}O_{2}$ -mediated catalysis for different immobilized species on a similar plasmonic core.

Time-resolved spectroscopy was used to determine the lifetime of $[Ru(bpy)_3]^{2+}$ triplet state and rationalized the influence of the shell thickness on the excitation of the photocatalyst. This study revealed that the presence of the plasmonic core induced the emergence of a short lifetime, followed by a longer lifetime similar to the one of $[Ru(bpy)_3]^{2+}$ immobilized on SiO₂ NPs without an Ag core. Ag@SiO₂-[Ru] with a 33 nm shell exhibited the longest lifetime of the series and the highest radiative decay rate. The time-resolved spectroscopy measurements therefore confirmed the observation made during steady-state luminescence studies.

While more studies are required to determine how the plasmon-induced field enhancement affects the excitation states and relaxation pathways of the photocatalysts, the luminescence measurements and photocatalytic test we performed using Ag@SiO₂-[Ru], Ag@SiO₂-MB and Ag@SiO₂-RB indicate that plasmonic antenna-reactor systems are versatile nanocatalysts but careful design of such hybrid structures is required to optimize the overall efficiency.

6.8 References

20. Yoon, T. P.; Ischay, M. A.; Du, J., Visible Light Photocatalysis as a Greener Approach to Photochemical Synthesis. *Nat. Chem.* **2010**, *2*(7), 527-532.

64. Cheng, L.; Wang, C.; Feng, L.; Yang, K.; Liu, Z., Functional Nanomaterials for Phototherapies of Cancer. *Chemical reviews* **2014**, *114*(21), 10869-10939.

69. Gelle, A.; Jin, T.; de la Garza, L.; Price, G. D.; Besteiro, L. V.; Moores, A., Applications of Plasmon-Enhanced Nanocatalysis to Organic Transformations. *Chemical Reviews* **2019**, *120*(2), 986-1041.

77. Planas, O.; Macia, N.; Agut, M.; Nonell, S.; Heyne, B., Distance-Dependent Plasmon-Enhanced Singlet Oxygen Production and Emission for Bacterial Inactivation. *J. Am. Chem. Soc.* **2016**, *138* (8), 2762-2768. 237. Mori, K.; Kawashima, M.; Che, M.; Yamashita, H., Enhancement of the Photoinduced Oxidation Activity of a Ruthenium(Ii) Complex Anchored on Silica-Coated Silver Nanoparticles by Localized Surface Plasmon Resonance. *Angew. Chem.* **2010**, *122* (46), 8780-8783.

466. Tambosco, B.; Segura, K.; Seyrig, C.; Cabrera, D.; Port, M.; Ferroud, C.; Amara, Z., Outer-Sphere Effects in Visible-Light Photochemical Oxidations with Immobilized and Recyclable Ruthenium Bipyridyl Salts. *ACS Catal.* **2018**, *8*(5), 4383-4389.

478. Giannini, V.; Fernández-Domínguez, A. I.; Heck, S. C.; Maier, S. A., Plasmonic Nanoantennas: Fundamentals and Their Use in Controlling the Radiative Properties of Nanoemitters. *Chem. Rev.* **2011**, *111*(6), 3888-3912.

479. Schuller, J. A.; Barnard, E. S.; Cai, W.; Jun, Y. C.; White, J. S.; Brongersma, M. L., Plasmonics for Extreme Light Concentration and Manipulation. *Nat. Mater.* **2010**, *9*, 193.

480. Barnes, W. L.; Dereux, A.; Ebbesen, T. W., Surface Plasmon Subwavelength Optics. *Nature* **2003**, *424*(6950), 824-830.

481. Kinkhabwala, A.; Yu, Z.; Fan, S.; Avlasevich, Y.; Müllen, K.; Moerner, W., Large Single-Molecule Fluorescence Enhancements Produced by a Bowtie Nanoantenna. *Nat. Photonics* **2009**, *3*(11), 654-657.

482. Wertz, E.; Isaacoff, B. P.; Flynn, J. D.; Biteen, J. S., Single-Molecule Super-Resolution Microscopy Reveals How Light Couples to a Plasmonic Nanoantenna on the Nanometer Scale. *Nano Lett.* **2015**, *15*(4), 2662-2670.

483. Darvill, D.; Centeno, A.; Xie, F., Plasmonic Fluorescence Enhancement by Metal Nanostructures: Shaping the Future of Bionanotechnology. *Phys. Chem. Chem. Phys* **2013**, *15*(38), 15709-15726.

484. Deng, W.; Goldys, E. M., Plasmonic Approach to Enhanced Fluorescence for Applications in Biotechnology and the Life Sciences. *Langmuir* **2012**, *28*(27), 10152-10163. 485. Deng, W.; Xie, F.; Baltar, H. T.; Goldys, E. M., Metal-Enhanced Fluorescence in the Life Sciences: Here, Now and Beyond. *Phys. Chem. Chem. Phys* **2013**, *15* (38), 15695-15708.

487. Willets, K. A.; Van Duyne, R. P., Localized Surface Plasmon Resonance Spectroscopy and Sensing. *Annu. Rev. Phys. Chem.* **2007**, *58*, 267-297.

488. Banholzer, M. J.; Millstone, J. E.; Qin, L.; Mirkin, C. A., Rationally Designed Nanostructures for Surface-Enhanced Raman Spectroscopy. *Chem. Soc. Rev.* **2008**, *37*(5), 885-897.

497. Macia, N.; Bresoli-Obach, R.; Nonell, S.; Heyne, B., Hybrid Silver Nanocubes for Improved Plasmon-Enhanced Singlet Oxygen Production and Inactivation of Bacteria. *J. Am. Chem. Soc.* **2018**, *141*(1), 684-692.

503. An, X.; Stelter, D.; Keyes, T.; Reinhard, B. M., Plasmonic Photocatalysis of Urea Oxidation and Visible-Light Fuel Cells. *Chem* **2019**, *5*(8), 2228-2242.

507. Wu, C.; Mosher, B. P.; Lyons, K.; Zeng, T., Reducing Ability and Mechanism for Polyvinylpyrrolidone (Pvp) in Silver Nanoparticles Synthesis. *J. Nanosci. Nanotechnol.* **2010**, *10*(4), 2342-2347.

508. Kobayashi, Y.; Katakami, H.; Mine, E.; Nagao, D.; Konno, M.; Liz-Marzán, L. M., Silica Coating of Silver Nanoparticles Using a Modified Stöber Method. *J. Colloid Interface Sci.* **2005**, *283*(2), 392-396.

509. Matsui, K.; Momose, F., Luminescence Properties of Tris (2, 2 '-Bipyridine) Ruthenium (Ii) in Sol– Gel Systems of Sio2. *Chem. Mater.* **1997**, *9*(11), 2588-2591.

510. Innocenzi, P.; Kozuka, H.; Yoko, T., Fluorescence Properties of the Ru (Bpy) 32+ Complex Incorporated in Sol– Gel-Derived Silica Coating Films. *J. Phys. Chem. B* **1997**, *101* (13), 2285-2291.

515. Abadeer, N. S.; Brennan, M. R.; Wilson, W. L.; Murphy, C. J., Distance and Plasmon Wavelength Dependent Fluorescence of Molecules Bound to Silica-Coated Gold Nanorods. *ACS Nano* **2014**, *8*(8), 8392-8406.

519. Banholzer, M. J.; Harris, N.; Millstone, J. E.; Schatz, G. C.; Mirkin, C. A., Abnormally Large Plasmonic Shifts in Silica-Protected Gold Triangular Nanoprisms. *J. Phys. Chem. C* **2010**, *114*(16), 7521-7526.

520. Rodríguez-Fernández, J.; Pastoriza-Santos, I.; Perez-Juste, J.; García de Abajo, F. J.; Liz-Marzan, L. M., The Effect of Silica Coating on the Optical Response of Sub-Micrometer Gold Spheres. *J. Phys. Chem.* C**2007**, *111*(36), 13361-13366.

521. Pastoriza-Santos, I.; Gomez, D.; Pérez-Juste, J.; Liz-Marzán, L. M.; Mulvaney, P., Optical Properties of Metal Nanoparticle Coated Silica Spheres: A Simple Effective Medium Approach. *Phys. Chem. Chem. Phys* **2004**, *6*(21), 5056-5060.

524. Cole-Hamilton, D. J.; Tooze, R. P., *Catalyst Separation, Recovery and Recycling: Chemistry and Process Design*. Springer Science & Business Media: 2006; Vol. 30.

525. Vankayala, R.; Sagadevan, A.; Vijayaraghavan, P.; Kuo, C.-L.; Hwang, K. C., Metal Nanoparticles Sensitize the Formation of Singlet Oxygen. *Angew. Chem. Int. Ed.* **2011**, *50* (45), 10640-10644.

526. Toftegaard, R.; Arnbjerg, J.; Daasbjerg, K.; Ogilby, P. R.; Dmitriev, A.; Sutherland, D. S.; Poulsen, L., Metal-Enhanced 1270 Nm Singlet Oxygen Phosphorescence. *Angew. Chem. Int. Ed.* **2008**, *47*(32), 6025-6027.

537. Anker, J.; Hall, P.; Lyandres, O.; Shah, N.; Zhao, J.; Van Duyne, R., Biosensing with Plasmonic Nanosensors. *J. Nanosci. Nanotechnol.*, 308-319.

538. Yeh, A. T.; Shank, C. V.; McCusker, J. K., Ultrafast Electron Localization Dynamics Following Photo-Induced Charge Transfer. *Science* **2000**, *289*(5481), 935-938.

539. Redmond, R. W.; Gamlin, J. N., A Compilation of Singlet Oxygen Yields from Biologically Relevant Molecules. *Photochemistry and photobiology* **1999**, *70*(4), 391-475. 540. Neckers, D., Rose Bengal. *Journal of Photochemistry and Photobiology A: Chemistry* **1989**, *47*(1), 1-29.

541. Yaraki, M. T.; Hu, F.; Rezaei, S. D.; Liu, B.; Tan, Y. N., Metal-Enhancement Study of Dual Functional Photosensitizers with Aggregation-Induced Emission and Singlet Oxygen Generation. *Nanoscale Advances* **2020**, *2*(7), 2859-2869.

542. Dragan, A. I.; Geddes, C. D., Metal-Enhanced Fluorescence: The Role of Quantum Yield, Q0, in Enhanced Fluorescence. *Applied Physics Letters* **2012**, *100*(9), 093115.

7 Chapter 7 – Conclusion and outlooks

7.1 Conclusion

While the discovery of plasmonic particles is not new, it is only recently that they have emerged as appealing photocatalysts, and their potential for catalytic applications keeps increasing due to the versatility of plasmon-based catalyst designs. In this thesis, we reported the use of Ag-based NPs as photo-nanocatalysts for various transformations using either the plasmon-induced hot electrons or field enhancement. Our results clearly demonstrated the potential of plasmon-mediated nanocatalysts, and have shined light on the importance of meticulous catalyst design. The work presented here aims at providing insights on how this new kind of heterogenous photocatalysts have the ability to be influential in the development of greener reaction conditions.

First, principles of green chemistry and photocatalysis were introduced, as well as the role plasmonic nanoparticles could undertake in these contexts. We then reviewed organic transformations catalyzed by plasmonic-based nanoparticles and the SPR-mediated catalytic activity of TiO_2 decorated with plasmonic metals, and explored different group XI nanoparticle design and bimetallic materials that have been used as plasmon-driven photonanocatalysts.

The ability of Ag NCs to activate H₂ and O₂ to perform oxidations of ethylene had been previous shown, and we explored the use of such nanostructures for other applications. Ag NCs proved to be extremely sensitive to the environmental conditions therefore the synthesis had to be optimized before performing catalytic tests. We reported a new protocol for the synthesis of Ag NCs and then demonstrated that Ag NCs can be used to perform oxidations of carbonyl using molecular oxygen mediated by hot electrons in a continuous flow reactor.

We also demonstrated that Ag NPs can act as nanoantennae and boost the catalytic activity of nearby homogeneous catalysts. The presence of a Ag plasmonic core was shown to alter the intensity of emission and the photocatalytic properties of $[Ru(bpy)_3]^{2+}$ toward the oxidation of alkene *via* singlet oxygen. This study also proved that the distance between the plasmonic surface and the photoactive species had a strong influence on the luminescence and photocatalytic properties. The existence of an optimal distance at which the luminescence and catalytic activity were maximal was demonstrated and a maximum increase up to 4-fold of the conversion was measured. Mapping of the decay of the plasmonic signal around the Ag core, using energy electron loss spectroscopy was used to study the surface plasmon and boundary elements method simulation, provided a rationale for the observed catalytic enhancement dependence on the silica coating thickness.

Finally, we compared the emission and catalytic properties of three series of silica coated Ag NPs decorated with homogeneous photocatalysts, namely $[Ru(bpy)_3]^{2+}$, Rose Bengal and Methylene Blue. This study provided insights into the importance of the spectral overlap between the excitation wavelength of the homogeneous catalyst and the plasmonic band on the overall catalytic activity, as well as the role of the QY. Comparison of the three series of Ag@SiO₂-[photocatalysts] also showed that the optimal silica layer providing the maximum luminescence and conversion was identical regardless of the photocatalyst. Real-time spectroscopy confirmed that the plasmonic core had an influence on the lifetime of $[Ru(bpy)_3]^{2+}$ and that it varied with the thickness of the silica layer.

In this thesis, we demonstrated that plasmonic-based NPs can be employed for a variety of reactions and the mechanisms driving the photocatalysis are also diverse. While we proved the efficiency of only a few systems based on Ag PNPs, the versatility of hybrid nanostructures and other plasmonic metals open the door to boundless photonanocatalysts exploration. The studies we conducted highlighted the potential of SPR-driven nanocatalysis and we emphasized the importance of catalyst design to make the most of the plasmonic properties for catalytic applications.

7.2 Outlooks

Given the growing interest for visible light-driven heterogeneous catalysis, and the many advantages plasmonic nanoparticles feature, we expect plasmon-induced catalysts to keep lighting up. Moreover a wide range of plasmonic nanostructures that can be synthesized and many have not yet been employed in many catalytic processes despite having appealing properties, whether as free standing nanoparticles or in hybrid systems, to mediate transformations *via* hot electrons or field enhancement.

SERS studies have revealed the potential of plasmonic surfaces to drive organic transformations but such reactivities were studied only detected as molecular events and remain mostly unexplored in catalytic processes in batch. Qualitative conversions are therefore required to validate the catalytic activity of such system on large scale, but SERS observations have already unraveled many other potential catalytic applications of plasmonic nanoparticles for organic transformations.

Our work on the oxidation of carbonyls in continuous flow reactor highlight the potential of such system to exploit plasmonic nanoparticles to the best of their ability by optimizing the irradiation and the mass transfer. Our promising flow chemistry results proved that such tube-in-tube reactors and irradiation settings can increase the yield of multiphasic photoreactions. This study also suggested that more work could be done to further optimize such system, and that other similar catalytic processes could see their performance increased when adapted in flow chemistry. Due to technical barriers, we have not yet performed hydrogenation using flow reactor but given the highly encouraging results obtained under oxidative conditions, it could be a venue worth pursuing.

Moreover, one major limitation of implementing plasmon-mediated catalysts at a larger scale is associated with the difficulty of providing homogeneous light exposure in wide reaction vessels. The use of continuous flow processes appears as a promising venue for

Chapter 7 - Conclusion and outlooks

light irradiation of significant volumes of solvents and thus industrial applications of plasmonic nanoparticles.

For our studies with Ag@SiO₂-[photocatalyst], we used a tailor reactor which allowed us to maximize the irradiation and to keep the system at a constant temperature, while introducing oxygen. Such a piece of equipment was essential for our studies and other photocatalytic testing would benefit from such glassware able to have uniform irradiation as well as efficient temperature control and gas transfer. Photocatalytic reactions are often performed in vials irradiated by unidimensional light source and the volume of solvent that can be used is very limited. Access to a variety of photoreactors, without having to rely on continuous flow reactors which are expensive and required substantial expertise to be used efficiently, would facilitate the growth of plasmon-driven nanocatalysis. Photoreactors would allow to optimize the reactions conditions and also ensure reproductivity.

Another limitation of the implementation of plasmonic catalysts is the synthesis of the NPs themselves. As described previously, the synthesis of such structures is challenging but also leads to small quantities of NPs and scaling up of NPs is delicate. The processes by which plasmonic nanoparticles are obtained are also not sustainable, thus the field of photonanocatalysis would benefit from greener and scalable NP syntheses. Development of Albased and Cu-based NPs, along with less common plasmon-active nanomaterials such as nitrides would also profit to the advancement of SPR-driven catalysts. Such nanomaterials made of abundant and cheap materials could also exhibit reactivity different from the ones already-reported for Ag- and Au-based catalysts. Moreover, synthesis of plasmon-active nanoparticles coupled with magnetic materials using Fe, Co, or Ni for core-shell or alloy structures have been reported^{293, 543-550} but has not yet been exploited for catalysis to the best of our knowledge and appear as appealing systems combining photocatalytic and recycling properties.

Chapter 7 - Conclusion and outlooks

We emphasized the importance of carefully designed nanocatalysts for field enhancedmediated catalysis when studying the luminescence and catalytic activity of [Ru(bpy)₃]²⁺, RB and MB immobilized on Ag@SiO₂ NPs. We based our studies on observations made for biological applications and theoretical studies, and we aimed at understanding how the alteration of the field in the vicinity of PNPs could be used for important organic transformations. Very few examples of field enhanced-boosted nanostructure have been reported for organic catalysis, and distance-dependent ¹O₂ production studies for catalysts are still rare whereas it has been investigated several times for biological applications. Despite the many systems studies in biological settings, the observations did not always relate to theoretical studies results. Thus there is still a lot to understand about the mechanisms driven such hybrid nanostructures.

Our results clearly demonstrated the potential of such hybrid nanocatalysts, thus more reactions and photocatalysts using nanoantenna-reactor NPs could be worth investigating and could provide useful information about the behavior of these systems, and the range of the applications of plasmonic nanoparticles for photocatalysis. The availability of photosensitizers that can be easily anchored, and the challenging synthesis of more complex NP morphologies with various SPR band limits the options of hybrid structures that can be studies, yet exploring other photosensitizers immobilized on Ag@SiO₂ NPs or [Ru(bpy)₃]²⁺, RB and MB on Au@SiO₂ NPs for example, would allow to understand more in depth the dynamics of antenna-reactors systems.

Despite the many plasmon-driven nanocatalysts reported over the last decades and the efforts made to understand the underlying mechanism of such photocatalysts, a lot of questions about the catalytic properties of these systems remain. Deciphering the role of thermal, electromagnetic or hot carrier effects on the reactivity of plasmonic catalysts is crucial for the development of more SPR-driven nanocatalysts, yet investigating the mechanisms of reported catalyst is often overlooked. Some theoretical and experimental studies have focused on identifying the mechanisms inducting transformations but more work is vital to understand in depth how plasmonic nanocatalysts operate. Moreover, has

highlighted by our antenna-reactors studies, even when the main plasmon-induced mechanism is identified, field-enhanced in our case, the underlying mechanisms by which the reactivity is improved remain unexplored.

Such studies would require cooperation of many fields of expertise and the use of instruments not commonly used for catalytic tests, in addition to computation and theoretical studies. Intersectional work would open prospects for a better understanding of plasmonic behavior and implementation of carefully designed photo-nanocatalysts. EELS experiments and simulation, and real-time spectroscopy measurements presented in this thesis provided crucial information about the behavior of the plasmonic structures. This kind of studies remain rare in the field of SPR-driven catalysis and more characterization of the photoactive properties of reported catalytic systems could guide future work. Better catalysts design would also benefit from in-situ characterization. It would be desirable to conduct real-time measurements in catalytic conditions, yet is currently limited by existing instrumentations and methods. In-situ techniques are expected to provide insightful information about the growth of NPs and their reactivity, thus assist in the development of new plasmon-based nanostructures and SPR-driven catalysts. Plasmonic nanoparticles have a bright future ahead of them.

7.3 References

293. Wu, Y.; Zhang, T.; Zheng, Z.; Ding, X.; Peng, Y., A Facile Approach to Fe3o4@Au Nanoparticles with Magnetic Recyclable Catalytic Properties. *Materials Research Bulletin* **2010**, *45*(4), 513-517.

543. Cortie, M. B.; McDonagh, A. M., Synthesis and Optical Properties of Hybrid and Alloy Plasmonic Nanoparticles. *Chemical Reviews* **2011**, *111*(6), 3713-3735.

544. Wang, L.; Wang, Z.; Li, L.; Zhang, J.; Liu, J.; Hu, J.; Wu, X.; Weng, Z.; Chu, X.; Li, J.; Qiao, Z., Magnetic–Plasmonic Ni@Au Core–Shell Nanoparticle Arrays and Their Sers Properties. *RSC Advances* **2020**, *10*(5), 2661-2669.

545. Lim, J.; Majetich, S. A., Composite Magnetic–Plasmonic Nanoparticles for Biomedicine: Manipulation and Imaging. *Nano Today* **2013**, *8*(1), 98-113.

546. She, H.; Chen, Y.; Chen, X.; Zhang, K.; Wang, Z.; Peng, D.-L., Structure, Optical and Magnetic Properties of Ni@Au and Au@Ni Nanoparticles Synthesized Via Non-Aqueous Approaches. *Journal of Materials Chemistry* **2012**, *22*(6), 2757-2765.

547. Song, H.-M.; Wei, Q.; Ong, Q. K.; Wei, A., Plasmon-Resonant Nanoparticles and Nanostars with Magnetic Cores: Synthesis and Magnetomotive Imaging. *ACS Nano* **2010**, *4*(9), 5163-5173.

548. Ravichandran, M.; Oza, G.; Velumani, S.; Ramirez, J. T.; Garcia-Sierra, F.; Andrade, N. B.; Vera, A.; Leija, L.; Garza-Navarro, M. A., Plasmonic/Magnetic Multifunctional Nanoplatform for Cancer Theranostics. *Scientific Reports* **2016**, *6*(1), 34874.

549. Souza, J. B.; Varanda, L. C., Magneto-Plasmonic Au-Coated Co Nanoparticles Synthesized Via Hot-Injection Method. *Nanotechnology* **2018**, *29*(6), 065604.

550. Levin, C. S.; Hofmann, C.; Ali, T. A.; Kelly, A. T.; Morosan, E.; Nordlander, P.; Whitmire, K. H.; Halas, N. J., Magnetic–Plasmonic Core–Shell Nanoparticles. *ACS Nano* **2009**, *3*(6), 1379-1388.

8.1 Supplementary information - Unveiling the potential of Ag NCs for plasmon-driven photochemistry

8.1.1 Ag NCs synthesis

All chemicals used in this work were purchased from Sigma-Aldrich. All ketones or aldehydes used for the reactions were purified using standard purification techniques found in "Purification of Laboratory Chemicals, 5th edition" and NMR was used to confirm that these were pure before use in catalytic reactions. Hydrogen gas used was purchased from Air Liquide Canada and used without further purification or drying. Standard Schlenk line techniques were used during the synthesis of the nanoparticles and for manipulations during catalytic tests. All glassware used for the catalytic reactions was dried for 24 hours at 140 °C in a glass drying oven. Fresh microwave vials were used for scope reactions to ensure that no other metal residue was found within the glass used in the reactions or cleaned using nitric acid and a base bath. The light sources used during the reactions were either a standard 60 W incandescent lightbulb or a 405 nm LED laser using a diverging lens to expand the laser source to desired irradiation area.

The synthesis of the nanoparticle catalyst was reproduced from a previous literature procedure with some modifications.

5 mL of ethylene glycol was transferred in a new 6 inch vial and was heated in an oil bath at 145 °C. While ethylene glycol was heated, three solutions were prepared: 0.1 M AgNO3, 0.15 M polyvinylpyrrolidone (PVP in terms of monomer, 55 k M.W.), and a 30 mM HCl. All solutions were prepared using ethylene glycol as the solvent and were shaken into solution using sonication and a shaker table. All solutions were kept covered under aluminum foil. The HCl solution was prepared using concentrated HCl. After 1.5 hours of heating, 100 μ L

of the 30 mM HCl solution was transferred to the heated Schleck flask and the stirring was regulated to 600 RPM. This solution was stirred for 10 minutes before proceeding. During this waiting period, a syringe pump was primed with 3 mL of the AgNO3 and PVP solutions in separate syringes. Once 10 minutes had passed, the syringe pump was turned on and the solutions were delivered at a rate of 0.74 mL/min. The solution changed from a clear, colorless solution to a deep, opaque purple color. Within 2 minutes, the color shifted to beige. After 21 hours, the reaction was cooled down then quenched with three times the volume of ethanol. The cubes were isolated by centrifugation at 9000 RPM for 20 minutes at room temperature and the supernatant was removed using a syringe. This procedure was repeated 5 times and the final solution of cubes were suspended in anhydrous ethanol with sonication. At this point, samples were taken for all characterization and the remaining material was stored in aluminum foil.

8.1.2 Hydrogenation catalytic tests reactions

A pre-dried 2-8 mL microwave vial from ChemGlass was equipped with 1-10 mmol of aldehyde or ketone, 5 mL of solvent, 1 mg of Ag NCs and a stirring bar. The reaction vessel was capped with a septum and Ar gas was bubbled through the reaction mixture for 20 minutes to ensure complete de-gassing. This procedure was performed in complete darkness. Then the septum was removed quickly and replaced with a microwave crimp top with a septum middle. The vial was evacuated *via* a needle attached to the Schlenk line, and a balloon of hydrogen was attached and injected. The reaction was then heated to a temperature of 40, 60, 80 or 100°C (depending on the entry) using an oil bath for 24 hours (Table 8-1). Depending on the entry, the vial was carefully left in the dark, or exposed for the whole duration of the test with the lightbulb or the laser. After the reaction was completed, the vial was cooled to room temperature and then sonicated for 20 minutes to ensure any product absorbed on Ag NCs was desorbed. The reaction mixture was then transferred to a centrifuge tube and centrifuged at 9000 rpm for 10 minutes. The supernatant was transferred to a pre-weighed round bottom flask and solvent was

removed *in vacuo*. The procedure was performed in triplicate. All reported yields were isolated yields, except for camphor where GCMS measurements using a standard curve were employed.

Temperature	Hydrogen Pressure	Light course	GC-MS
(°C)	(atm)	Light source	(% yield of product)
40	1	405 nm laser	29%
40	1	None	N/R
40	1	Light bulb	17%
60	1	405 nm laser	47%
60	1	None	Trace
60	1	Light bulb	29%
80	1	405 nm laser	87%
80	1	None	Trace
80	1	Light bulb	42%
100	1	405 nm laser	81%
100	1	None	6%
100	1	Light bulb	57%
80	Argon	405 nm laser	N/R
100	1	405 nm laser	N/R without cubes.
100	1	532 nm laser	5%
100	1	633 nm laser	N/R

Table 8-1 -Results for the hydrogenation of camphor with Ag NCs as catalyst as a function of temperature, H_2 pressure, and light exposure.

Reaction conditions: $500 \ \mu L$ of $0.04 \ mg/mL$ Ag NCs solution in ethanol, 1 mmol of camphor and 1 mL of dioxane, 24 hours. Control experiments presented here involve using offplasmon excitation, using argon as a reagent gas and performing these reactions in the dark.

8.1.3 Oxidation catalytic tests

To a pre-dried 2-8 mL microwave vial from ChemGlass, 5 mmol of p-hydroxybenzaldehyde was added and dissolved in 5 mL of p-dioxane. 5 mg of silver nanocubes was added to the reaction vessel and a stirring bar was added along with a crimp cap with a septum. A double balloon of air was attached and added to the top. The reaction was then heated in an oil bath to 80°C and exposed to 405 nm light for 18 hours. After the reaction was completed, the vial was cooled to room temperature and then sonicated for 20 minutes to ensure any absorbed product was removed from the surface of the particles. The reaction mixture was transferred to a centrifuge tube and was centrifuged at 9000 rpm for 10 minutes. The supernatant as transferred to a pre-weighed round bottom flask. This procedure is preformed two times more and the resulting solution is rotary evaporated to dryness.

Table 8-2 - Table comparing optimization conditions for the standard photo-oxidation reaction. Control experiments showed no reactivity when the catalyst was not present, or when the reagent gas was not air.

Temperature	Reagent Gas	Catalyst Load	Light source	NMR vield	
(°C)		(mg)	g., cour co		
60	Air (1 atm)	5	Light bulb	95%	
60	Air (1 atm)	5	Dark	34%	
60	Air (1 atm)	5	405 nm laser	95%	
80	Air (1 atm)	5	Light bulb	96%	
80	Air (1 atm)	5	Dark	46%	
80	Air (1 atm)	5	405 nm laser	97%	
80	Argon	5	405 nm laser	N/R	
80	Air (1 atm)	0	405 nm laser	N/R	

8.1.4 Continuous flow

In a typical experiment, the syringe pump is connected to an injection loop, which is in turn connected to the tube-in-tube and the coil reactor with the LED tower. Solutions of the substrate and the NPs were prepared in acetonitrile. The end of the tubing was placed in a vial or round-bottom flask for collection. VapourTec module connected and a PFA coil (1mm I.D.) were used.

8.1.5 Characterization



Figure 8-1 - SEM images of Ag NCs



Figure 8-2 - BFSTEM images of Ag NCs on Cu/ lacey carbon grid



Figure 8-3 - STEM image (top left) and EDS spectra (top right and bottom) of Ag NCs. The bottom view focuses on the silver region, where the silver contribution is provided in orange over the total count in yellow.

Samples of the Ag NCs were taken from a batch after suspended in ethanol and dried overnight in a vacuum oven at 80 °C. After the sample seemed dry, the tubes containing the sample were loaded into a Schlenk flask and dried overnight under high vacuum to remove and residual water. Once fully dried, the samples were crushed into a powder and placed onto copper tape and analyzed using a Thermo Scientific K-Alpha instrument.



Figure 8-4 - XPS full scan (A) and closeup on Cl2p scan (B), Ag3d scan (C) and C1s (D) of Ag NCs.

Element	Peak BE	Height CPS	FWHM	Area (P) CPE	Atomic %		
			(eV)	(eV)	(%)	Q	
Ag3d	368.92	181182.98	2.62	941706.57	20.90	1	

Table 8-3 - Elemental identification and quantification of Ag NCs by XPS.

C1s	286.05	37003.85	3.68	154975.37	59.77	1
O1s	532.80	18975.27	4.26	87931.07	13.29	1
Cl2p	198.78	2016.10	4.76	11153.52	1.81	1
N1s	401.13	5092.16	3.11	18589.85	4.23	1

8.2 Supplementary information - Enhancing singlet oxygen photocatalysis with plasmonic nanoparticles

8.2.1 Synthesis of Ag NPs

Silver nanospheres were prepared using the protocol reported by Zhao *et al.*⁵⁵¹ with slight modifications. 18,0 mL of ethylene glycol (EG) was used to dissolved 0,90 g of polyvinylpyrrolidone (PVP) 30K MW 40K in a round bottom flask previously washed with aqua regia. 200 mg of AgNO₃ dissolved in 2,0 mL of EG were added to the PVP solution at room temperature. After stirring at 145 °C for 4 h, 5 mL of acetone and 5 mL of ethanol were added, and the reaction mixture was let to cool down. The solution turned from colorless to green-brown when reaching the set temperature and the final solution was beige. The Ag NPs were washed three times using 30 mL of 50:50 acetone and ethanol mixture and centrifuged at 12 000 rpm at ambient conditions for 15 min. The resulting pellets were easily to suspend in ethanol and were dried in a vacuum oven at room temperature.

8.2.2 Synthesis of Ag@SiO₂ NPs

The Ag@SiO₂ NPs were obtained *via* base-catalyzed Stöber process. In a typical synthesis, 25 mg of Ag NPs were added to a round bottom flask containing 40 mL of ethanol, 10 mL of ultra-pure water and 1.25 mL of NH₄OH 30%. 25 μ L of TEOS were added to the vigorously stirring solution at room temperature every 12 h until the SiO₂ layer reached the thickness

wanted. Ag@SiO₂ NPs were isolated and purified by adding 20 mL of ethanol and centrifuged at 8 000 rpm for 10 min. The nanoparticles were washed two more times using 30 mL of ethanol and 10 mL of water prior to be suspended in ethanol and dried in a vacuum oven. The reaction was scaled up to 125 mg of Ag NPs by increasing the amount of reagents and solvents accordingly.

8.2.3 Immobilization of [Ru(bpy)₃]²⁺ to form Ag@SiO₂-Ru NPs

Immobilization of $[Ru(bpy)_3]Cl_2$ on Ag@SiO₂ NPs was realized following a procedure previously reported by the Amara group.⁴⁶⁶

Briefly, an aqueous stock solution of [Ru(bpy)₃]Cl₂.6H₂O 0.4 mM was prepared. A varied volume of this solution was then added to 20 mg of dried Ag@SiO₂ NPs suspended in a total volume of 3 mL of water. The volume added was calculated depending on the BET surface area in order to obtain the desired loading and surface coverage, which was identical of each nanomaterial. The solution was sonicated then stirred in the dark overnight. The final material was washed three times with water and dried by lyophilization. Complete immobilizations resulted in a colorless supernatant, which was confirmed by UV-Vis spectroscopy.

8.2.4 Surface loading and surface coverage

The total area of the nanosupport covered by the photosensitizer, called surface coverage, was calculated using the BET surface area and the area of a single photosensitized was determined using the software Avogadro (Equations 1-3). The area occupied by one $[Ru(bpy)_3]^{2+}$ was considered to be a circle of diameter equal to the distance between the two farthest atoms of the structure, plus the van der Waals radii of the two atoms in the extremities.(Figure 8-5)

 $A = \pi r^2 = \pi (1.425 \, nm)^2 = 6.38 \, nm^2$

Equation 8-1 - Area of one $Ru(bpy)_3^{2+}$

 $A = (6.38nm^2)(6.022.10^{23}mol^{-1}) = 3.84.10^6m^2mol^{-1}$

Equation 8-2 - Area of occupied by one mol of $Ru(bpy)_3^{2+}$ ions

 $Surface coverage = \left(\frac{(n Ru(bpy)_3^{2+})[mol](3.84.10^6)[m^2mol^{-1}]}{(surface area of support)[m^2g^{-1}](mass of support)[g]}\right) (100\%)$

Equation 8-3 - Surface coverage



Figure 8-5 - Structure and measurement of $Ru(bpy)_3^{2+}$ radius for determination of the surface coverage

8.2.5 Mathlab

The experimental conditions were recreated in-silico using the MNPBEM17 Matlab® toolbox.^{535, 552} An 80 nm spheres is generated, with the sphere's interior dielectric constant assigned to the values of silver.⁵⁵³ A second co-centric sphere is used as a shell layer, with then inside of the shell given the dielectric properties of amorphous silica.⁵⁵³ The outside of

the shell is given the dielectric properties of the testing environment (vacuum for electron microscopy, water and acetonitrile for photocatalytic tests).^{554, 555} The effect of the shell thickness is investigated by running a series of simulations, from no shell to a shell of 45 nm, in on nm increments. Due to the symmetry of the simulated geometry, a radial line scan across the shell of the particle yields a global picture of the plasmon excitations of the sample.

In the present work, two frames of references are used. The first is the energy loss spectra at the shell surface, for all shell thicknesses. Plotting the spectra for all the thicknesses highlights the red shift, as well as the general loss of intensity of the plasmon that occurs with increasing the thickness of the shell layer. The second frame of reference is the intensity of the plasmon as a function of the distance from the surface of the core. This allows a good visualisation of the relative intensity profiles as a function of shell thickness.



Figure 8-6 - Simulations, Laurentzian multi linear least squared fit and residuals of the plasmonic excitations of a 80 nm silver sphere with varying thickness of silica shell, in water and acetonitrile.

The simulated spectra show complex peak structures. In all cases, two regions of interest are visible. A lower, broad energy peak and a higher energy complex peak. A linear combination of Lorentzian distributions yields a good fit of the simulated data. The fit is performed using the SciPy. Optimize python method.⁵⁵⁶ For each shell thickness after the first fit, the previous fit results are used as initial fit values. Using this constraint accelerates the fitting process. The best fit is achieved with four Laurentzians for the vacuum case, and

with five in the water and acetonitrile cases. The simulations in water and acetonitrile yield similar results, which is to be expected, since the dielectric properties of both liquids are similar. The simulations in vacuum do show significantly different trends than the two liquids, especially at small shell thicknesses.



Figure 8-7 - Energy (color) and intensity of the fitted peaks for vacuum and CH_3CN at varying shell thickness. A red shift is present on all the peaks but is much more significant in the vacuum environment then in the acetonitrile.

The small shell thickness simulations show higher energies for all the peaks, while the spectra become similar as the shell thickness increases. A stronger red shift is therefore visible in the vacuum than in the acetonitrile simulations.

8.2.6 Discussion synthesis and optimization of materials

8.2.6.1 Plasmonic core: metal and size NPs

In this design, Ag was selected as the plasmonic metal, since it had been shown to exhibit better field enhancement performances than Au, which was proven to be key for metalenhanced luminescence.^{476, 511, 512} We initially optimized the plasmonic core diameter to maximize its antenna property. Large Ag NPs were synthesized for this study due to their

substantial scattering properties. Previous studies suggested that larger NPs exhibit more intense MEL due to a higher scattering effect,^{483, 504, 515} which is supported by theoretical evidences that the effect of the enhanced field at the vicinity of plasmonic nanoparticles is stronger for Ag than other metals, and increases with size.⁵²⁰ It was showed that both near-(field enhancement) and far-field (scattering) effects contribute to MEL.^{521, 525} In the following work, we kept the size of the metallic core constant, while varying the silica shell thickness. Moreover, the SPR signal should overlap effectively with [Ru(bpy)₃]²⁺, which absorbs at 450 nm, for an optimal metal-enhanced singlet oxygen production. Indeed, recent studies showed MEL was strongly favored by a good overlap between the SPR band and the excitation band of the sensitizer.^{77, 482, 504, 527}

However, the SPR band shifts upon growth of the silica layer. This is why we wanted to identify the thickness range that will provide both a SPR centered around 450 nm but also will maximize the luminescence of the photosensitizer hence optimizing the effect of the MEL. The optimal for ratio between the Ag core diameter and the SiO₂ thickness was found by screening for the highest emission intensity. This initial study allowed to identify an Ag core of 80 nm in diameter, with a shell of 25-35 nm, as a good fit to achieve both points.

8.2.6.2 Surface loading: determination optimal surface coverage

As mentioned previously, all the nanomaterials feature the same surface coverage (ie the distance between two photosensitizers is identical between two PNPs). The optimal molecular catalytic loading value was determined by measuring the intensity of luminescence of the nanomaterial at various surface loadings. The optimized value of $6.5E-5 \text{ mmol of } [\text{Ru}(\text{bpy})_3]^{2+}/\text{m}^2$ of support was kept constant for all Ag@SiO₂ NP samples. Indeed, it is well known that photoactive molecules may undergo self-quenching when they are in close proximity, thus this parameter was considered the most important one to lock for comparison purposes.

The optimal surface loading was confirmed by running catalytic tests.

8.2.7 Nanoparticle Characterization

The nanoparticles were washed and isolated by centrifugation (Thermo Scientific Sorvall Legend XF) and the nanoparticle solutions were well sonicated before each characterization. The size and the morphology of all of the nanoparticles were investigated with a transmission electron microscope (Philips CM200 200 kV). The samples were dropcasted on onto a Cu grid with a carbon mesh grids. The particle size distribution was evaluated by analyzing the images with ImageJ using on average 100 particles. EDS experiments were carried out in a Thermo Scientific Talos F200X S/TEM operated at 200 keV, with high brightness XFEG Schottky source. EDS carried out with a SuperX G2 energy dispersive spectroscopy detector comprising four windowless SSDs, dwell time 20 µs per pixel and probe current 236 pA. Data was processed using Gatan Digital Micrograph[®] software. The UV-visible extinction spectra were recorded with a spectrophotometer (Cary 50, Varian, Palo Alto, CA). The zeta potential was measured using a Zetasizer (BrookHaven Instrument Corp., ZetaPlus). The spectrum imaging (SI) EELS acquisitions were achieved using a Hitachi SU-9000 cold-field emission SEM in STEM mode fitted with an EEL spectrometer consisting in a charge-coupled device (CCD) of 1024 (dispersion axis) × 256 pixels. An energy dispersion of 0.055 eV/channel was used to provide maximum energy resolution which was estimated to be around 0.55 eV from the zero-loss peak full width at half maximum.⁵³¹ The line profiles were extracted from the SI data by integrating the collected intensity over an energy window of 2 eV centered on the peak maximum of the total LSP peak. Each individual spectrum was normalized with the absolute ZLP intensity in vacuum, which accounts for the probe current variations. This allowed to obtain comparable intensity profiles for each sample investigated. The conversion was determined by GC-MS (Agilent technologies 7890A coupled with Agilent technologies 5975C inert XL MSD with triple-axis detector) and by NMR (Bruker AVIIIHD 500 MHz NMR spectrometer).

8.2.7.1 BET surface area

SiO ₂	thickness	BET	surfac	e	area
(nm)		(m²/g)			
7		4.984	2 ± 0.19	937	
10		7.2817 ± 0.2264			
15		11.3062 ± 0.2870			
19		13.3037 ± 0.3529			
25		14.7687±0.3710			
28		16.8502 ± 0.4649			
30		16.9728 ± 0.4908			
33		17.4269 ± 0.2683			
37		18.5098 ± 0.3208			
45		20.91	73	± 0.2	2919

Table 8-4 -BET surface area of Ag@SiO₂NPs with various silica thickness shell

8.2.7.2 ζ-potential

Table 8-5 – ζ -potential of Ag@SiO2 NPs with 28 and 33 nm shell before and after immobilization of [Ru(bpy)₃]²⁺

Ag@SiO2_28nm	Ag@SiO2_33nm	Ag@SiO2_28nm-Ru	Ag@SiO2_33nm-
			Ru
-25.67 ± 0.8	-32.34 ± 0.9	-15.79 ± 0.72	-18.52 ± 1.02

Each sample was measured 3 times and each measurement is the average of 10 cycles. Values are in mV.

8.2.7.3 UV Vis absorption



Figure 8-8 - Extinction spectra of naked Ag NPs and with SiO₂ shell upon 6 TEOS additions



Figure 8-9 - A) Shift of the SPR band observed upon 6 TEOS additions and B) corresponding thickness of the SiO_2 shell measured by TEM

8.2.7.4 Luminescence



Figure 8-10– Emission of $Ru(bpy)_3]^{2+}$ for similar surface loadings (6.5E-5 mmol of $[Ru(bpy)_3]^{2+}/m^2$) with various thickness of silica. The quantity of $Ru(bpy)_3]^{2+}$ in solution was kept constant.

Annex



Figure 8-11 – Emission of $Ru(bpy)_3$ ²⁺ for similar silica layers (Ag@SiO₂_28nm NPs) with various surface loadings of photosensitizer. The quantity of NPs in solution was kept constant.





Figure 8-12 - EELS spectra of a single naked Ag NP and Ag@SiO₂_28nm NP with different plasmon modes between 5, 8 and 25 eV. LSP was measured at 3.4 eV (365 nm).

8.2.8 Photocatalytic tests

8.2.8.1 Mechanism



Figure 8-13 - Detailed mechanism of the citronellol photooxidation reaction.⁵¹⁸

8.2.8.2 Experimental conditions

Photooxidation of citronellol was performed in a 125 mL 3-neck jacketed with a condenser, a thermometer and a balloon filed with oxygen were connected to the 3 necks, and the reactor was maintained at 20 °C using a water recirculatory. The reactor was illuminated by white LED strips (MINGER White Strip Light LED 6000K Bright White Daylight) positioned on a cylindrical support of about 30 cm diameter and 10 cm height and the whole set up was covered with aluminum foil.

In a typical procedure, 0.33 mmol of b-citronellol and 0.20 mmol of orthodimethoxybenzene (internal standard) were dissolved in 20 mL of acetonitrile, using part of the solvent to suspend 2.0 mg of Ag@SiO₂-Ru with a silica shell of 28 nm and surface loading equal to 6.5E-5 mmol of $[Ru(bpy)_3]^{2+}/m^2$. The amount of reagents was adapted to keep the concentration of molecular catalytic loading the same for all experiment while

maintaining the concentration of PNPs identical, hence the opacity of the solution the same for all experiments.

For the kinetic studies, aliquots were taken every hour and quenched with 1.2 molar equivalent of triphenylphosphine and analyzed by GC-MS. After 3h, the reaction mixture was quenched with triphenylphosphine, concentrated by rotary evaporation and dissolved in CDCl₃ for ¹H NMR analysis.

Conversions were calculated using the ratio between the internal standard (orthodimethoxybenzene) and the reactant peak areas given by GC-MS at a given time, compared to the one at the beginning of the reaction. The conversion was also calculated using NMR by the ratio of the integration for the product and the internal standard. The reactions were performed in triplicate.



Figure 8-14 - Photograph of the photoreactor used.
Annex



Figure 8-15 -Sample gas chromatogram for a crude reaction product showing the internal standard, remaining reagent, the two product peaks and also the quenching agent and its oxidized form.

Conditions	Conversion by GC-MS	Conversion by NMR		
Conditions	(%)	(%)		
No catalyst	5	6		
No light	3	5		
Ag NPs	4	5		
Homogeneous Ru(bpy) ₃ Cl ₂	37	41		
Homogeneous Ru(bpy) ₃ Cl ₂ with Ag	10	12		
SiO ₂ -Ru NPs	23	25		
Ag@SiO ₂ _28nm-Ru NPs	66	68		

Table 8-6 - Conversions for the oxidation of citronellol under various reaction conditions

Standard reaction conditions: 0.33 mmol citronellol, acetonitrile, 3 h, O_2 balloon, catalyst: 0.0034 mol% in Ru.





Figure 8-16 - Conversion of citronellol as determined by GC-MS (green) and NMR (blue) after 3h of reaction in comparison with the intensity of the fluorescence measured for Ag@SiO₂-Ru NPs (orange), plotted as a function of SiO₂ shell thickness. Conversion by NMR for [Ru(bpy)₃]Cl₂ homogeneous (★) and [Ru(bpy)₃]Cl₂ immobilized on commercial SiO₂ NPs (♦). The molecular catalyst loading of photosensitizers was identical for each reaction (0.0034 mol%) independently of the nanomaterial used.

Annex



Figure 8-17 – Conversation by GC-MS over time or $[Ru(bpy)_3]^{2+}$ homogeneous or immobilized on various nanomaterial





Figure 8-18 - Conversion determined by NMR for various thickness of silica and surface loadings of [Ru(bpy)₃]²⁺ immobilized on Ag@SiO₂_28 nm NPs

Annex

8.2.9 Comparison with previous studies

Table 8-7- Comparison of the different separation distances used for various core-shelland photosensitizer systems studied

Nanosphora, studiod			Separation		
and core diameter	Photosensitizer	Method	distance	Reference	
and core diameter			(nm)		
۵۹۵۵۶۱۵		Emission	33		
80 nm	[Ru(bpy)₃]²+	Catalytic conversion	28	This work	
Ag@SiO ₂ 60 nm	[Ru(bpy) ₃] ²⁺	Not optimized	3	237	
A		Emission RB	20		
	Rose Bengal	Emission ¹ O ₂	11	77	
40 nm		Quantity ¹ O ₂	22		
Ag@SiO2 75 nm	Fluorescein isothiocyanate	Emission Fluorescein isothiocyanate	21	501	
Ag@SiO2 50 nm	[Ru(bpy) ₃] ²⁺	Emission [Ru(bpy) ₃] ²⁺	10	499	
Ag@SiO ₂ 45 nm	CYe	Emission Cye	24	500	
Au@SiO ₂ 30 nm	CYe	Emission Cye	25	500	
Ag@octadecanethiol- lipid layer	[Ru(bpy) ₃] ²⁺	Potential of mean force	2-5 nm	503	

8.3 Supplementary information - Rational for the antenna-reactor design using Ag PNPs to boost photocatalysis

8.3.1 Experimental section

8.3.1.1 Synthesis of SiO₂ NPs

Silver nanospheres were prepared using the protocol reported by Zhao *et al.*⁵⁵⁷ with slight modifications. 18,0 mL of ethylene glycol (EG) was used to dissolved 0,90 g of polyvinylpyrrolidone (PVP) 30K MW 40K in a round bottom flask previously washed with aqua regia. 200 mg of AgNO₃ dissolved in 2,0 mL of EG were added to the PVP solution at room temperature. After stirring at 145 °C for 4 h, 5 mL of acetone and 5 mL of ethanol were added, and the reaction mixture was let to cool down. The solution turned from colorless to green-brown when reaching the set temperature and the final solution was beige. The Ag NPs were washed three times using 30 mL of 50:50 acetone and ethanol mixture and centrifuged at 12 000 rpm at ambient conditions for 15 min. The resulting pellets were easily to suspend in ethanol and were dried in a vacuum oven at room temperature.

The Ag@SiO₂ NPs were obtained *via* base-catalyzed Stober process. In a typical synthesis, 25 mg of Ag NPs were added to a round bottom flask containing 40 mL of ethanol, 10 mL of ultra-pure water and 1.25 mL of NH₄OH 30%. 25 μ L of TEOS were added to the vigorously stirring solution at room temperature every 12 h until the SiO₂ layer reached the thickness wanted. Ag@SiO₂ NPs were isolated and purified by adding 20 mL of ethanol and centrifuged at 8 000 rpm for 10 min. The nanoparticles were washed two more times using 30 mL of ethanol and 10 mL of water prior to be suspended in ethanol and dried in a vacuum oven. The reaction was scaled up to 125 mg of Ag NPs by increasing the amount of reagents and solvents accordingly.

8.3.1.2 Synthesis of SiO₂@Ag-[Ru] NPs and SiO₂@Ag-MB NPs

Immobilization of $[Ru(bpy)_3]Cl_2$ on Ag@SiO₂ NPs was realized following a procedure previously reported by the Amara group.⁴⁶⁶ Briefly, an aqueous stock solution of $[Ru(bpy)_3]Cl_2.6H_2O$ 0.4 mM was prepared. A varied volume of this solution was then added to 20 mg of dried Ag@SiO₂ NPs suspended in a total volume of 3 mL of water. The volume added was calculated depending on the

BET surface area in order to obtain the desired loading and surface coverage, which was identical of each nanomaterial. The solution was sonicated then stirred in the dark overnight. The final material was washed three times with water and dried by lyophilization. Complete immobilizations resulted in a colorless supernatant, which was confirmed by UV-Vis spectroscopy.

A similar protocol was used to immobilized MB on SiO₂@Ag NPs to achieve the identical desired loading and surface coverage.

8.3.2 Synthesis of SiO₂@Ag-RB NPs

SiO₂@Ag NPs were first functionalized with amino moieties prior to the anchorage of Rose Bengal (RB). 10 mg of SiO2@Ag NPs and 1 mL of NH4OH 30% were added to 20 mL of isopropanol. After vigorous stirring for 30 min and sonicating several times to obtain a homogeneous colloidal suspension, 5 μ L of (3-Aminopropyl)triethoxysilane (APTES) were added to the mixture. 3 h later, the solvent was removed following centrifugation at 12 00 rpm for 15 min and the nanoparticles were resuspended in 2 mL of a 2-ethanesulfonic acid (MES) 0.1 M buffer. In a separate vial, 8 mg of 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and the volume of RB needed to reach the identical desired loading and surface coverage were added to 3 mL of MES buffer. After 20 min of stirring, the solutions were combined and let to react for 3 h. SiO2@Ag-RB NPs were isolated and purified by three cycles of centrifugation (12 000 rpm, 10 min) using 10 mL of ultra-pure water then dried by lyophilization.

8.3.2.1 Nanoparticle Characterization

The nanoparticles were washed and isolated by centrifugation (Thermo Scientific Sorvall Legend XF) and the nanoparticle solutions were well sonicated before each characterization. The size and the morphology of all of the nanoparticles were investigated with a transmission electron microscope (Philips CM200 200 kV). The samples were drop-casted on onto a Cu grid with a carbon mesh grids. The particle size distribution was evaluated by analyzing the images with ImageJ using on average 100 particles. EDS experiments were carried out in a Thermo Scientific Talos F200X S/TEM operated at 200 keV, with high brightness XFEG Schottky source. EDS carried out with a

Annex

SuperX G2 energy dispersive spectroscopy detector comprising four windowless SSDs, dwell time 20 µs per pixel and probe current 236 pA. Data was processed using Gatan Digital Micrograph[®] software. The UV-visible extinction spectra were recorded with a spectrophotometer (Cary 50, Varian, Palo Alto, CA). The zeta potential was measured using a Zetasizer (BrookHaven Instrument Corp., ZetaPlus). The conversion was determined by GC-MS (Agilent technologies 7890A coupled with Agilent technologies 5975C inert XL MSD with triple-axis detector) and by NMR (Bruker AVIIIHD 500 MHz NMR spectrometer).

8.3.2.2 Catalytic tests

Photooxidation of citronellol was performed in a 125 mL 3-neck jacketed with a condenser, a thermometer and a balloon filed with oxygen were connected to the 3 necks, and the reactor was maintained at 20 °C using a water recirculatory (Figure S9). The reactor was illuminated by white LED strips (Ustellar UT33301) with a daylight white color (6000 K) positioned on a cylindrical support of about 30 cm diameter and 10 cm height and the whole set up was covered with aluminum foil.

In a typical procedure, 0.33 mmol of b-citronellol and 0.20 mmol of ortho-dimethoxybenzene (internal standard) were dissolved in 20 mL of acetonitrile, using part of the solvent to suspend 2.0 mg of Ag@SiO₂-Ru with a silica shell of 28 nm and surface loading equal to 6.5E-5 mmol of $[Ru(bpy)_3]^{2+}/m^2$. The amount of reagents was adapted to keep the concentration of molecular catalytic loading the same for all experiment while maintaining the concentration of PNPs identical, hence the opacity of the solution the same for all experiments. For MB, 0.42 mmol of b-citronellol and 0.36 mmol of ortho-dimethoxybenzene (internal standard) were dissolved in 20 mL of isopropanol, using part of the solvent to suspend 2.0 mg of Ag@SiO₂-RB with a silica shell of 28 nm and surface loading equal to 6.5E-5 mmol of MB /m². For RB, 0.42 mmol of b-citronellol and 0.36 mmol of ortho-dimethoxybenzene (internal standard) were dissolved in 20 mL of isopropanol, using part of the solvent to suspend 2.0 mg of Ag@SiO₂-RB with a silica shell of 28 nm and surface loading equal to 6.5E-5 mmol of MB /m². For RB, 0.42 mmol of b-citronellol and 0.36 mmol of ortho-dimethoxybenzene (internal standard) were dissolved in 20 mL of isopropanol, using part of the solvent to suspend 2.0 mg of Ag@SiO₂-RB with a silica shell of 28 nm and surface loading equal to 6.5E-5 mmol of MB /m². For RB, 0.42 mmol of b-citronellol and 0.36 mmol of ortho-dimethoxybenzene (internal standard) were dissolved in 20 mL of isopropanol, using part of the solvent to suspend 2.0 mg of Ag@SiO₂-NB with a silica shell of 28 nm and surface loading equal to 6.5E-5 mmol of MB /m². For RB, 0.42 mmol of b-citronellol and 0.36 mmol of ortho-dimethoxybenzene (internal standard) were dissolved in 20 mL of isopropanol, using part of the solvent to suspend 2.0 mg of Ag@SiO₂-NB with a silica shell of 28 nm and surface loading equal to 6.5E-5 mmol of RB /m².

For the kinetic studies, aliquots were taken every hour and quenched with 1.2 molar equivalent of triphenylphosphine and analyzed by GC-MS. After 3h, the reaction mixture was quenched with

triphenylphosphine, concentrated by rotary evaporation and dissolved in $CDCl_3$ for ¹H NMR analysis.

Conversions were calculated using the ratio between the internal standard (orthodimethoxybenzene) and the reactant peak areas given by GC-MS at a given time, compared to the one at the beginning of the reaction. The conversion was also calculated using NMR by the ratio of the integration for the product and the internal standard. The reactions were performed in triplicate.

8.3.2.3 Time-resolved spectroscopy

Emission lifetime data was obtained on an Edinburgh Instruments FLS1000 photoluminescence spectrometer with an EPL-510 nm pulse diode 5 mW LASER excitation source, monitoring at 610 nm. Catalyst samples were purged under nitrogen for 30 minutes to remove oxygen quenching in a 1 cm pathlength cell cuvette before spectra were obtained. Samples were run to 5,000 counts with an instrument response function to remove source laser decay scattering. The data was fit with a bi-exponential tail fitting function to generate the t_1 and t_2 emission lifetimes with respective β_1 and β_2 contribution amplitude values.

8.3.3 BET surface area

SiO ₂ thickness (nm)	BET surface area (m²/g)				
7	4.9842 ± 0.1937				
10	7.2817 ± 0.2264				
15	11.3062 ± 0.2870				
19	13.3037 ± 0.3529				
25	14.7687 ± 0.3710				
28	16.8502 ± 0.4649				
30	16.9728 ± 0.4908				
33	17.4269 ± 0.2683				
37	18.5098 ± 0.3208				
45	20.9174 ± 0.2919				

Table 8-8 - BET surface area of Ag@SiO2 NPs with various silica thickness shell

8.3.4 ζ-potential

Table 8-9 – ζ -potential of Ag@SiO2 NPs with 28 and 33 nm shell before and after immobilization of [Ru(bpy)₃]²⁺

	Ag@SiO2_28nm	Ag@SiO2_33nm			
Naked	-25.67 ± 0.8	-32.34 ± 0.9			
With [Ru]	-15.79 ± 0.7	-18.52 ± 1.0			
With APTES	-11.76 ± 1.0	-13.18 ± 1.1			
With RB	-18.98 ± 1.0	-19.14 ± 1.2			





Figure 8-19 - Time resolved emission for $[Ru(bpy)_3]^{2+}$ @SiO₂ standard with 5 microsecond pulse rate and acquisition window.

Annex



Figure 8-20 - Experimental data for the emission of $[Ru(bpy)_3]^{2+}$ immobilized on commercial SiO₂ NPs and Ag@SiO₂ NPs with different thicknesses, and fitting of the lifetime. Insert on 2B shows the lifetime short component.

Annex

$$\tau_{Avg} = \frac{B_1 \tau_1^2 + B_2 \tau_2^2}{B_1 \tau_1 + B_2 \tau_2}$$

Equation 8-4 - Relationship between the lifetime (T avg) and the fitting functions, with t_1 and t_2 emission lifetimes with respective β_1 and β_2 contribution amplitude values

Quantum yield of emission values along with the rates of radiative and non-radiative decay processes were calculated using the formulae, with the quantum yield of [$Ru(bpy)_3$]²⁺ in water taken to be 0.042

 $Emission_{Enhancement} * \Phi Rubpy = \Phi Ag@SiO2 - Rubpy Samples$

$$\Phi$$
 Sample = K_{radiative} * t_{average}

$$t_{average} = \frac{1}{K_{radiative} + K_{non-radiative}}$$

$$K_{non-radiative} = \frac{1}{t_{average}} - K_{radiative}$$

Equation 8-5A-D- relationships between the emission enhancement, the quantum yield Φ , the radiative (Kr) and non-radiative (Knr) decay rates and th lifetime (t average)

Annex

Table 8-10 - Measured lifetimes, amplitudes, and residuals for each sample as well as the
calculated average lifetime, radiative and non-radiative decay rates

Sample	T _{average}	T ₁	T ₂	B ₁	B ₂	EF	Φluminescence	K Radiative	k _{Non-}	EF
		-				lum			Radiative	catalysis
	ns	ns	ns				%	10 ⁶ s ⁻¹	10 ⁶ s ⁻¹	
Rubpy@SiO ₂ _7 nm	379	93	479	310	173	0.18	0.007	0.02	2.62	0.67
Rubpy@SiO ₂ _19 nm	340	50	456	252	68	1.18	0.032	0.15	2.80	1.22
Rubpy@SiO ₂ _28 nm	416	70	484	990	725	3.53	0.148	0.35	2.04	2.72
Rubpy@SiO2_33 nm	476	88	552	145	119	4.12	0.173	0.36	1.73	1.84
Rubpy@SiO2_45 nm	486	38	545	83	44	0.82	0.035	0.07	1.98	1.24
Rubpy@SiO₂ comm	596	N/A	596	N/A	3615	1.00	0.042	0.07	1.61	1.00

8.4 References

77. Planas, O.; Macia, N.; Agut, M.; Nonell, S.; Heyne, B., Distance-Dependent Plasmon-Enhanced Singlet Oxygen Production and Emission for Bacterial Inactivation. *J. Am. Chem. Soc.* **2016**, *138* (8), 2762-2768.

237. Mori, K.; Kawashima, M.; Che, M.; Yamashita, H., Enhancement of the Photoinduced Oxidation Activity of a Ruthenium(Ii) Complex Anchored on Silica-Coated Silver Nanoparticles by Localized Surface Plasmon Resonance. *Angew. Chem.* **2010**, *122* (46), 8780-8783.

466. Tambosco, B.; Segura, K.; Seyrig, C.; Cabrera, D.; Port, M.; Ferroud, C.; Amara, Z., Outer-Sphere Effects in Visible-Light Photochemical Oxidations with Immobilized and Recyclable Ruthenium Bipyridyl Salts. *ACS Catal.* **2018**, *8*(5), 4383-4389.

476. Gellé, A.; Jin, T.; de la Garza, L.; Price, G. D.; Besteiro, L. V.; Moores, A., Applications of Plasmon-Enhanced Nanocatalysis to Organic Transformations. *Chemical Reviews* 2019.
482. Wertz, E.; Isaacoff, B. P.; Flynn, J. D.; Biteen, J. S., Single-Molecule Super-Resolution Microscopy Reveals How Light Couples to a Plasmonic Nanoantenna on the Nanometer Scale. *Nano Lett.* 2015, *15*(4), 2662-2670.

483. Darvill, D.; Centeno, A.; Xie, F., Plasmonic Fluorescence Enhancement by Metal Nanostructures: Shaping the Future of Bionanotechnology. *Phys. Chem. Chem. Phys* **2013**, *15*(38), 15709-15726.

499. Yin, N.; Liu, Y.; Liu, L.; Lei, J.; Jiang, T.; Wang, H.; Zhu, L.; Xu, X., Fluorescence Enhancement of Ru(Bpy)32+ by Core–Shell Ag@Sio2 Nanocomposites. *J. Alloys Compd.* **2013**, *581*, 6-10.

500. Tovmachenko, O. G.; Graf, C.; van den Heuvel, D. J.; van Blaaderen, A.; Gerritsen, H. C., Fluorescence Enhancement by Metal-Core/Silica-Shell Nanoparticles. *Adv. Mater.* **2006**, *18*(1), 91-95.

501. Cheng, D.; Xu, Q.-H., Separation Distance Dependent Fluorescence Enhancement of Fluorescein Isothiocyanate by Silver Nanoparticles. *Chem. Commun.* **2007**, (3), 248-250.

503. An, X.; Stelter, D.; Keyes, T.; Reinhard, B. M., Plasmonic Photocatalysis of Urea Oxidation and Visible-Light Fuel Cells. *Chem* **2019**, *5*(8), 2228-2242.

504. Chen, Y.; Munechika, K.; Ginger, D. S., Dependence of Fluorescence Intensity on the Spectral Overlap between Fluorophores and Plasmon Resonant Single Silver Nanoparticles. *Nano Lett.* **2007**, *7*(3), 690-696.

511. Macia, N.; Kabanov, V.; Côté-Cyr, M.; Heyne, B., Roles of near and Far Fields in Plasmon-Enhanced Singlet Oxygen Production. *J. Phys. Chem. Let.* **2019**, *10* (13), 3654-3660.

512. Szmacinski, H.; Lakowicz, J. R.; Catchmark, J. M.; Eid, K.; Anderson, J. P.; Middendorf, L., Correlation between Scattering Properties of Silver Particle Arrays and Fluorescence Enhancement. *Appl. Spectrosc.* **2008**, *62*(7), 733-738.

515. Abadeer, N. S.; Brennan, M. R.; Wilson, W. L.; Murphy, C. J., Distance and Plasmon Wavelength Dependent Fluorescence of Molecules Bound to Silica-Coated Gold Nanorods. *ACS Nano* **2014**, *8*(8), 8392-8406.

518. Terra, J. C.; Desgranges, A.; Monnereau, C.; Sanchez, E. H.; De Toro, J. A.; Amara, Z.; Moores, A., Photocatalysis Meets Magnetism: Designing Magnetically Recoverable Supports for Visible-Light Photocatalysis. *ACS Appl. Mater. Inter.* **2020**, *12* (22), 24895-24904.

520. Rodríguez-Fernández, J.; Pastoriza-Santos, I.; Perez-Juste, J.; García de Abajo, F. J.; Liz-Marzan, L. M., The Effect of Silica Coating on the Optical Response of Sub-Micrometer Gold Spheres. *J. Phys. Chem.* C**2007**, *111*(36), 13361-13366.

521. Pastoriza-Santos, I.; Gomez, D.; Pérez-Juste, J.; Liz-Marzán, L. M.; Mulvaney, P., Optical Properties of Metal Nanoparticle Coated Silica Spheres: A Simple Effective Medium Approach. *Phys. Chem. Chem. Phys* **2004**, *6* (21), 5056-5060.

525. Vankayala, R.; Sagadevan, A.; Vijayaraghavan, P.; Kuo, C.-L.; Hwang, K. C., Metal Nanoparticles Sensitize the Formation of Singlet Oxygen. *Angew. Chem. Int. Ed.* **2011**, *50* (45), 10640-10644.

527. Huang, Y. F.; Zhang, M.; Zhao, L. B.; Feng, J. M.; Wu, D. Y.; Ren, B.; Tian, Z. Q., Activation of Oxygen on Gold and Silver Nanoparticles Assisted by Surface Plasmon Resonances. *Angew. Chem. Int. Ed.* **2014**, *53*(9), 2353-2357.

531. Brodusch, N.; Demers, H.; Gellé, A.; Moores, A.; Gauvin, R., Electron Energy-Loss Spectroscopy (Eels) with a Cold-Field Emission Scanning Electron Microscope at Low Accelerating Voltage in Transmission Mode. *Ultramicroscopy* **2019**, *203*, 21-36.

535. Hohenester, U., Simulating Electron Energy Loss Spectroscopy with the Mnpbem Toolbox. *Comput. Phys. Commun.* **2014**, *185*(3), 1177-1187.

551. Zhao, T.; Sun, R.; Yu, S.; Zhang, Z.; Zhou, L.; Huang, H.; Du, R., Size-Controlled Preparation of Silver Nanoparticles by a Modified Polyol Method. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2010**, *366* (1-3), 197-202.

552. Hohenester, U.; Trügler, A., Mnpbem - a Matlab Toolbox for the Simulation of Plasmonic Nanoparticles. *Computer Physics Communications* **2012**, *183*(2), 370-381.

553. Palik, E. D., *Handbook of Optical Constants of Solids*. Academic press: 1998; Vol. 3.

554. Hayashi, H.; Hiraoka, N., Accurate Measurements of Dielectric and Optical Functions of Liquid Water and Liquid Benzene in the Vuv Region (1–100 Ev) Using Small-Angle Inelastic X-Ray Scattering. *The Journal of Physical Chemistry* **B2015**, *119*(17), 5609-5623.

555. Moutzouris, K.; Papamichael, M.; Betsis, S. C.; Stavrakas, I.; Hloupis, G.; Triantis, D., Refractive, Dispersive and Thermo-Optic Properties of Twelve Organic Solvents in the Visible and near-Infrared. *Applied Physics B***2014**, *116*(3), 617-622.

556. Virtanen, P.; Gommers, R.; Oliphant, T. E.; Haberland, M.; Reddy, T.; Cournapeau, D.; Burovski, E.; Peterson, P.; Weckesser, W.; Bright, J., Scipy 1.0: Fundamental Algorithms for Scientific Computing in Python. *Nature methods* **2020**, *17*(3), 261-272.

557. Zhao, T.; Sun, R.; Yu, S.; Zhang, Z.; Zhou, L.; Huang, H.; Du, R., Size-Controlled Preparation of Silver Nanoparticles by a Modified Polyol Method. *Colloids Surf. A Physicochem. Eng.* **2010**, *366* (1-3), 197-202.

9 Bibliographie

1. Ciamician, G., The Photochemistry of the Future. *Science* **1912**, *36*(926), 385-394.

2. Palmisano, G.; Augugliaro, V.; Pagliaro, M.; Palmisano, L., Photocatalysis: A Promising Route for 21st Century Organic Chemistry. *Chemical Communications* **2007**, (33), 3425-3437.

3. Roth, H. D., The Beginnings of Organic Photochemistry. *Angewandte Chemie International Edition in English* **1989**, *28*(9), 1193-1207.

4. Albini, A.; Fagnoni, M., 1908: Giacomo Ciamician and the Concept of Green Chemistry. *ChemSusChem* **2008**, *1*(1-2), 63-66.

5. Acar, C.; Dincer, I.; Naterer, G. F., Review of Photocatalytic Water-Splitting Methods for Sustainable Hydrogen Production. *International Journal of Energy Research* **2016**, *40* (11), 1449-1473.

6. Jafari, T.; Moharreri, E.; Amin, A. S.; Miao, R.; Song, W.; Suib, S. L., Photocatalytic Water Splitting—the Untamed Dream: A Review of Recent Advances. *Molecules* **2016**, *21* (7), 900.

7. Fajrina, N.; Tahir, M., A Critical Review in Strategies to Improve Photocatalytic Water Splitting Towards Hydrogen Production. *International Journal of Hydrogen Energy* **2019**, *44*(2), 540-577.

8. Nicewicz, D. A.; Nguyen, T. M., Recent Applications of Organic Dyes as Photoredox Catalysts in Organic Synthesis. ACS Publications: 2014.

9. Nicewicz, D. A.; MacMillan, D. W., Merging Photoredox Catalysis with Organocatalysis: The Direct Asymmetric Alkylation of Aldehydes. *Science* **2008**, *322* (5898), 77-80.

10. Al-Mamun, M.; Kader, S.; Islam, M.; Khan, M., Photocatalytic Activity Improvement and Application of Uv-Tio2 Photocatalysis in Textile Wastewater Treatment: A Review. *Journal of Environmental Chemical Engineering* **2019**, *7*(5), 103248.

11. Ahmed, S. N.; Haider, W., Heterogeneous Photocatalysis and Its Potential Applications in Water and Wastewater Treatment: A Review. *Nanotechnology* **2018**, *29* (34), 342001.

12. Ge, J.; Zhang, Y.; Heo, Y.-J.; Park, S.-J., Advanced Design and Synthesis of Composite Photocatalysts for the Remediation of Wastewater: A Review. *Catalysts* **2019**, *9*(2), 122.

13. Romero, N. A.; Nicewicz, D. A., Organic Photoredox Catalysis. *Chemical reviews* **2016**, *116*(17), 10075-10166.

14. Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J., Visible Light Photoredox-Controlled Reactions of N-Radicals and Radical Ions. *Chemical Society Reviews* **2016**, *45* (8), 2044-2056.

15. Schweitzer, C.; Schmidt, R., Physical Mechanisms of Generation and Deactivation of Singlet Oxygen. *Chemical reviews* **2003**, *103*(5), 1685-1758.

16. Ghogare, A. A.; Greer, A., Using Singlet Oxygen to Synthesize Natural Products and Drugs. *Chem. Rev.* **2016**, *116*(17), 9994-10034.

17. Ravelli, D.; Fagnoni, M.; Albini, A., Photoorganocatalysis. What For? *Chemical Society Reviews* **2013**, *42*(1), 97-113.

18. Ravelli, D.; Protti, S.; Fagnoni, M., Carbon–Carbon Bond Forming Reactions Via Photogenerated Intermediates. *Chemical reviews* **2016**, *116*(17), 9850-9913.

19. Schultz, D. M.; Yoon, T. P., Solar Synthesis: Prospects in Visible Light Photocatalysis. *Science* **2014**, *343*(6174).

20. Yoon, T. P.; Ischay, M. A.; Du, J., Visible Light Photocatalysis as a Greener Approach to Photochemical Synthesis. *Nat. Chem.* **2010**, *2*(7), 527-532.

21. Hoffmann, N., Photochemical Reactions as Key Steps in Organic Synthesis. *Chemical Reviews* **2008**, *108*(3), 1052-1103.

22. Karkas, M. D.; Porco Jr, J. A.; Stephenson, C. R., Photochemical Approaches to Complex Chemotypes: Applications in Natural Product Synthesis. *Chemical Reviews* **2016**, *116*(17), 9683-9747.

23. Shaw, M. H.; Twilton, J.; MacMillan, D. W., Photoredox Catalysis in Organic Chemistry. *The Journal of organic chemistry* **2016**, *81*(16), 6898-6926.

24. Zhou, D.; Chen, Z.; Gao, T.; Niu, F.; Qin, L.; Huang, Y., Hydrogen Generation from Water Splitting on Tio2 Nanotube-Array-Based Photocatalysts. *Energy Technology* **2015**, *3*(9), 888-895.

25. Fox, M. A.; Dulay, M. T., Heterogeneous Photocatalysis. *Chemical reviews* **1993**, *93* (1), 341-357.

26. Sharma, S.; Sharma, A., Recent Advances in Photocatalytic Manipulations of Rose Bengal in Organic Synthesis. *Org. Biomol. Chem.* **2019**, *17*(18), 4384-4405.

27. Hari, D. P.; König, B., Synthetic Applications of Eosin Y in Photoredox Catalysis. *Chemical Communications* **2014**, *50*(51), 6688-6699.

28. Joshi-Pangu, A.; Lévesque, F. o.; Roth, H. G.; Oliver, S. F.; Campeau, L.-C.; Nicewicz, D.; DiRocco, D. A., Acridinium-Based Photocatalysts: A Sustainable Option in Photoredox Catalysis. *The Journal of Organic Chemistry* **2016**, *81* (16), 7244-7249.

29. Chen, Y.; Li, A.; Huang, Z.-H.; Wang, L.-N.; Kang, F., Porphyrin-Based Nanostructures for Photocatalytic Applications. *Nanomaterials* **2016**, *6*(3), 51.

30. Ravelli, D.; Fagnoni, M., Dyes as Visible Light Photoredox Organocatalysts. *ChemCatChem* **2012**, *4*(2), 169-171.

31. DeRosa, M. C.; Crutchley, R. J., Photosensitized Singlet Oxygen and Its Applications. *Coordination Chemistry Reviews* **2002**, *233*, 351-371.

32. You, Y., Chemical Tools for the Generation and Detection of Singlet Oxygen. *Organic & biomolecular chemistry* **2018**, *16*(22), 4044-4060.

33. Pibiri, I.; Buscemi, S.; Piccionello, A. P.; Pace, A., Photochemically Produced Singlet Oxygen: Applications and Perspectives. *ChemPhotoChem* **2018**, *2*(7), 535-547.

34. Fukuzumi, S.; Ohkubo, K., Organic Synthetic Transformations Using Organic Dyes as Photoredox Catalysts. *Organic & Biomolecular Chemistry* **2014**, *12*(32), 6059-6071.

35. Teegardin, K.; Day, J. I.; Chan, J.; Weaver, J., Advances in Photocatalysis: A Microreview of Visible Light Mediated Ruthenium and Iridium Catalyzed Organic Transformations. *Org. Proc. Res. Dev.* **2016**, *20*(7), 1156-1163.

36. Michelin, C. m.; Hoffmann, N., Photosensitization and Photocatalysis—Perspectives in Organic Synthesis. *ACS Catalysis* **2018**, *8*(12), 12046-12055.

37. Narayanam, J. M.; Stephenson, C. R., Visible Light Photoredox Catalysis: Applications in Organic Synthesis. *Chemical Society Reviews* **2011**, *40*(1), 102-113.

38. Arias-Rotondo, D. M.; McCusker, J. K., The Photophysics of Photoredox Catalysis: A Roadmap for Catalyst Design. *Chemical Society Reviews* **2016**, *45* (21), 5803-5820.

39. Guo, S.; Chen, K.-K.; Dong, R.; Zhang, Z.-M.; Zhao, J.; Lu, T.-B., Robust and Long-Lived Excited State Ru (Ii) Polyimine Photosensitizers Boost Hydrogen Production. *ACS Catalysis* **2018**, *8*(9), 8659-8670.

40. Parada, G. A.; Fredin, L. A.; Santoni, M.-P.; Jäger, M.; Lomoth, R.; Hammarström, L.; Johansson, O.; Persson, P.; Ott, S., Tuning the Electronics of Bis (Tridentate) Ruthenium (Ii) Complexes with Long-Lived Excited States: Modifications to the Ligand Skeleton Beyond Classical Electron Donor or Electron Withdrawing Group Decorations. *Inorganic Chemistry* **2013**, *52*(9), 5128-5137.

41. Krinsky, N. I., Singlet Oxygen in Biological Systems. *Trends in Biochemical Sciences* **1977**, *2*(2), 35-38.

42. Abdel-Shafi, A. A.; Worrall, D. R.; Ershov, A. Y., Photosensitized Generation of Singlet Oxygen from Ruthenium (Ii) and Osmium (Ii) Bipyridyl Complexes. *Dalton Transactions* **2004**, (1), 30-36.

43. Abdel-Shafi, A. A.; Beer, P. D.; Mortimer, R. J.; Wilkinson, F., Photosensitized Generation of Singlet Oxygen from (Substituted Bipyridine) Ruthenium (Ii) Complexes. *Helvetica Chimica Acta* **2001**, *84*(9), 2784-2795.

44. Gutiérrez, M. I.; Martínez, C. G.; García-Fresnadillo, D.; Castro, A. M.; Orellana, G.; Braun, A. M.; Oliveros, E., Singlet Oxygen (1δg) Production by Ruthenium (Ii) Complexes in Microheterogeneous Systems. *The Journal of Physical Chemistry A* **2003**, *107*(18), 3397-3403.

45. Adam, W.; Brünker, H.-G.; Kumar, A. S.; Peters, E.-M.; Peters, K.; Schneider, U.; von Schnering, H. G., Diastereoselective Singlet Oxygen Ene Reaction (Schenck Reaction) and Diastereoselective Epoxidations of Heteroatom-Substituted Acyclic Chiral Olefins: A Mechanistic Comparison. *Journal of the American Chemical Society* **1996**, *118* (8), 1899-1905.

46. Prein, M.; Adam, W., The Schenck Ene Reaction: Diastereoselective Oxyfunctionalization with Singlet Oxygen in Synthetic Applications. *Angewandte Chemie International Edition in English* **1996**, *35*(5), 477-494.

47. Amara, Z.; Bellamy, J. F.; Horvath, R.; Miller, S. J.; Beeby, A.; Burgard, A.; Rossen, K.; Poliakoff, M.; George, M. W., Applying Green Chemistry to the Photochemical Route to Artemisinin. *Nat. Chem.* **2015**, *7*(6), 489-495.

48. Markham, S. C., Photocatalytic Properties of Oxides. ACS Publications: 1955.

49. Fujishima, A.; Honda, K., Electrochemical Photolysis of Water at a Semiconductor Electrode. *nature* **1972**, *238*(5358), 37-38.

50. Kudo, A.; Miseki, Y., Heterogeneous Photocatalyst Materials for Water Splitting. *Chemical Society Reviews* **2009**, *38*(1), 253-278.

51. Pelaez, M.; Nolan, N. T.; Pillai, S. C.; Seery, M. K.; Falaras, P.; Kontos, A. G.; Dunlop, P. S.; Hamilton, J. W.; Byrne, J. A.; O'shea, K., A Review on the Visible Light Active Titanium Dioxide Photocatalysts for Environmental Applications. *Applied Catalysis B: Environmental* **2012**, *125*, 331-349.

52. Serpone, N.; Emeline, A., Semiconductor Photocatalysis: Past, Present, and Future Outlook. ACS Publications: 2012.

53. Li, S.; Shelar, D. P.; Hou, C.-C.; Chen, Q.-Q.; Deng, P.; Chen, Y., Wo3 Nanospheres with Improved Catalytic Activity for Visible Light Induced Cross Dehydrogenative Coupling Reactions. *Journal of Photochemistry and Photobiology A: Chemistry* **2018**, *363*, 44-50.

54. Mills, A.; Davies, R. H.; Worsley, D., Water Purification by Semiconductor Photocatalysis. *Chemical Society Reviews* **1993**, *22*(6), 417-425.

55. Demyanenko, A. V.; Bogomolov, A. S.; Dozmorov, N. V.; Svyatova, A. I.; Pyryaeva, A. P.; Goldort, V. G.; Kochubei, S. A.; Baklanov, A. V., Singlet Oxygen 1o2 in Photocatalysis on Tio2. Where Does It Come From? *The Journal of Physical Chemistry* **C2019**, *123*(4), 2175-2181.

56. Daimon, T.; Nosaka, Y., Formation and Behavior of Singlet Molecular Oxygen in Tio2 Photocatalysis Studied by Detection of near-Infrared Phosphorescence. *The Journal of Physical Chemistry* C**2007**, *111*(11), 4420-4424.

57. Moniz, S. J.; Shevlin, S. A.; Martin, D. J.; Guo, Z.-X.; Tang, J., Visible-Light Driven Heterojunction Photocatalysts for Water Splitting-a Critical Review. *Energy & Environmental Science* **2015**, *8*(3), 731-759.

58. Ni, M.; Leung, M. K.; Leung, D. Y.; Sumathy, K., A Review and Recent Developments in Photocatalytic Water-Splitting Using Tio2 for Hydrogen Production. *Renewable and Sustainable Energy Reviews* **2007**, *11*(3), 401-425.

59. Tang, J.; Durrant, J. R.; Klug, D. R., Mechanism of Photocatalytic Water Splitting in Tio2. Reaction of Water with Photoholes, Importance of Charge Carrier Dynamics, and Evidence for Four-Hole Chemistry. *Journal of the American Chemical Society* **2008**, *130* (42), 13885-13891.

60. Kisch, H., Semiconductor Photocatalysis—Mechanistic and Synthetic Aspects. *Angewandte Chemie International Edition* **2013**, *52*(3), 812-847.

61. de Aberasturi, D. J.; Serrano-Montes, A. B.; Liz-Marzán, L. M., Modern Applications of Plasmonic Nanoparticles: From Energy to Health. *Adv. Opt. Mater.* **2015**, *3*(5), 602-617.

62. Song, M.; Wang, D.; Peana, S.; Choudhury, S.; Nyga, P.; Kudyshev, Z. A.; Yu, H.; Boltasseva, A.; Shalaev, V. M.; Kildishev, A. V., Colors with Plasmonic Nanostructures: A Full-Spectrum Review. *Applied Physics Reviews* **2019**, *6*(4), 041308.

63. Masson, J.-F., Surface Plasmon Resonance Clinical Biosensors for Medical Diagnostics. *ACS sensors* **2017**, *2*(1), 16-30.

64. Cheng, L.; Wang, C.; Feng, L.; Yang, K.; Liu, Z., Functional Nanomaterials for Phototherapies of Cancer. *Chemical reviews* **2014**, *114*(21), 10869-10939.

65. Wang, D.; Wang, W.; Knudson, M. P.; Schatz, G. C.; Odom, T. W., Structural Engineering in Plasmon Nanolasers. *Chemical reviews* **2017**, *118*(6), 2865-2881.

66. Clavero, C., Plasmon-Induced Hot-Electron Generation at Nanoparticle/Metal-Oxide Interfaces for Photovoltaic and Photocatalytic Devices. *Nature Photonics* **2014**, *8* (2), 95-103.

67. Kuppe, C.; Rusimova, K. R.; Ohnoutek, L.; Slavov, D.; Valev, V. K., "Hot" in Plasmonics: Temperature-Related Concepts and Applications of Metal Nanostructures. *Advanced Optical Materials* **2020**, *8*(1), 1901166.

68. Cardinal, M. F.; Vander Ende, E.; Hackler, R. A.; McAnally, M. O.; Stair, P. C.; Schatz, G. C.; Van Duyne, R. P., Expanding Applications of Sers through Versatile Nanomaterials Engineering. *Chemical Society Reviews* **2017**, *46* (13), 3886-3903.

69. Gellé, A.; Jin, T.; de la Garza, L.; Price, G. D.; Besteiro, L. V.; Moores, A., Applications of Plasmon-Enhanced Nanocatalysis to Organic Transformations. *Chemical Reviews* **2019**, *120*(2), 986-1041.

70. Moores, A.; Goettmann, F., The Plasmon Band in Noble Metal Nanoparticles: An Introduction to Theory and Applications. *New J. Chem.* **2006**, *30*(8), 1121-1132.

71. Brongersma, M. L.; Halas, N. J.; Nordlander, P., Plasmon-Induced Hot Carrier Science and Technology. *Nature nanotechnology* **2015**, *10*(1), 25-34.

72. Zhang, Z.; Zhang, C.; Zheng, H.; Xu, H., Plasmon-Driven Catalysis on Molecules and Nanomaterials. *Accounts of chemical research* **2019**, *52*(9), 2506-2515.

73. Zhang, Y.; He, S.; Guo, W.; Hu, Y.; Huang, J.; Mulcahy, J. R.; Wei, W. D., Surface-Plasmon-Driven Hot Electron Photochemistry. *Chemical reviews* **2017**, *118* (6), 2927-2954.

74. Mukherjee, S.; Libisch, F.; Large, N.; Neumann, O.; Brown, L. V.; Cheng, J.; Lassiter, J. B.; Carter, E. A.; Nordlander, P.; Halas, N. J., Hot Electrons Do the Impossible: Plasmon-Induced Dissociation of H2 on Au. *Nano letters* **2013**, *13*(1), 240-247.

75. Swearer, D. F.; Zhao, H.; Zhou, L.; Zhang, C.; Robatjazi, H.; Martirez, J. M. P.; Krauter, C. M.; Yazdi, S.; McClain, M. J.; Ringe, E., Heterometallic Antenna– Reactor Complexes for Photocatalysis. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113*(32), 8916-8920.

76. Gellé, A.; Moores, A., Water Splitting Catalyzed by Titanium Dioxide Decorated with Plasmonic Nanoparticles. *Pure and Applied Chemistry* **2017**, *89*(12), 1817-1827.

77. Planas, O.; Macia, N.; Agut, M.; Nonell, S.; Heyne, B., Distance-Dependent Plasmon-Enhanced Singlet Oxygen Production and Emission for Bacterial Inactivation. *J. Am. Chem. Soc.* **2016**, *138* (8), 2762-2768.

78. Clark, J. H., Green Chemistry: Challenges and Opportunities. *Green Chemistry* **1999**, *1*(1), 1-8.

79. Anastas, P. T.; Warner, J. C., Principles of Green Chemistry. *Green chemistry: Theory and practice* **1998**, 29-56.

80. Taylor, D. A., Principles into Practice Setting the Bar for Green Chemistry. National Institute of Environmental Health Sciences: 2010.

81. Sheldon, R. A., Green Chemistry and Resource Efficiency: Towards a Green Economy. *Green Chemistry* **2016**, *18*(11), 3180-3183.

82. Sanderson, K., It's Not Easy Being Green: In the Past Two Decades, the Green-Chemistry Movement Has Helped Industry Become Much Cleaner. But Mindsets Change Slowly, and the Revolution Still Has a Long Way to Go. *Nature* **2011**, *469*(7328), 18-21.

83. Roschangar, F.; Colberg, J.; Dunn, P. J.; Gallou, F.; Hayler, J. D.; Koenig, S. G.; Kopach, M. E.; Leahy, D. K.; Mergelsberg, I.; Tucker, J. L., A Deeper Shade of Green: Inspiring Sustainable Drug Manufacturing. *Green Chemistry* **2017**, *19*(1), 281-285.

84. Poliakoff, M.; Fitzpatrick, J. M.; Farren, T. R.; Anastas, P. T., Green Chemistry: Science and Politics of Change. *Science* **2002**, *297*(5582), 807-810.

85. Sheldon, R. A., Metrics of Green Chemistry and Sustainability: Past, Present, and Future. *ACS Sustainable Chemistry & Engineering* **2018**, *6*(1), 32-48.

86. Roschangar, F.; Sheldon, R.; Senanayake, C., Overcoming Barriers to Green Chemistry in the Pharmaceutical Industry–the Green Aspiration Level[™] Concept. *Green Chemistry* **2015**, *17*(2), 752-768.

87. Anastas, P. T.; Kirchhoff, M. M.; Williamson, T. C., Catalysis as a Foundational Pillar of Green Chemistry. *Applied Catalysis A: General* **2001**, *221* (1-2), 3-13.

88. Albini, A.; Fagnoni, M., Green Chemistry and Photochemistry Were Born at the Same Time. *Green Chemistry* **2004**, *6*(1), 1-6.

89. Marzo, L.; Pagire, S. K.; Reiser, O.; König, B., Visible-Light Photocatalysis: Does It Make a Difference in Organic Synthesis? *Angewandte Chemie International Edition* **2018**, *57*(32), 10034-10072.

90. Zhou, Q. Q.; Zou, Y. Q.; Lu, L. Q.; Xiao, W. J., Visible-Light-Induced Organic Photochemical Reactions through Energy-Transfer Pathways. *Angewandte Chemie International Edition* **2019**, *58*(6), 1586-1604.

91. Ogilby, P. R., Singlet Oxygen: There Is Indeed Something New under the Sun. *Chemical Society Reviews* **2010**, *39*(8), 3181-3209.

92. Jo, W.-K.; Tayade, R. J., New Generation Energy-Efficient Light Source for Photocatalysis: Leds for Environmental Applications. *Industrial & Engineering Chemistry Research* **2014**, *53*(6), 2073-2084.

93. Chavez, S.; Aslam, U.; Linic, S., Design Principles for Directing Energy and Energetic Charge Flow in Multicomponent Plasmonic Nanostructures. *ACS Energy Lett.* **2018**, *3*(7), 1590-1596.

94. Burnham, A.; Han, J.; Clark, C. E.; Wang, M.; Dunn, J. B.; Palou-Rivera, I., Life-Cycle Greenhouse Gas Emissions of Shale Gas, Natural Gas, Coal, and Petroleum. *Environmental Science & Technology* **2012**, *46*(2), 619-627.

95. Armaroli, N.; Balzani, V., The Future of Energy Supply: Challenges and Opportunities. *Angewandte Chemie-International Edition* **2007**, *46* (1-2), 52-66.

96. Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C., Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chemical Reviews* **2013**, *113*(7), 5322-5363.

97. Ni, M.; Leung, M. K. H.; Leung, D. Y. C.; Sumathy, K., A Review and Recent Developments in Photocatalytic Water-Splitting Using Tio2 for Hydrogen Production. *Renewable & Sustainable Energy Reviews* **2007**, *11*(3), 401-425.

98. Hisatomi, T.; Kubota, J.; Domen, K., Recent Advances in Semiconductors for Photocatalytic and Photoelectrochemical Water Splitting. *Chemical Society Reviews* **2014**, *43*(22), 7520-7535.

99. Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W., Environmental Applications of Semiconductor Photocatalysis. *Chemical Reviews* **1995**, *95*(1), 69-96.

100. Han, F.; Kambala, V. S. R.; Srinivasan, M.; Rajarathnam, D.; Naidu, R., Tailored Titanium Dioxide Photocatalysts for the Degradation of Organic Dyes in Wastewater Treatment: A Review. *Applied Catalysis a-General* **2009**, *359*(1-2), 25-40.

101. Smith, J. G.; Faucheaux, J. A.; Jain, P. K., Plasmon Resonances for Solar Energy Harvesting: A Mechanistic Outlook. *Nano Today* **2015**, *10*(1), 67-80.

102. Papaioannou, S.; Kalavrouziotis, D.; Vyrsokinos, K.; Weeber, J. C.; Hassan, K.; Markey, L.; Dereux, A.; Kumar, A.; Bozhevolnyi, S. I.; Baus, M.; Tekin, T.; Apostolopoulos, D.; Avramopoulos, H.; Pleros, N., Active Plasmonics in Wdm Traffic Switching Applications. *Scientific Reports* **2012**, *2*.

103. Tian, Y.; Tatsuma, T., Mechanisms and Applications of Plasmon-Induced Charge Separation at Tio2 Films Loaded with Gold Nanoparticles. *Journal of the American Chemical Society* **2005**, *127*(20), 7632-7637.

104. Awazu, K.; Fujimaki, M.; Rockstuhl, C.; Tominaga, J.; Murakami, H.; Ohki, Y.; Yoshida, N.; Watanabe, T., A Plasmonic Photocatalyst Consisting of Silver Nanoparticles Embedded in Titanium Dioxide. *J. Am. Chem. Soc.* **2008**, *130*(5), 1676-1680.

105. Astruc, D.; Lu, F.; Aranzaes, J. R., Nanoparticles as Recyclable Catalysts: The Frontier between Homogeneous and Heterogeneous Catalysis. *Angewandte Chemie-International Edition* **2005**, *44*(48), 7852-7872.

106. Fihri, A.; Bouhrara, M.; Nekoueishahraki, B.; Basset, J. M.; Polshettiwar, V., Nanocatalysts for Suzuki Cross-Coupling Reactions. *Chemical Society Reviews* **2011**, *40* (10), 5181-5203.

107. Polshettiwar, V.; Varma, R. S., Green Chemistry by Nano-Catalysis. *Green Chemistry* **2010**, *12*(5), 743-754.

108. Roldan Cuenya, B., Synthesis and Catalytic Properties of Metal Nanoparticles: Size, Shape, Support, Composition, and Oxidation State Effects. *Thin Solid Films* **2010**, *518*(12), 3127-3150.

109. Ricciardi, R.; Huskens, J.; Verboom, W., Nanocatalysis in Flow. *Chemsuschem* **2015**, *8*(16), 2586-2605.

110. Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H. B.; Bouhrara, M.; Bassett, J. M., Magnetically Recoverable Nanocatalysts. *Chemical Reviews* **2011**, *111*(5), 3036-3075.

111. Hudson, R.; Feng, Y. T.; Varma, R. S.; Moores, A., Bare Magnetic Nanoparticles: Sustainable Synthesis and Applications in Catalytic Organic Transformations. *Green Chemistry* **2014**, *16*(10), 4493-4505.

112. Gonella, F.; Mazzoldi, P., *Handbook of Nanostructured Materials and Nanotechnology*. Elsevier: 2000.

113. Louis, C., Gold Nanoparticles in the Past: Before the Nanotechnology Era. In *Gold Nanoparticles for Physics, Chemistry and Biology*, 2012.

114. Garnett, J. M., Colours in Metal Glasses and in Metallic Films. *Philos. Trans. R. Soc. London* **1904**, *203*, 359-371.

115. Garnett, J. M., Colours in Metal Glasses, in Metallic Films, and in Metallic Solutions. *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character* **1906**, *205*, 387-401.

116. Mie, G., Beiträge Zur Optik Trüber Medien, Speziell Kolloidaler Metallösungen. *Annalen der Physik* **1908**, *330*(3), 377-445.

117. Kreibig, U.; Vollmer, M., *Optical Properties of Metal Clusters*. Springer: Berlin, 1995.
118. Drude, P., Zur Elektronentheorie Der Metalle. *Annalen der Physik* 1900, *306* (3), 566-613.

119. Solis, D. M.; Taboada, J. M.; Obelleiro, F.; Liz-Marzan, L. M.; García de Abajo, F. J., Toward Ultimate Nanoplasmonics Modeling. *Acs Nano* **2014**, *8*(8), 7559-7570.

120. Maier, S. A., *Plasmonics: Fundamentals and Applications*. Springer Science & Business Media: 2007.

121. Pelton, M.; Bryant, G. W., *Introduction to Metal-Nanoparticle Plasmonics*. Wiley: 2013.

122. van de Hulst, H. C., *Light Scattering by Small Particles*. Dover Publications: 1981.

123. Yu, R.; Liz-Marzán, L. M.; García de Abajo, F. J., Universal Analytical Modeling of Plasmonic Nanoparticles. *Chemical Society Reviews* **2017**, *46*(22), 6710-6724.

124. Merlen, A.; Lagugné-Labarthet, F., Imaging the Optical near Field in Plasmonic Nanostructures. *Applied spectroscopy* **2014**, *68*(12), 1307-1326.

125. Moores, A.; Le Floch, P., Metal Nanoparticle Plasmon Band as a Powerful Tool for Chemo and Biosensing. In *Biosensing Using Nanomaterials*, Merkoçi, A., Ed. Wiley & Sons: 2009; pp 137-170.

126. Anker, J. N.; Hall, P.; Lyandres, O.; Shah, N. C.; Zhao, J.; Van Duyne, R. P., Biosensing with Plasmonic Nanosensors. In *Nanoscience and Technology*, Nature, Ed. 2010; pp 308-319.

127. Moskovits, M., Surface-Enhanced Raman Spectroscopy: A Brief Retrospective. *Journal of Raman Spectroscopy* **2005**, *36*(6-7), 485-496.

128. Tam, F.; Goodrich, G. P.; Johnson, B. R.; Halas, N. J., Plasmonic Enhancement of Molecular Fluorescence. *Nano Letters* **2007**, *7*(2), 496-501.

129. Bauch, M.; Toma, K.; Toma, M.; Zhang, Q.; Dostalek, J., Plasmon-Enhanced Fluorescence Biosensors: A Review. *Plasmonics* **2014**, *9*(4), 781-799.

130. Willets, K. A.; Duyne, R. P. V., Localized Surface Plasmon Resonance Spectroscopy and Sensing. *Annual Review of Physical Chemistry* **2007**, *58*(1), 267-297.

131. Sonnefraud, Y.; Verellen, N.; Sobhani, H.; Vandenbosch, G. A. E.; Moshchalkov, V. V.; Van Dorpe, P.; Nordlander, P.; Maier, S. A., Experimental Realization of Subradiant, Superradiant, and Fano Resonances in Ring/Disk Plasmonic Nanocavities. *ACS Nano* **2010**, *4*(3), 1664-1670.

132. Zorić, I.; Zäch, M.; Kasemo, B.; Langhammer, C., Gold, Platinum, and Aluminum Nanodisk Plasmons: Material Independence, Subradiance, and Damping Mechanisms. *ACS Nano* **2011**, *5*(4), 2535-2546.

133. Govorov, A. O.; Richardson, H. H., Generating Heat with Metal Nanoparticles. *Nano today* **2007**, *2*(1), 30-38.

134. Lal, S.; Clare, S. E.; Halas, N. J., Nanoshell-Enabled Photothermal Cancer Therapy: Impending Clinical Impact. *Accounts of Chemical Research* **2008**, *41* (12), 1842-1851.

135. Huang, X.; Jain, P. K.; El-Sayed, I. H.; El-Sayed, M. A., Plasmonic Photothermal Therapy (Pptt) Using Gold Nanoparticles. *Lasers in medical science* **2008**, *23*(3), 217-218.

136. Xiao, M.; Jiang, R.; Wang, F.; Fang, C.; Wang, J.; Jimmy, C. Y., Plasmon-Enhanced Chemical Reactions. *J. Mater. Chem. A* **2013**, *1*(19), 5790-5805.

137. Qiu, J. J.; Wei, W. D., Surface Plasmon-Mediated Photothermal Chemistry. *Journal of Physical Chemistry C***2014**, *118*(36), 20735-20749.

138. Hartland, G. V.; Besteiro, L. V.; Johns, P.; Govorov, A. O., What's So Hot About Electrons in Metal Nanoparticles? *ACS Energy Letters* **2017**, *2*(7), 1641-1653.

139. Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C., The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *The Journal of Physical Chemistry B* **2003**, *107*(3), 668-677.

140. Chikkaraddy, R.; de Nijs, B.; Benz, F.; Barrow, S. J.; Scherman, O. A.; Rosta, E.; Demetriadou, A.; Fox, P.; Hess, O.; Baumberg, J. J., Single-Molecule Strong Coupling at Room Temperature in Plasmonic Nanocavities. *Nature* **2016**, *535*, 127-130.

141. Prodan, E.; Radloff, C.; Halas, N. J.; Nordlander, P., A Hybridization Model for the Plasmon Response of Complex Nanostructures. *Science* **2003**, *302*(5644), 419-422.

142. Wang, H.; Brandl, D. W.; Nordlander, P.; Halas, N. J., Plasmonic Nanostructures: Artificial Molecules. *Accounts of Chemical Research* **2007**, *40*(1), 53-62.

143. Enoch, S.; Bonod, N., *Plasmonics: From Basics to Advanced Topics*. Springer: 2012.

144. Liz-Marzan, L. M., Tailoring Surface Plasmons through the Morphology and Assembly of Metal Nanoparticles. *Langmuir* **2006**, *22*(1), 32-41.

145. Wu, Y. Y.; Li, G. L.; Camden, J. P., Probing Nanoparticle Plasmons with Electron Energy Loss Spectroscopy. *Chemical Reviews* **2018**, *118*(6), 2994-3031.

146. Brodusch, N.; Demers, H.; Gellé, A.; Moores, A.; Gauvin, R., Electron Energy-Loss Spectroscopy (Eels) with a Cold-Field Emission Scanning Electron Microscope at Low Accelerating Voltage in Transmission Mode. *Ultramicroscopy* **2018**, *203*, 21-36.

147. Nelayah, J.; Kociak, M.; Stéphan, O.; de Abajo, F. J. G.; Tencé, M.; Henrard, L.; Taverna, D.; Pastoriza-Santos, I.; Liz-Marzán, L. M.; Colliex, C., Mapping Surface Plasmons on a Single Metallic Nanoparticle. *Nature Physics* **2007**, *3*(5), 348-353.

148. Faraday, M., On the Color of Colloidal Gold. *Phil. Trans. R. Soc. London* **1857**, *147*, 145-181.

149. Daniel, M.-C.; Astruc, D., Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology. *Chemical reviews* **2004**, *104*(1), 293-346.

150. Rycenga, M.; Cobley, C. M.; Zeng, J.; Li, W.; Moran, C. H.; Zhang, Q.; Qin, D.; Xia, Y., Controlling the Synthesis and Assembly of Silver Nanostructures for Plasmonic Applications. *Chemical reviews* **2011**, *111*(6), 3669-3712.

151. Thanh, N. T. K.; Maclean, N.; Mahiddine, S., Mechanisms of Nucleation and Growth of Nanoparticles in Solution. *Chemical Reviews* **2014**, *114*(15), 7610-7630.

152. Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E., Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angewandte Chemie International Edition* **2009**, *48*(1), 60-103.

153. LaMer, V. K.; Dinegar, R. H., Theory, Production and Mechanism of Formation of Monodispersed Hydrosols. *Journal of the American Chemical Society* **1950**, *72*(11), 4847-4854.

154. Kang, H.; Buchman, J. T.; Rodriguez, R. S.; Ring, H. L.; He, J.; Bantz, K. C.; Haynes, C. L., Stabilization of Silver and Gold Nanoparticles: Preservation and Improvement of Plasmonic Functionalities. *Chemical Reviews* **2019**, *119*(1), 664-699.

155. Lee, P.; Meisel, D., Adsorption and Surface-Enhanced Raman of Dyes on Silver and Gold Sols. *The Journal of Physical Chemistry* **1982**, *86*(17), 3391-3395.

156. Henglein, A.; Giersig, M., Formation of Colloidal Silver Nanoparticles: Capping Action of Citrate. *The Journal of Physical Chemistry B***1999**, *103*(44), 9533-9539.

157. Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A., Chemistry and Properties of Nanocrystals of Different Shapes. *Chemical Reviews* **2005**, *105*(4), 1025-1102.

158. Turkevich, J.; Stevenson, P. C.; Hillier, J., A Study of the Nucleation and Growth Processes in the Synthesis of Colloidal Gold. *Discussions of the Faraday Society* **1951**, *11* (0), 55-75.

159. Frens, G., Controlled Nucleation for the Regulation of the Particle Size in Monodisperse Gold Suspensions. *Nature physical science* **1973**, *241*(105), 20-22.

160. Mayer, K. M.; Hafner, J. H., Localized Surface Plasmon Resonance Sensors. *Chemical Reviews* **2011**, *111*(6), 3828-3857.

161. Turner, A. P. F., Biosensors: Sense and Sensibility. *Chemical Society Reviews* **2013**, *42* (8), 3184-3196.

162. Gellé, A.; Moores, A., Plasmonic Nanoparticles: Photocatalysts with a Bright Future. *Current Opinion in Green and Sustainable Chemistry* **2019**, *15*, 60-66.

163. Sun, Y.; Xia, Y., Shape-Controlled Synthesis of Gold and Silver Nanoparticles. *Science* **2002**, *298* (5601), 2176-2179.

164. Zhou, J.; An, J.; Tang, B.; Xu, S.; Cao, Y.; Zhao, B.; Xu, W.; Chang, J.; Lombardi, J. R., Growth of Tetrahedral Silver Nanocrystals in Aqueous Solution and Their Sers Enhancement. *Langmuir* **2008**, *24*(18), 10407-10413.

165. Ditlbacher, H.; Hohenau, A.; Wagner, D.; Kreibig, U.; Rogers, M.; Hofer, F.; Aussenegg, F. R.; Krenn, J. R., Silver Nanowires as Surface Plasmon Resonators. *Physical review letters* **2005**, *95*(25), 257403.

166. Chen, S.; Carroll, D. L., Synthesis and Characterization of Truncated Triangular Silver Nanoplates. *Nano Letters* **2002**, *2*(9), 1003-1007.

167. Pietrobon, B.; Kitaev, V., Photochemical Synthesis of Monodisperse Size-Controlled Silver Decahedral Nanoparticles and Their Remarkable Optical Properties. *Chemistry of Materials* **2008**, *20*(16), 5186-5190.

168. Liu, X.; Huang, R.; Zhu, J., Functional Faceted Silver Nano-Hexapods: Synthesis, Structure Characterizations, and Optical Properties. *Chemistry of Materials* **2008**, *20*(1), 192-197.

169. Wiley, B.; Herricks, T.; Sun, Y.; Xia, Y., Polyol Synthesis of Silver Nanoparticles: Use of Chloride and Oxygen to Promote the Formation of Single-Crystal, Truncated Cubes and Tetrahedrons. *Nano Letters* **2004**, *4*(9), 1733-1739.

170. Wiley, B. J.; Xiong, Y.; Li, Z.-Y.; Yin, Y.; Xia, Y., Right Bipyramids of Silver: A New Shape Derived from Single Twinned Seeds. *Nano letters* **2006**, *6*(4), 765-768.

171. Wiley, B. J.; Chen, Y.; McLellan, J. M.; Xiong, Y.; Li, Z.-Y.; Ginger, D.; Xia, Y., Synthesis and Optical Properties of Silver Nanobars and Nanorice. *Nano letters* **2007**, *7*(4), 1032-1036.

172. Wiley, B.; Sun, Y.; Xia, Y., Synthesis of Silver Nanostructures with Controlled Shapes and Properties. *Accounts of chemical research* **2007**, *40*(10), 1067-1076.

173. Skrabalak, S. E.; Wiley, B. J.; Kim, M.; Formo, E. V.; Xia, Y., On the Polyol Synthesis of Silver Nanostructures: Glycolaldehyde as a Reducing Agent. *Nano letters* **2008**, *8*(7), 2077-2081.

174. Im, S. H.; Lee, Y. T.; Wiley, B.; Xia, Y. N., Large-Scale Synthesis of Silver Nanocubes: The Role of Hcl in Promoting Cube Perfection and Monodispersity. *Angewandte Chemie-International Edition* **2005**, *44*(14), 2154-2157.

175. Al-Saidi, W. A.; Feng, H. J.; Fichthorn, K. A., Adsorption of Polyvinylpyrrolidone on Ag Surfaces: Insight into a Structure-Directing Agent. *Nano Letters* **2012**, *12*(2), 997-1001. 176. Saidi, W. A.; Feng, H. J.; Fichthorn, K. A., Binding of Polyvinylpyrrolidone to Ag Surfaces: Insight into a Structure-Directing Agent from Dispersion-Corrected Density Functional Theory. *Journal of Physical Chemistry C***2013**, *117*(2), 1163-1171. 177. Sun, Y.; Yin, Y.; Mayers, B. T.; Herricks, T.; Xia, Y., Uniform Silver Nanowires Synthesis by Reducing Agno3 with Ethylene Glycol in the Presence of Seeds and Poly(Vinyl Pyrrolidone). *Chemistry of Materials* **2002**, *14*(11), 4736-4745.

178. Ghosh, S.; Manna, L., The Many "Facets" of Halide Ions in the Chemistry of Colloidal Inorganic Nanocrystals. *Chemical reviews* **2018**, *118*(16), 7804-7864.

179. Chen, Z.; Balankura, T.; Fichthorn, K. A.; Rioux, R. M., Revisiting the Polyol Synthesis of Silver Nanostructures: Role of Chloride in Nanocube Formation. *ACS Nano* **2019**, *13*(2), 1849-1860.

180. Cobley, C. M.; Rycenga, M.; Zhou, F.; Li, Z.-Y.; Xia, Y., Controlled Etching as a Route to High Quality Silver Nanospheres for Optical Studies. *The Journal of Physical Chemistry C***2009**, *113*(39), 16975-16982.

181. Jin, R.; Cao, Y. C.; Hao, E.; Métraux, G. S.; Schatz, G. C.; Mirkin, C. A., Controlling Anisotropic Nanoparticle Growth through Plasmon Excitation. *Nature* **2003**, *425* (6957), 487-490.

182. Haynes, C. L.; Van Duyne, R. P., Nanosphere Lithography: A Versatile Nanofabrication Tool for Studies of Size-Dependent Nanoparticle Optics. *The Journal of Physical Chemistry* **B2001**, *105*(24), 5599-5611.

183. Kim, F.; Connor, S.; Song, H.; Kuykendall, T.; Yang, P., Platonic Gold Nanocrystals. *Angewandte Chemie International Edition* **2004**, *43*(28), 3673-3677.

184. Li, C.; Shuford, K. L.; Park, Q.-H.; Cai, W.; Li, Y.; Lee, E. J.; Cho, S. O., High-Yield Synthesis of Single-Crystalline Gold Nano-Octahedra. *Angewandte Chemie International Edition* **2007**, *46* (18), 3264-3268.

185. Seo, D.; Park, J. C.; Song, H., Polyhedral Gold Nanocrystals with Oh Symmetry: From Octahedra to Cubes. *Journal of the American Chemical Society* **2006**, *128* (46), 14863-14870.

186. Seo, D.; Yoo, C. I.; Park, J. C.; Park, S. M.; Ryu, S.; Song, H., Directed Surface Overgrowth and Morphology Control of Polyhedral Gold Nanocrystals. *Angewandte Chemie* **2008**, *120*(4), 775-779.

187. Magano, J.; Dunetz, J. R., Large-Scale Carbonyl Reductions in the Pharmaceutical Industry. *Organic Process Research & Development* **2012**, *16*(6), 1156-1184.

188. Evans, W. L.; Day, J. E., The Oxidation of Ethyl Alcohol by Means of Potassium Permanganate. *Journal of the American Chemical Society* **1916**, *38*(2), 375-381.

189. Lee, D. G.; Spitzer, U. A., Aqueous Dichromate Oxidation of Primary Alcohols. *The Journal of Organic Chemistry* **1970**, *35*(10), 3589-3590.

190. Travis, B. R.; Sivakumar, M.; Hollist, G. O.; Borhan, B., Facile Oxidation of Aldehydes to Acids and Esters with Oxone. *Organic Letters* **2003**, *5*(7), 1031-1034.

191. Han, L.; Xing, P.; Jiang, B., Selective Aerobic Oxidation of Alcohols to Aldehydes, Carboxylic Acids, and Imines Catalyzed by a Ag-Nhc Complex. *Organic Letters* **2014**, *16* (13), 3428-3431.

192. González-Arellano, C.; Campelo, J. M.; Macquarrie, D. J.; Marinas, J. M.; Romero, A. A.; Luque, R., Efficient Microwave Oxidation of Alcohols Using Low-Loaded Supported Metallic Iron Nanoparticles. *ChemSusChem* **2008**, *1* (8-9), 746-750.

193. Mallat, T.; Baiker, A., Oxidation of Alcohols with Molecular Oxygen on Solid Catalysts. *Chemical Reviews* **2004**, *104*(6), 3037-3058.

194. Roduner, E.; Kaim, W.; Sarkar, B.; Urlacher, V. B.; Pleiss, J.; Gläser, R.; Einicke, W.-D.; Sprenger, G. A.; Beifuß, U.; Klemm, E.; Liebner, C.; Hieronymus, H.; Hsu, S.-F.; Plietker, B.; Laschat, S., Selective Catalytic Oxidation of C H Bonds with Molecular Oxygen. *ChemCatChem* **2013**, *5*(1), 82-112.

195. Huang, Y.-F.; Zhang, M.; Zhao, L.-B.; Feng, J.-M.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q., Activation of Oxygen on Gold and Silver Nanoparticles Assisted by Surface Plasmon Resonances. *Angewandte Chemie International Edition* **2014**, *53*(9), 2353-2357.

196. Rodríguez-González, V.; Zanella, R.; del Angel, G.; Gómez, R., Mtbe Visible-Light Photocatalytic Decomposition over Au/Tio2 and Au/Tio2-Al2o3 Sol-Gel Prepared Catalysts. *Journal of Molecular Catalysis A: Chemical* **2008**, *281*(1), 93-98.

197. Li, H.; Bian, Z.; Zhu, J.; Huo, Y.; Li, H.; Lu, Y., Mesoporous Au/Tio2 Nanocomposites with Enhanced Photocatalytic Activity. *Journal of the American Chemical Society* **2007**, *129*(15), 4538-4539.

198. Kowalska, E.; Abe, R.; Ohtani, B., Visible Light-Induced Photocatalytic Reaction of Gold-Modified Titanium(Iv) Oxide Particles: Action Spectrum Analysis. *Chemical Communications* **2009**, (2), 241-243.

199. Kowalska, E.; Mahaney, O. O. P.; Abe, R.; Ohtani, B., Visible-Light-Induced Photocatalysis through Surface Plasmon Excitation of Gold on Titania Surfaces. *Physical Chemistry Chemical Physics* **2010**, *12*(10), 2344-2355.

200. Naya, S.-i.; Inoue, A.; Tada, H., Self-Assembled Heterosupramolecular Visible Light Photocatalyst Consisting of Gold Nanoparticle-Loaded Titanium(Iv) Dioxide and Surfactant. *Journal of the American Chemical Society* **2010**, *132*(18), 6292-6293.

201. Tsukamoto, D.; Shiraishi, Y.; Sugano, Y.; Ichikawa, S.; Tanaka, S.; Hirai, T., Gold Nanoparticles Located at the Interface of Anatase/Rutile Tio2 Particles as Active Plasmonic Photocatalysts for Aerobic Oxidation. *Journal of the American Chemical Society* **2012**, *134* (14), 6309-6315.

202. Tanaka, A.; Hashimoto, K.; Kominami, H., Selective Photocatalytic Oxidation of Aromatic Alcohols to Aldehydes in an Aqueous Suspension of Gold Nanoparticles Supported on Cerium(Iv) Oxide under Irradiation of Green Light. *Chemical Communications* **2011**, *47*(37), 10446-10448.

203. Tanaka, A.; Hashimoto, K.; Kominami, H., Preparation of Au/Ceo2 Exhibiting Strong Surface Plasmon Resonance Effective for Selective or Chemoselective Oxidation of Alcohols to Aldehydes or Ketones in Aqueous Suspensions under Irradiation by Green Light. *Journal of the American Chemical Society* **2012**, *134*(35), 14526-14533.

204. Zhai, W.; Xue, S.; Zhu, A.; Luo, Y.; Tian, Y., Plasmon-Driven Selective Oxidation of Aromatic Alcohols to Aldehydes in Water with Recyclable Pt/Tio2 Nanocomposites. *ChemCatChem* **2011**, *3*(1), 127-130.

205. Liu, L.; Ouyang, S.; Ye, J., Gold-Nanorod-Photosensitized Titanium Dioxide with Wide-Range Visible-Light Harvesting Based on Localized Surface Plasmon Resonance. *Angewandte Chemie* **2013**, *125* (26), 6821-6825.

206. Nadeem, M. A.; Idriss, H., Photo-Thermal Reactions of Ethanol over Ag/Tio2 Catalysts. The Role of Silver Plasmon Resonance in the Reaction Kinetics. *Chemical Communications* **2018**, *54*(41), 5197-5200.

207. Hallett-Tapley, G. L.; Silvero, M. J.; González-Béjar, M.; Grenier, M.; Netto-Ferreira, J. C.; Scaiano, J. C., Plasmon-Mediated Catalytic Oxidation of Sec-Phenethyl and Benzyl Alcohols. *The Journal of Physical Chemistry* **C2011**, *115*(21), 10784-10790.

208. Hallett-Tapley, G. L.; Silvero, M. J.; Bueno-Alejo, C. J.; González-Béjar, M.; McTiernan, C. D.; Grenier, M.; Netto-Ferreira, J. C.; Scaiano, J. C., Supported Gold Nanoparticles as Efficient Catalysts in the Solventless Plasmon Mediated Oxidation of Sec-Phenethyl and Benzyl Alcohol. *The Journal of Physical Chemistry C***2013**, *117*(23), 12279-12288.

209. Landry, M. J.; Gellé, A.; Meng, B. Y.; Barrett, C. J.; Moores, A., Surface-Plasmon-Mediated Hydrogenation of Carbonyls Catalyzed by Silver Nanocubes under Visible Light. *ACS Catalysis* **2017**, *7*(9), 6128-6133.

210. Sugano, Y.; Shiraishi, Y.; Tsukamoto, D.; Ichikawa, S.; Tanaka, S.; Hirai, T., Supported Au–Cu Bimetallic Alloy Nanoparticles: An Aerobic Oxidation Catalyst with Regenerable Activity by Visible-Light Irradiation. *Angewandte Chemie* **2013**, *125* (20), 5403-5407.

211. Jiang, T.; Jia, C.; Zhang, L.; He, S.; Sang, Y.; Li, H.; Li, Y.; Xu, X.; Liu, H., Gold and Gold– Palladium Alloy Nanoparticles on Heterostructured Tio2 Nanobelts as Plasmonic Photocatalysts for Benzyl Alcohol Oxidation. *Nanoscale* **2015**, *7*(1), 209-217.

212. Sarina, S.; Zhu, H.; Jaatinen, E.; Xiao, Q.; Liu, H.; Jia, J.; Chen, C.; Zhao, J., Enhancing Catalytic Performance of Palladium in Gold and Palladium Alloy Nanoparticles for Organic Synthesis Reactions through Visible Light Irradiation at Ambient Temperatures. *Journal of the American Chemical Society* **2013**, *135*(15), 5793-5801.

213. Huang, X.; Li, Y.; Chen, Y.; Zhou, H.; Duan, X.; Huang, Y., Plasmonic and Catalytic Aupd Nanowheels for the Efficient Conversion of Light into Chemical Energy. *Angewandte Chemie* **2013**, *125* (23), 6179-6183.

214. Colmenares, J. C.; Lisowski, P.; Łomot, D.; Chernyayeva, O.; Lisovytskiy, D., Sonophotodeposition of Bimetallic Photocatalysts Pd–Au/Tio2: Application to Selective Oxidation of Methanol to Methyl Formate. *ChemSusChem* **2015**, *8*(10), 1676-1685.

215. Long, R.; Mao, K.; Gong, M.; Zhou, S.; Hu, J.; Zhi, M.; You, Y.; Bai, S.; Jiang, J.; Zhang, Q.; Wu, X.; Xiong, Y., Tunable Oxygen Activation for Catalytic Organic Oxidation: Schottky Junction Versus Plasmonic Effects. *Angewandte Chemie International Edition* **2014**, *53* (12), 3205-3209.

216. Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F., Improved Utilisation of Renewable Resources: New Important Derivatives of Glycerol. *Green Chemistry* **2008**, *10* (1), 13-30.

217. Schünemann, S.; Dodekatos, G.; Tüysüz, H., Mesoporous Silica Supported Au and Aucu Nanoparticles for Surface Plasmon Driven Glycerol Oxidation. *Chemistry of Materials* **2015**, *27*(22), 7743-7750.

218. Dodekatos, G.; Tüysüz, H., Plasmonic Au/Tio2 Nanostructures for Glycerol Oxidation. *Catalysis Science & Technology* **2016**, *6*(19), 7307-7315.

219. Guo, L.; Sun, Q.; Marcus, K.; Hao, Y.; Deng, J.; Bi, K.; Yang, Y., Photocatalytic Glycerol Oxidation on Auxcu–Cus@Tio2 Plasmonic Heterostructures. *Journal of Materials Chemistry A* **2018**, *6* (44), 22005-22012.

220. Chehadi, Z.; Girardon, J.-S.; Capron, M.; Dumeignil, F.; Jradi, S., Thermoplasmonic-Induced Energy-Efficient Catalytic Oxidation of Glycerol over Gold Supported Catalysts Using Visible Light at Ambient Temperature. *Applied Catalysis A: General* **2019**, *572*, 9-14. 221. Rasmussen, M.; Serov, A.; Artyushkova, K.; Chen, D.; Rose, T. C.; Atanassov, P.; Harris, J. M.; Minteer, S. D., Enhancement of Electrocatalytic Oxidation of Glycerol by Plasmonics. *ChemElectroChem* **2019**, *6*(1), 241-245.

222. Peng, T.; Miao, J.; Gao, Z.; Zhang, L.; Gao, Y.; Fan, C.; Li, D., Reactivating Catalytic Surface: Insights into the Role of Hot Holes in Plasmonic Catalysis. *Small* **2018**, *14* (12), 1703510.

223. Zhang, L.; Jia, C.; He, S.; Zhu, Y.; Wang, Y.; Zhao, Z.; Gao, X.; Zhang, X.; Sang, Y.; Zhang, D.; Xu, X.; Liu, H., Hot Hole Enhanced Synergistic Catalytic Oxidation on Pt-Cu Alloy Clusters. *Advanced Science* **2017**, *4*(6), 1600448.

224. Boltersdorf, J.; Forcherio, G. T.; McClure, J. P.; Baker, D. R.; Leff, A. C.; Lundgren, C., Visible Light-Promoted Plasmon Resonance to Induce "Hot" Hole Transfer and Photothermal Conversion for Catalytic Oxidation. *The Journal of Physical Chemistry C* **2018**, *122*(50), 28934-28948.

225. Li, H.; Qin, F.; Yang, Z.; Cui, X.; Wang, J.; Zhang, L., New Reaction Pathway Induced by Plasmon for Selective Benzyl Alcohol Oxidation on Biocl Possessing Oxygen Vacancies. *Journal of the American Chemical Society* **2017**, *139*(9), 3513-3521.

226. Lee, S.-H.; Jo, J.-S.; Park, J. H.; Lee, S. W.; Jang, J.-W., A Hot-Electron-Triggered Catalytic Oxidation Reaction of Plasmonic Silver Nanoparticles Evidenced by Surface Potential Mapping. *Journal of Materials Chemistry A* **2018**, *6*(42), 20939-20946.

227. Xu, H.; Song, P.; Yan, B.; Wang, J.; Guo, J.; Du, Y., Surface-Plasmon-Enhanced Photo-Electrocatalytic Ethylene Glycol Oxidation Based on Highly Open Auag Nanobowls. *ACS Sustainable Chemistry & Engineering* **2018**, *6*(3), 4138-4146.

228. Xu, H.; Song, P.; Fernandez, C.; Wang, J.; Shiraishi, Y.; Wang, C.; Du, Y., Surface Plasmon Enhanced Ethylene Glycol Electrooxidation Based on Hollow Platinum-Silver Nanodendrites Structures. *Journal of the Taiwan Institute of Chemical Engineers* **2018**, *91*, 316-322.

229. Wang, M.; Wang, P.; Li, C.; Li, H.; Jin, Y., Boosting Electrocatalytic Oxygen Evolution Performance of Ultrathin Co/Ni-Mof Nanosheets Via Plasmon-Induced Hot Carriers. *ACS Applied Materials & Interfaces* **2018**, *10*(43), 37095-37102.

230. Plotkin, J. S. Beyond the Ethylene Steam Cracker. <u>https://www.acs.org/content/acs/en/pressroom/cutting-edge-chemistry/beyond-the-</u>ethylene-steam-cracker.html (accessed February 27, 2019).

231. Jones, T. E.; Wyrwich, R.; Böcklein, S.; Carbonio, E. A.; Greiner, M. T.; Klyushin, A. Y.; Moritz, W.; Locatelli, A.; Menteş, T. O.; Niño, M. A.; Knop-Gericke, A.; Schlögl, R.; Günther, S.; Wintterlin, J.; Piccinin, S., The Selective Species in Ethylene Epoxidation on Silver. *ACS Catalysis* **2018**, *8*(5), 3844-3852.

232. Institute, G. C. Ethylene Oxide Production. https://hub.globalccsinstitute.com/publications/ccs-roadmap-industry-high-purity-co2-

<u>sources-sectoral-assessment-%E2%80%93-final-draft-report-2</u> (accessed February 27, 2019).

233. Ozbek, M. O.; Onal, I.; van Santen, R. A., Why Silver Is the Unique Catalyst for Ethylene Epoxidation. *Journal of Catalysis* **2011**, *284*(2), 230-235.

234. Christopher, P.; Xin, H.; Linic, S., Visible-Light-Enhanced Catalytic Oxidation Reactions on Plasmonic Silver Nanostructures. *Nature chemistry* **2011**, *3*(6), 467-472.

235. Marimuthu, A.; Zhang, J.; Linic, S., Tuning Selectivity in Propylene Epoxidation by Plasmon Mediated Photo-Switching of Cu Oxidation State. *Science* **2013**, *339* (6127), 1590-1593.

236. Zhang, X.; Kumari, G.; Heo, J.; Jain, P. K., In situ Formation of Catalytically Active Graphene in Ethylene Photo-Epoxidation. *Nature Communications* **2018**, *9*(1), 3056.

237. Mori, K.; Kawashima, M.; Che, M.; Yamashita, H., Enhancement of the Photoinduced Oxidation Activity of a Ruthenium(Ii) Complex Anchored on Silica-Coated Silver Nanoparticles by Localized Surface Plasmon Resonance. *Angew. Chem.* **2010**, *122* (46), 8780-8783.

238. Ide, Y.; Matsuoka, M.; Ogawa, M., Efficient Visible-Light-Induced Photocatalytic Activity on Gold-Nanoparticle-Supported Layered Titanate. *Journal of the American Chemical Society* **2010**, *132*(47), 16762-16764.

239. Wee, T.-L.; Schmidt, L. C.; Scaiano, J. C., Photooxidation of 9-Anthraldehyde Catalyzed by Gold Nanoparticles: Solution and Single Nanoparticle Studies Using Fluorescence Lifetime Imaging. *The Journal of Physical Chemistry C* **2012**, *116* (45), 24373-24379.

240. Zheng, Z.; Huang, B.; Qin, X.; Zhang, X.; Dai, Y.; Whangbo, M.-H., Facile in Situ Synthesis of Visible-Light Plasmonic Photocatalysts M@Tio2 (M = Au, Pt, Ag) and Evaluation of Their Photocatalytic Oxidation of Benzene to Phenol. *Journal of Materials Chemistry* **2011**, *21*(25), 9079-9087.

241. Xiao, Y.; Liu, J.; Mai, J.; Pan, C.; Cai, X.; Fang, Y., High-Performance Silver Nanoparticles Coupled with Monolayer Hydrated Tungsten Oxide Nanosheets: The Structural Effects in Photocatalytic Oxidation of Cyclohexane. *Journal of Colloid and Interface Science* **2018**, *516*, 172-181.

242. Egli, R.; Peter, A.; Freeman, H., *Colour Chemistry: The Design and Synthesis of Organic Dyes and Pigments*. Springer: 1991.

243. Murahashi, S.-I., Synthetic Aspects of Metal-Catalyzed Oxidations of Amines and Related Reactions. *Angewandte Chemie International Edition in English* **1995**, *34* (22), 2443-2465.

244. Nicolaou, K. C.; Mathison, C. J. N.; Montagnon, T., New Reactions of Ibx: Oxidation of Nitrogen- and Sulfur-Containing Substrates to Afford Useful Synthetic Intermediates. *Angewandte Chemie International Edition* **2003**, *42*(34), 4077-4082.

245. Naya, S.-i.; Kimura, K.; Tada, H., One-Step Selective Aerobic Oxidation of Amines to Imines by Gold Nanoparticle-Loaded Rutile Titanium(Iv) Oxide Plasmon Photocatalyst. *ACS Catalysis* **2013**, *3*(1), 10-13.

246. Sato, Y.; Naya, S.-i.; Tada, H., A New Bimetallic Plasmonic Photocatalyst Consisting of Gold(Core)-Copper(Shell) Nanoparticle and Titanium(Iv) Oxide Support. *APL Materials* **2015**, *3*(10), 104502.

247. Zhai, Z.-Y.; Guo, X.-N.; Jin, G.-Q.; Guo, X.-Y., Visible Light-Induced Selective Photocatalytic Aerobic Oxidation of Amines into Imines on Cu/Graphene. *Catalysis Science & Technology* **2015**, *5* (8), 4202-4207.

248. Wang, J.; Ando, R. A.; Camargo, P. H. C., Controlling the Selectivity of the Surface Plasmon Resonance Mediated Oxidation of P-Aminothiophenol on Au Nanoparticles by Charge Transfer from Uv-Excited Tio2. *Angewandte Chemie* **2015**, *127*(23), 7013-7016.

249. da Silva, A. G. M.; Rodrigues, T. S.; Correia, V. G.; Alves, T. V.; Alves, R. S.; Ando, R. A.; Ornellas, F. R.; Wang, J.; Andrade, L. H.; Camargo, P. H. C., Plasmonic Nanorattles as Next-Generation Catalysts for Surface Plasmon Resonance-Mediated Oxidations Promoted by Activated Oxygen. *Angewandte Chemie International Edition* **2016**, *55* (25), 7111-7115.

250. Zhu, K.; Wang, C.; Camargo, P. H. C.; Wang, J., Investigating the Effect of Mno2 Band Gap in Hybrid Mno2–Au Materials over the Spr-Mediated Activities under Visible Light. *Journal of Materials Chemistry A* **2019**, *7*(3), 925-931.

251. Zhao, L.-B.; Liu, X.-X.; Zhang, M.; Liu, Z.-F.; Wu, D.-Y.; Tian, Z.-Q., Surface Plasmon Catalytic Aerobic Oxidation of Aromatic Amines in Metal/Molecule/Metal Junctions. *The Journal of Physical Chemistry C*2016, *120*(2), 944-955.

252. Wang, J.; Alves, T. V.; Trindade, F. J.; de Aquino, C. B.; Pieretti, J. C.; Domingues, S. H.; Ando, R. A.; Ornellas, F. R.; Camargo, P. H. C., Theoretical Design and Experimental Realization of Quasi Single Electron Enhancement in Plasmonic Catalysis. *Angewandte Chemie* **2015**, *127*(48), 14635-14639.

253. Woodham, A. P.; Meijer, G.; Fielicke, A., Activation of Molecular Oxygen by Anionic Gold Clusters. *Angewandte Chemie International Edition* **2012**, *51*(18), 4444-4447.

254. Lin, W.; Cao, E.; Zhang, L.; Xu, X.; Song, Y.; Liang, W.; Sun, M., Electrically Enhanced Hot Hole Driven Oxidation Catalysis at the Interface of a Plasmon-Exciton Hybrid. *Nanoscale* **2018**, *10*(12), 5482-5488.

255. Novello, P.; Varanasi, C. V.; Liu, J., Effects of Light on Catalytic Activities and Lifetime of Plasmonic Au Catalysts in the Co Oxidation Reaction. *ACS Catalysis* **2019**, *9*(1), 578-586.

256. An, N.; Li, S.; Duchesne, P. N.; Wu, P.; Zhang, W.; Lee, J.-F.; Cheng, S.; Zhang, P.; Jia, M.; Zhang, W., Size Effects of Platinum Colloid Particles on the Structure and Co Oxidation Properties of Supported Pt/Fe2o3 Catalysts. *The Journal of Physical Chemistry C* **2013**, *117*(41), 21254-21262.

257. Bamwenda, G. R.; Tsubota, S.; Nakamura, T.; Haruta, M., The Influence of the Preparation Methods on the Catalytic Activity of Platinum and Gold Supported on Tio2 for Co Oxidation. *Catalysis Letters* **1997**, *44*(1), 83-87.

258. Jia, C.-J.; Liu, Y.; Bongard, H.; Schüth, F., Very Low Temperature Co Oxidation over Colloidally Deposited Gold Nanoparticles on Mg(Oh)2 and Mgo. *Journal of the American Chemical Society* **2010**, *132*(5), 1520-1522.

259. Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N., Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature Far Below 0 °C. *Chemistry Letters* **1987**, *16*(2), 405-408.

260. Lee, S. W.; Lee, C.; Goddeti, K. C.; Kim, S. M.; Park, J. Y., Surface Plasmon-Driven Catalytic Reactions on a Patterned Co3o4/Au Inverse Catalyst. *RSC Advances* **2017**, *7*(88), 56073-56080.

261. Kim, S. M.; Lee, C.; Goddeti, K. C.; Park, J. Y., Hot Plasmonic Electron-Driven Catalytic Reactions on Patterned Metal-Insulator-Metal Nanostructures. *Nanoscale* **2017**, *9*(32), 11667-11677.

262. Lee, S. W.; Hong, J. W.; Lee, H.; Wi, D. H.; Kim, S. M.; Han, S. W.; Park, J. Y., The Surface Plasmon-Induced Hot Carrier Effect on the Catalytic Activity of Co Oxidation on a Cu2o/Hexoctahedral Au Inverse Catalyst. *Nanoscale* **2018**, *10*(23), 10835-10843.

263. Kim, S. M.; Lee, S. J.; Kim, S. H.; Kwon, S.; Yee, K. J.; Song, H.; Somorjai, G. A.; Park, J. Y., Hot Carrier-Driven Catalytic Reactions on Pt–Cdse–Pt Nanodumbbells and Pt/Gan under Light Irradiation. *Nano Letters* **2013**, *13*(3), 1352-1358.

264. Park, J. Y.; Baker, L. R.; Somorjai, G. A., Role of Hot Electrons and Metal-Oxide Interfaces in Surface Chemistry and Catalytic Reactions. *Chemical Reviews* **2015**, *115*(8), 2781-2817.

265. Zhang, Y.; Li, Q.; Liu, C.; Shan, X.; Chen, X.; Dai, W.; Fu, X., The Promoted Effect of a Metal-Organic Frameworks (Zif-8) on Au/Tio2 for Co Oxidation at Room Temperature Both in Dark and under Visible Light Irradiation. *Applied Catalysis B: Environmental* **2018**, *224*, 283-294.

266. Swearer, D. F.; Zhao, H. Q.; Zhou, L. N.; Zhang, C.; Robatjazi, H.; Martirez, J. M. P.; Krauter, C. M.; Yazdi, S.; McClain, M. J.; Ringe, E.; Carter, E. A.; Nordlander, P.; Halas, N. J., Heterometallic Antenna-Reactor Complexes for Photocatalysis. *Proceedings of the National Academy of Sciences of the United States of America* **2016**, *113*(32), 8916-8920. 267. Zhang, C.; Zhao, H.; Zhou, L.; Schlather, A. E.; Dong, L.; McClain, M. J.; Swearer, D.

F.; Nordlander, P.; Halas, N. J., Al-Pd Nanodisk Heterodimers as Antenna-Reactor Photocatalysts. *Nano Lett.* **2016**, *16*(10), 6677-6682.

268. Spata, V. A.; Carter, E. A., Mechanistic Insights into Photocatalyzed Hydrogen Desorption from Palladium Surfaces Assisted by Localized Surface Plasmon Resonances. *ACS nano* **2018**, *12*(4), 3512-3522.

269. Quiroz, J.; Barbosa, E. C.; Araujo, T. P.; Fiorio, J. L.; Wang, Y.-C.; Zou, Y.-C.; Mou, T.; Alves, T. V.; de Oliveira, D. C.; Wang, B.; Haigh, S.; Rossi, L.; Camargo, P. H., Controlling Reaction Selectivity over Hybrid Plasmonic Nanocatalysts. *Nano Letters* **2018**, *18* (11), 7289-7297.

270. Schnepf, M. J.; Mayer, M.; Kuttner, C.; Tebbe, M.; Wolf, D.; Dulle, M.; Altantzis, T.; Formanek, P.; Förster, S.; Bals, S.; König, T. A. F.; Fery, A., Nanorattles with Tailored Electric Field Enhancement. *Nanoscale* **2017**, *9*(27), 9376-9385.

271. Zhao, X. Y.; Long, R.; Liu, D.; Luo, B. B.; Xiong, Y. J., Pd-Ag Alloy Nanocages: Integration of Ag Plasmonic Properties with Pd Active Sites for Light-Driven Catalytic Hydrogenation. *Journal of Materials Chemistry A* **2015**, *3*(18), 9390-9394.

272. Gangishetty, M. K.; Fontes, A. M.; Malta, M.; Kelly, T. L.; Scott, R. W. J., Improving the Rates of Pd-Catalyzed Reactions by Exciting the Surface Plasmons of Aupd Bimetallic Nanotriangles. *RSC Advances* **2017**, *7*(64), 40218-40226.

273. Hao, C.-H.; Guo, X.-N.; Pan, Y.-T.; Chen, S.; Jiao, Z.-F.; Yang, H.; Guo, X.-Y., Visible-Light-Driven Selective Photocatalytic Hydrogenation of Cinnamaldehyde over Au/Sic Catalysts. *Journal of the American Chemical Society* **2016**, *138* (30), 9361-9364.

274. Li, A. Y.; Gellé, A.; Segalla, A.; Moores, A., Silver Nanoparticles in Organic Transformations. In *Silver Catalysis in Organic Synthesis*, Li, C. J., Bi, Xihe., Ed. Wiley: 2019. 275. Mukherjee, S.; Zhou, L.; Goodman, A. M.; Large, N.; Ayala-Orozco, C.; Zhang, Y.; Nordlander, P.; Halas, N. J., Hot-Electron-Induced Dissociation of H2 on Gold Nanoparticles Supported on Sio2. *Journal of the American Chemical Society* **2014**, *136*(1), 64-67.

276. Zhou, L.; Zhang, C.; McClain, M. J.; Manavacas, A.; Krauter, C. M.; Tian, S.; Berg, F.; Everitt, H. O.; Carter, E. A.; Nordlander, P.; Halas, N. J., Aluminum Nanocrystals as a Plasmonic Photocatalyst for Hydrogen Dissociation. *Nano Letters* **2016**, *16* (2), 1478-1484.

277. Pradhan, N.; Pal, A.; Pal, T., Catalytic Reduction of Aromatic Nitro Compounds by Coinage Metal Nanoparticles. *Langmuir* **2001**, *17*(5), 1800-1802.

278. Wu, X.-Q.; Wu, X.-W.; Huang, Q.; Shen, J.-S.; Zhang, H.-W., In Situ Synthesized Gold Nanoparticles in Hydrogels for Catalytic Reduction of Nitroaromatic Compounds. *Applied Surface Science* **2015**, *331*, 210-218.

279. Shah, D.; Kaur, H., Resin-Trapped Gold Nanoparticles: An Efficient Catalyst for Reduction of Nitro Compounds and Suzuki-Miyaura Coupling. *Journal of Molecular Catalysis A: Chemical* **2014**, *381*, 70-76.

280. Cui, Q.; Xia, B.; Mitzscherling, S.; Masic, A.; Li, L.; Bargheer, M.; Möhwald, H., Preparation of Gold Nanostars and Their Study in Selective Catalytic Reactions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2015**, *465*, 20-25.

281. Mori, K.; Verma, P.; Hayashi, R.; Fuku, K.; Yamashita, H., Color-Controlled Ag Nanoparticles and Nanorods within Confined Mesopores: Microwave-Assisted Rapid Synthesis and Application in Plasmonic Catalysis under Visible-Light Irradiation. *Chemistry–A European Journal* **2015**, *21* (33), 11885-11893.

282. Pradhan, N.; Pal, A.; Pal, T., Silver Nanoparticle Catalyzed Reduction of Aromatic Nitro Compounds. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2002**, *196* (2-3), 247-257.

283. Vadakkekara, R.; Chakraborty, M.; Parikh, P. A., Reduction of Aromatic Nitro Compounds on Colloidal Hollow Silver Nanospheres. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2012**, *399*, 11-17.

284. Hajfathalian, M.; Gilroy, K. D.; Yaghoubzade, A.; Sundar, A.; Tan, T.; Hughes, R. A.; Neretina, S., Photocatalytic Enhancements to the Reduction of 4-Nitrophenol by Resonantly Excited Triangular Gold-Copper Nanostructures. *The Journal of Physical Chemistry* **C2015**, *119*(30), 17308-17315.

285. He, R.; Wang, Y.-C.; Wang, X.; Wang, Z.; Liu, G.; Zhou, W.; Wen, L.; Li, Q.; Wang, X.; Chen, X.; Zeng, J.; Hou, J. G., Facile Synthesis of Pentacle Gold–Copper Alloy Nanocrystals and Their Plasmonic and Catalytic Properties. *Nature Communications* **2014**, *5*, 4327.

286. Haldar, K. K.; Kundu, S.; Patra, A., Core-Size-Dependent Catalytic Properties of Bimetallic Au/Ag Core-Shell Nanoparticles. *ACS applied materials & interfaces* **2014**, *6* (24), 21946-21953.

287. Wu, W.; Lei, M.; Yang, S.; Zhou, L.; Liu, L.; Xiao, X.; Jiang, C.; Roy, V. A., A One-Pot Route to the Synthesis of Alloyed Cu/Ag Bimetallic Nanoparticles with Different Mass Ratios for Catalytic Reduction of 4-Nitrophenol. *Journal of Materials Chemistry A* **2015**, *3* (7), 3450-3455.

288. Xiao, Q.; Sarina, S.; Waclawik, E. R.; Jia, J.; Chang, J.; Riches, J. D.; Wu, H.; Zheng, Z.; Zhu, H., Alloying Gold with Copper Makes for a Highly Selective Visible-Light Photocatalyst for the Reduction of Nitroaromatics to Anilines. *ACS Catalysis* **2016**, *6* (3), 1744-1753.

289. Vysakh, A.; Babu, C. L.; Vinod, C., Demonstration of Synergistic Catalysis in Au@ Ni Bimetallic Core–Shell Nanostructures. *The Journal of Physical Chemistry* **C2015**, *119*(15), 8138-8146.

290. Essner, J. B.; Laber, C. H.; Baker, G. A., Carbon Dot Reduced Bimetallic Nanoparticles: Size and Surface Plasmon Resonance Tunability for Enhanced Catalytic Applications. *Journal of Materials Chemistry A* **2015**, *3*(31), 16354-16360.

291. Shin, K. S.; Cho, Y. K.; Choi, J.-Y.; Kim, K., Facile Synthesis of Silver-Deposited Silanized Magnetite Nanoparticles and Their Application for Catalytic Reduction of Nitrophenols. *Applied Catalysis A: General* **2012**, *413-414*, 170-175.

292. Zhu, H.; Ke, X.; Yang, X.; Sarina, S.; Liu, H., Reduction of Nitroaromatic Compounds on Supported Gold Nanoparticles by Visible and Ultraviolet Light. *Angewandte Chemie* **2010**, *122*(50), 9851-9855.

293. Wu, Y.; Zhang, T.; Zheng, Z.; Ding, X.; Peng, Y., A Facile Approach to Fe3o4@Au Nanoparticles with Magnetic Recyclable Catalytic Properties. *Materials Research Bulletin* **2010**, *45*(4), 513-517.

294. Barbosa, E. C. M.; Fiorio, J. L.; Mou, T.; Wang, B.; Rossi, L. M.; Camargo, P. H. C., Reaction Pathway Dependence in Plasmonic Catalysis: Hydrogenation as a Model Molecular Transformation. *Chemistry – A European Journal* **2018**, *24*(47), 12330-12339.

295. Naya, S.-i.; Niwa, T.; Kume, T.; Tada, H., Visible-Light-Induced Electron Transport from Small to Large Nanoparticles in Bimodal Gold Nanoparticle-Loaded Titanium(Iv) Oxide. *Angewandte Chemie International Edition* **2014**, *53*(28), 7305-7309.

296. Ding, Q.; Chen, M.; Fang, Y.; Zhang, Z.; Sun, M., Plasmon-Driven Diazo Coupling Reactions of P-Nitroaniline Via –Nh2 or –No2 in Atmosphere Environment. *The Journal of Physical Chemistry* C**2017**, *121*(9), 5225-5231.

297. Zhao, L.-B.; Zhang, M.; Huang, Y.-F.; Williams, C. T.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q., Theoretical Study of Plasmon-Enhanced Surface Catalytic Coupling Reactions of Aromatic Amines and Nitro Compounds. *The Journal of Physical Chemistry Letters* **2014**, *5*(7), 1259-1266.

298. Liu, Z.; Huang, Y.; Xiao, Q.; Zhu, H., Selective Reduction of Nitroaromatics to Azoxy Compounds on Supported Ag–Cu Alloy Nanoparticles through Visible Light Irradiation. *Green Chemistry* **2016**, *18*(3), 817-825.

299. Guo, X.; Hao, C.; Jin, G.; Zhu, H.-Y.; Guo, X.-Y., Copper Nanoparticles on Graphene Support: An Efficient Photocatalyst for Coupling of Nitroaromatics in Visible Light. *Angewandte Chemie International Edition* **2014**, *53*(7), 1973-1977.

300. Huang, Y.-F.; Zhu, H.-P.; Liu, G.-K.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q., When the Signal Is Not from the Original Molecule to Be Detected: Chemical Transformation of Para-Aminothiophenol on Ag During the Sers Measurement. *Journal of the American Chemical Society* **2010**, *132*(27), 9244-9246.

301. Ren, X.; Cao, E.; Lin, W.; Song, Y.; Liang, W.; Wang, J., Recent Advances in Surface Plasmon-Driven Catalytic Reactions. *RSC Advances* **2017**, *7*(50), 31189-31203.

302. Bailo, E.; Deckert, V., Tip-Enhanced Raman Scattering. *Chemical Society Reviews* **2008**, *37*(5), 921-930.

303. Hartman, T.; Wondergem, C. S.; Kumar, N.; van den Berg, A.; Weckhuysen, B. M., Surface-and Tip-Enhanced Raman Spectroscopy in Catalysis. *The journal of physical chemistry letters* **2016**, *7*(8), 1570-1584.

304. Kundu, S.; Mandal, M.; Ghosh, S. K.; Pal, T., Photochemical Deposition of Sers Active Silver Nanoparticles on Silica Gel and Their Application as Catalysts for the Reduction of

Aromatic Nitro Compounds. *Journal of colloid and interface science* **2004**, *272*(1), 134-144.

305. Xie, W.; Walkenfort, B.; Schlücker, S., Label-Free Sers Monitoring of Chemical Reactions Catalyzed by Small Gold Nanoparticles Using 3d Plasmonic Superstructures. *Journal of the American Chemical Society* **2012**, *135*(5), 1657-1660.

306. Ren, X.; Tan, E.; Lang, X.; You, T.; Jiang, L.; Zhang, H.; Yin, P.; Guo, L., Observing Reduction of 4-Nitrobenzenthiol on Gold Nanoparticles in Situ Using Surface-Enhanced Raman Spectroscopy. *Physical Chemistry Chemical Physics* **2013**, *15* (34), 14196-14201.

307. Zhang, Z.; Kinzel, D.; Deckert, V., Photo-Induced or Plasmon-Induced Reaction: Investigation of the Light-Induced Azo-Coupling of Amino Groups. *The Journal of Physical Chemistry* **C2016**, *120*(37), 20978-20983.

308. Cho, F.-H.; Kuo, S.-C.; Lai, Y.-H., Surface-Plasmon-Induced Azo Coupling Reaction between Nitro Compounds on Dendritic Silver Monitored by Surface-Enhanced Raman Spectroscopy. *RSC Advances* **2017**, *7*(17), 10259-10265.

309. Huang, Y.-F.; Wu, D.-Y.; Zhu, H.-P.; Zhao, L.-B.; Liu, G.-K.; Ren, B.; Tian, Z.-Q., Surface-Enhanced Raman Spectroscopic Study of P-Aminothiophenol. *Physical Chemistry Chemical Physics* **2012**, *14*(24), 8485-8497.

310. Tamao, K.; Sumitani, K.; Kumada, M., Selective Carbon-Carbon Bond Formation by Cross-Coupling of Grignard Reagents with Organic Halides. Catalysis by Nickel-Phosphine Complexes. *Journal of the American Chemical Society* **1972**, *94*(12), 4374-4376.

311. Lundgren, R. J.; Stradiotto, M., Addressing Challenges in Palladium-Catalyzed Cross-Coupling Reactions through Ligand Design. *Chemistry – A European Journal* **2012**, *18*(32), 9758-9769.

312. Mpungose, P.; Vundla, Z.; Maguire, G.; Friedrich, H., The Current Status of Heterogeneous Palladium Catalysed Heck and Suzuki Cross-Coupling Reactions. *Molecules* **2018**, *23*(7), 1676-1699.

313. Hussain, I.; Capricho, J.; Yawer, M. A., Synthesis of Biaryls Via Ligand-Free Suzuki-Miyaura Cross-Coupling Reactions: A Review of Homogeneous and Heterogeneous Catalytic Developments. *Advanced Synthesis & Catalysis* **2016**, *358* (21), 3320-3349.

314. Lakshminarayana, B.; Mahendar, L.; Ghosal, P.; Satyanarayana, G.; Subrahmanyam, C., Nano-Sized Recyclable Pdo Supported Carbon Nanostructures for Heck Reaction: Influence of Carbon Materials. *Chemistryselect* **2017**, *2*(9), 2700-2707.

315. Gu, Q.; Jia, Q.; Long, J.; Gao, Z., Heterogeneous Photocatalyzed C–C Cross-Coupling Reactions under Visible-Light and near-Infrared Light Irradiation. *ChemCatChem* **2019**, *11* (2), 669-683.

316. González-Béjar, M.; Peters, K.; Hallett-Tapley, G. L.; Grenier, M.; Scaiano, J. C., Rapid One-Pot Propargylamine Synthesis by Plasmon Mediated Catalysis with Gold Nanoparticles on Zno under Ambient Conditions. *Chemical Communications* **2013**, *49*(17), 1732-1734.

317. Dos Santos, C. G.; Marquez, D. T.; Crites, C.-O. L.; Netto-Ferreira, J. C.; Scaiano, J. C., Plasmon Heating Mediated Friedel-Crafts Alkylation of Anisole Using Supported Aunp@Nb2o5 Catalysts. *Tetrahedron Letters* **2017**, *58*(5), 427-431.
318. Yu, S.; Wilson, A. J.; Heo, J.; Jain, P. K., Plasmonic Control of Multi-Electron Transfer and C–C Coupling in Visible-Light-Driven Co2 Reduction on Au Nanoparticles. *Nano letters* **2018**, *18*(4), 2189-2194.

319. Hopkinson, M. N.; Sahoo, B.; Li, J.-L.; Glorius, F., Dual Catalysis Sees the Light: Combining Photoredox with Organo-, Acid, and Transition-Metal Catalysis. *Chemistry – A European Journal* **2014**, *20*(14), 3874-3886.

320. Liu, Q.; Dong, X.; Li, J.; Xiao, J.; Dong, Y.; Liu, H., Recent Advances on Palladium Radical Involved Reactions. *ACS Catalysis* **2015**, *5*(10), 6111-6137.

321. Wu, X.; Jaatinen, E.; Sarina, S.; Zhu, H. Y., Direct Photocatalysis of Supported Metal Nanostructures for Organic Synthesis. *Journal of Physics D: Applied Physics* **2017**, *50*(28), 283001.

322. Xiao, Q.; Sarina, S.; Jaatinen, E.; Jia, J.; Arnold, D. P.; Liu, H.; Zhu, H., Efficient Photocatalytic Suzuki Cross-Coupling Reactions on Au–Pd Alloy Nanoparticles under Visible Light Irradiation. *Green Chemistry* **2014**, *16*(9), 4272-4285.

323. Eremin, D. B.; Ananikov, V. P., Understanding Active Species in Catalytic Transformations: From Molecular Catalysis to Nanoparticles, Leaching, "Cocktails" of Catalysts and Dynamic Systems. *Coordination Chemistry Reviews* **2017**, *346*, 2-19.

324. Thathagar, M. B.; ten Elshof, J. E.; Rothenberg, G., Pd Nanoclusters in C C Coupling Reactions: Proof of Leaching. *Angewandte Chemie International Edition* **2006**, *45* (18), 2886-2890.

325. MacQuarrie, S.; Horton, J. H.; Barnes, J.; McEleney, K.; Loock, H.-P.; Crudden, C. M., Visual Observation of Redistribution and Dissolution of Palladium During the Suzuki-Miyaura Reaction. *Angewandte Chemie International Edition* **2008**, *47*(17), 3279-3282.

326. Verkaaik, M.; Grote, R.; Meulendijks, N.; Sastre, F.; Weckhuysen, B. M.; Buskens, P., Suzuki-Miyaura Cross-Coupling Using Plasmonic Pd-Decorated Au Nanorods as Catalyst: A Study on the Contribution of Laser Illumination. *ChemCatChem* **2019**, *11*, 1-8.

327. Wang, F.; Li, C.; Chen, H.; Jiang, R.; Sun, L.-D.; Li, Q.; Wang, J.; Yu, J. C.; Yan, C.-H., Plasmonic Harvesting of Light Energy for Suzuki Coupling Reactions. *Journal of the American Chemical Society* **2013**, *135*(15), 5588-5601.

328. Zhang, S.; Chang, C.; Huang, Z.; Ma, Y.; Gao, W.; Li, J.; Qu, Y., Visible-Light-Activated Suzuki-Miyaura Coupling Reactions of Aryl Chlorides over the Multifunctional Pd/Au/Porous Nanorods of Ceo2 Catalysts. *ACS Catalysis* **2015**, *5* (11), 6481-6488.

329. Wen, M.; Takakura, S.; Fuku, K.; Mori, K.; Yamashita, H., Enhancement of Pd-Catalyzed Suzuki-Miyaura Coupling Reaction Assisted by Localized Surface Plasmon Resonance of Au Nanorods. *Catalysis Today* **2015**, *242*, 381-385.

330. Han, D.; Bao, Z.; Xing, H.; Yang, Y.; Ren, Q.; Zhang, Z., Fabrication of Plasmonic Au-Pd Alloy Nanoparticles for Photocatalytic Suzuki-Miyaura Reactions under Ambient Conditions. *Nanoscale* **2017**, *9*(18), 6026-6032.

331. Zhu, X.; Jia, H.; Zhu, X.-M.; Cheng, S.; Zhuo, X.; Qin, F.; Yang, Z.; Wang, J., Selective Pd Deposition on Au Nanobipyramids and Pd Site-Dependent Plasmonic Photocatalytic Activity. *Advanced Functional Materials* **2017**, *27*(22), 1700016.

332. Su, G.; Jiang, H.; Zhu, H.; Lv, J.-J.; Yang, G.; Yan, B.; Zhu, J.-J., Controlled Deposition of Palladium Nanodendrites on the Tips of Gold Nanorods and Their Enhanced Catalytic Activity. *Nanoscale* **2017**, *9*(34), 12494-12502.

333. Nemygina, N. A.; Nikoshvili, L. Z.; Tiamina, I. Y.; Bykov, A. V.; Smirnov, I. S.; LaGrange, T.; Kaszkur, Z.; Matveeva, V. G.; Sulman, E. M.; Kiwi-Minsker, L., Au Core-Pd Shell Bimetallic Nanoparticles Immobilized within Hyper-Cross-Linked Polystyrene for Mechanistic Study of Suzuki Cross-Coupling: Homogeneous or Heterogeneous Catalysis? *Organic Process Research & Development* **2018**, *22*(12), 1606-1613.

334. Kozuch, S.; Shaik, S., A Combined Kinetic–Quantum Mechanical Model for Assessment of Catalytic Cycles: Application to Cross-Coupling and Heck Reactions. *Journal of the American Chemical Society* **2006**, *128*(10), 3355-3365.

335. Guo, J.; Zhang, Y.; Shi, L.; Zhu, Y.; Mideksa, M. F.; Hou, K.; Zhao, W.; Wang, D.; Zhao, M.; Zhang, X.; Lv, J.; Zhang, J.; Wang, X.; Tang, Z., Boosting Hot Electrons in Hetero-Superstructures for Plasmon-Enhanced Catalysis. *Journal of the American Chemical Society* **2017**, *139*(49), 17964-17972.

336. Verma, P.; Kuwahara, Y.; Mori, K.; Yamashita, H., Pd/Ag and Pd/Au Bimetallic Nanocatalysts on Mesoporous Silica for Plasmon-Mediated Enhanced Catalytic Activity under Visible Light Irradiation. *Journal of Materials Chemistry A* **2016**, *4* (26), 10142-10150.

337. Trinh, T. T.; Sato, R.; Sakamoto, M.; Fujiyoshi, Y.; Haruta, M.; Kurata, H.; Teranishi, T., Visible to near-Infrared Plasmon-Enhanced Catalytic Activity of Pd Hexagonal Nanoplates for the Suzuki Coupling Reaction. *Nanoscale* **2015**, *7*(29), 12435-12444.

338. Sharma, K.; Kumar, M.; Bhalla, V., Aggregates of the Pentacenequinone Derivative as Reactors for the Preparation of Ag@Cu2o Core-Shell Nps: An Active Photocatalyst for Suzuki and Suzuki Type Coupling Reactions. *Chemical Communications* **2015**, *51* (63), 12529-12532.

339. Xiao, Q.; Sarina, S.; Bo, A.; Jia, J.; Liu, H.; Arnold, D. P.; Huang, Y.; Wu, H.; Zhu, H., Visible Light-Driven Cross-Coupling Reactions at Lower Temperatures Using a Photocatalyst of Palladium and Gold Alloy Nanoparticles. *ACS Catalysis* **2014**, *4*(6), 1725-1734.

340. Guo, X.-W.; Hao, C.-H.; Wang, C.-Y.; Sarina, S.; Guo, X.-N.; Guo, X.-Y., Visible Light-Driven Photocatalytic Heck Reaction over Carbon Nanocoil Supported Pd Nanoparticles. *Catalysis Science & Technology* **2016**, *6* (21), 7738-7743.

341. Lanterna, A. E.; Elhage, A.; Scaiano, J. C., Heterogeneous Photocatalytic C-C Coupling: Mechanism of Plasmon-Mediated Reductive Dimerization of Benzyl Bromides by Supported Gold Nanoparticles. *Catalysis Science & Technology* **2015**, *5*(9), 4336-4340.

342. Pineda, A.; Gomez, L.; Balu, A. M.; Sebastian, V.; Ojeda, M.; Arruebo, M.; Romero, A. A.; Santamaria, J.; Luque, R., Laser-Driven Heterogeneous Catalysis: Efficient Amide Formation Catalysed by Au/Sio2 Systems. *Green Chemistry* **2013**, *15*(8), 2043-2049.

343. Wei, C. M.; Li, C. J., A Highly Efficient Three-Component Coupling of Aldehyde, Alkyne, and Amines Via C - H Activation Catalyzed by Gold in Water. *Journal of the American Chemical Society* **2003**, *125* (32), 9584-9585.

344. Gu, J.; Yan, Y.; Krizan, J. W.; Gibson, Q. D.; Detweiler, Z. M.; Cava, R. J.; Bocarsly, A.

B., P-Type Curho2 as a Self-Healing Photoelectrode for Water Reduction under Visible

Light. Journal of the American Chemical Society **2014**, *136*(3), 830-833.

345. Cartlidge, E., Saving for a Rainy Day. American Association for the Advancement of Science: 2011.

346. Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S., Solar Water Splitting Cells. *Chemical reviews* **2010**, *110*(11), 6446-6473.

347. Fechete, I.; Wang, Y.; Védrine, J. C., The Past, Present and Future of Heterogeneous Catalysis. *Catalysis Today* **2012**, *189*(1), 2-27.

348. Dholam, R.; Patel, N.; Adami, M.; Miotello, A., Hydrogen Production by Photocatalytic Water-Splitting Using Cr-or Fe-Doped Tio2 Composite Thin Films Photocatalyst. *International Journal of Hydrogen Energy* **2009**, *34*(13), 5337-5346.

349. Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y., Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides. *science* **2001**, *293* (5528), 269-271.

350. Youngblood, W. J.; Lee, S.-H. A.; Maeda, K.; Mallouk, T. E., Visible Light Water Splitting Using Dye-Sensitized Oxide Semiconductors. *Accounts of chemical research* **2009**, *42*(12), 1966-1973.

351. Momeni, M. M.; Ghayeb, Y., Photoelectrochemical Water Splitting on Chromium-Doped Titanium Dioxide Nanotube Photoanodes Prepared by Single-Step Anodizing. *Journal of Alloys and Compounds* **2015**, *637*, 393-400.

352. Chen, X.; Mao, S. S., Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chemical reviews* **2007**, *107*(7), 2891-2959.

353. Chen, J.-J.; Wu, J. C.; Wu, P. C.; Tsai, D. P., Plasmonic Photocatalyst for H2 Evolution in Photocatalytic Water Splitting. *The Journal of Physical Chemistry C***2011**, *115*(1), 210-216.

354. Hartland, G. V., Optical Studies of Dynamics in Noble Metal Nanostructures. *Chemical Reviews* **2011**, *111*(6), 3858-3887.

355. Warren, S. C.; Thimsen, E., Plasmonic Solar Water Splitting. *Energy & Environmental Science* **2012**, *5*(1), 5133-5146.

356. Chen, H. M.; Chen, C. K.; Liu, R.-S.; Zhang, L.; Zhang, J.; Wilkinson, D. P., Nano-Architecture and Material Designs for Water Splitting Photoelectrodes. *Chemical Society Reviews* **2012**, *41*(17), 5654-5671.

357. Baffou, G.; Quidant, R., Nanoplasmonics for Chemistry. *Chemical Society Reviews* **2014**, *43*(11), 3898-3907.

358. Chen, X.; Liu, L.; Huang, F., Black Titanium Dioxide (Tio2) Nanomaterials. *Chemical Society Reviews* **2015**, *44*(7), 1861-1885.

359. Gratzel, M., Photoelectrochemical Cells. *Nature* **2001**, *414* (6861), 338-345.

360. Linic, S.; Aslam, U.; Boerigter, C.; Morabito, M., Photochemical Transformations on Plasmonic Metal Nanoparticles. *Nature materials* **2015**, *14*(6), 567-576.

361. Jain, P. K.; Huang, X.; El-Sayed, I. H.; El-Sayed, M. A., Review of Some Interesting Surface Plasmon Resonance-Enhanced Properties of Noble Metal Nanoparticles and Their Applications to Biosystems. *Plasmonics* **2007**, *2*(3), 107-118.

362. Linic, S.; Christopher, P.; Ingram, D. B., Plasmonic-Metal Nanostructures for Efficient Conversion of Solar to Chemical Energy. *Nat. Mater.* **2011**, *10*(12), 911.

363. Long, R.; Li, Y.; Song, L.; Xiong, Y., Coupling Solar Energy into Reactions: Materials Design for Surface Plasmon-Mediated Catalysis. *Small* **2015**, *11* (32), 3873-3889.

364. Halas, N. J.; Lal, S.; Chang, W. S.; Link, S.; Nordlander, P., Plasmons in Strongly Coupled Metallic Nanostructures. *Chemical Reviews* **2011**, *111*(6), 3913-3961.

365. Bai, S.; Yin, W.; Wang, L.; Li, Z.; Xiong, Y., Surface and Interface Design in Cocatalysts for Photocatalytic Water Splitting and Co2 Reduction. *RSC advances* **2016**, *6*(62), 57446-57463.

366. Bai, S.; Jiang, W.; Li, Z.; Xiong, Y., Surface and Interface Engineering in Photocatalysis. *ChemNanoMat* **2015**, *1*(4), 223-239.

367. DuChene, J. S.; Sweeny, B. C.; Johnston-Peck, A. C.; Su, D.; Stach, E. A.; Wei, W. D., Prolonged Hot Electron Dynamics in Plasmonic-Metal/Semiconductor Heterostructures with Implications for Solar Photocatalysis. *Angewandte Chemie International Edition* **2014**, *53*(30), 7887-7891.

368. Tian, Y.; Tatsuma, T., Plasmon-Induced Photoelectrochemistry at Metal Nanoparticles Supported on Nanoporous Tio 2. *Chemical communications* **2004**, (16), 1810-1811.

369. Yu, K.; Tian, Y.; Tatsuma, T., Size Effects of Gold Nanaoparticles on Plasmon-Induced Photocurrents of Gold–Tio 2 Nanocomposites. *Physical Chemistry Chemical Physics* **2006**, *8*(46), 5417-5420.

370. Wang, C. L.; Astruc, D., Nanogold Plasmonic Photocatalysis for Organic Synthesis and Clean Energy Conversion. *Chemical Society Reviews* **2014**, *43*(20), 7188-7216.

371. Lang, X. J.; Chen, X. D.; Zhao, J. C., Heterogeneous Visible Light Photocatalysis for Selective Organic Transformations. *Chemical Society Reviews* **2014**, *43*(1), 473-486.

372. Lee, J.; Mubeen, S.; Ji, X. L.; Stucky, G. D.; Moskovits, M., Plasmonic Photoanodes for Solar Water Splitting with Visible Light. *Nano Letters* **2012**, *12*(9), 5014-5019.

373. Wu, B.; Liu, D.; Mubeen, S.; Chuong, T. T.; Moskovits, M.; Stucky, G. D., Anisotropic Growth of Tio2 onto Gold Nanorods for Plasmon-Enhanced Hydrogen Production from Water Reduction. *Journal of the American Chemical Society* **2016**, *138*(4), 1114-1117.

374. Tanaka, A.; Teramura, K.; Hosokawa, S.; Kominami, H.; Tanaka, T., Visible Light-Induced Water Splitting in an Aqueous Suspension of a Plasmonic Au/Tio 2 Photocatalyst with Metal Co-Catalysts. *Chemical science* **2017**, *8*(4), 2574-2580.

375. Pu, Y.-C.; Wang, G.; Chang, K.-D.; Ling, Y.; Lin, Y.-K.; Fitzmorris, B. C.; Liu, C.-M.; Lu, X.; Tong, Y.; Zhang, J. Z., Au Nanostructure-Decorated Tio2 Nanowires Exhibiting Photoactivity across Entire Uv-Visible Region for Photoelectrochemical Water Splitting. *Nano letters* **2013**, *13*(8), 3817-3823.

376. Takakura, R.; Oshikiri, T.; Ueno, K.; Shi, X.; Kondo, T.; Masuda, H.; Misawa, H., Water Splitting Using a Three-Dimensional Plasmonic Photoanode with Titanium Dioxide Nano-Tunnels. *Green Chemistry* **2017**, *19*(10), 2398-2405.

377. Zhang, Z.; Zhang, L.; Hedhili, M. N.; Zhang, H.; Wang, P., Plasmonic Gold Nanocrystals Coupled with Photonic Crystal Seamlessly on Tio2 Nanotube Photoelectrodes for Efficient Visible Light Photoelectrochemical Water Splitting. *Nano Letters* **2013**, *13*(1), 14-20.

378. Roy, P.; Berger, S.; Schmuki, P., Tio2 Nanotubes: Synthesis and Applications. *Angewandte Chemie International Edition* **2011**, *50*(13), 2904-2939.

379. Wang, H.; You, T.; Shi, W.; Li, J.; Guo, L., Au/Tio2/Au as a Plasmonic Coupling Photocatalyst. *The Journal of Physical Chemistry* C**2012**, *116*(10), 6490-6494.

380. Zhan, Z.; An, J.; Zhang, H.; Hansen, R. V.; Zheng, L., Three-Dimensional Plasmonic Photoanodes Based on Au-Embedded Tio2 Structures for Enhanced Visible-Light Water Splitting. *ACS applied materials & interfaces* **2014**, *6*(2), 1139-1144.

381. Zhang, X.; Liu, Y.; Lee, S.-T.; Yang, S.; Kang, Z., Coupling Surface Plasmon Resonance of Gold Nanoparticles with Slow-Photon-Effect of Tio 2 Photonic Crystals for Synergistically Enhanced Photoelectrochemical Water Splitting. *Energy & Environmental Science* **2014**, *7*(4), 1409-1419.

382. Baba, T., Slow Light in Photonic Crystals. *Nature photonics* **2008**, *2*(8), 465-473.

383. Chen, J. I.; von Freymann, G.; Choi, S. Y.; Kitaev, V.; Ozin, G. A., Amplified Photochemistry with Slow Photons. *Advanced Materials* **2006**, *18*(14), 1915-1919.

384. Peerakiatkhajohn, P.; Butburee, T.; Yun, J.-H.; Chen, H.; Richards, R. M.; Wang, L., A Hybrid Photoelectrode with Plasmonic Au@ Tio 2 Nanoparticles for Enhanced Photoelectrochemical Water Splitting. *Journal of Materials Chemistry A* **2015**, *3* (40), 20127-20133.

385. Valdes, A.; Brillet, J.; Grätzel, M.; Gudmundsdottir, H.; Hansen, H. A.; Jonsson, H.; Klüpfel, P.; Kroes, G.-J.; Le Formal, F.; Man, I. C., Solar Hydrogen Production with Semiconductor Metal Oxides: New Directions in Experiment and Theory. *Physical Chemistry Chemical Physics* **2012**, *14*(1), 49-70.

386. Pany, S.; Naik, B.; Martha, S.; Parida, K., Plasmon Induced Nano Au Particle Decorated over S, N-Modified Tio2 for Exceptional Photocatalytic Hydrogen Evolution under Visible Light. *ACS applied materials & interfaces* **2014**, *6*(2), 839-846.

387. Sathish, M.; Viswanathan, B.; Viswanath, R.; Gopinath, C. S., Synthesis, Characterization, Electronic Structure, and Photocatalytic Activity of Nitrogen-Doped Tio2 Nanocatalyst. *Chemistry of materials* **2005**, *17*(25), 6349-6353.

388. Mubeen, S.; Lee, J.; Singh, N.; Krämer, S.; Stucky, G. D.; Moskovits, M., An Autonomous Photosynthetic Device in Which All Charge Carriers Derive from Surface Plasmons. *Nature nanotechnology* **2013**, *8*(4), 247-251.

389. Christopher, P.; Ingram, D. B.; Linic, S., Enhancing Photochemical Activity of Semiconductor Nanoparticles with Optically Active Ag Nanostructures: Photochemistry Mediated by Ag Surface Plasmons. *The Journal of Physical Chemistry C* **2010**, *114* (19), 9173-9177.

390. Christopher, P.; Linic, S., Shape-and Size-Specific Chemistry of Ag Nanostructures in Catalytic Ethylene Epoxidation. *ChemCatChem* **2010**, *2*(1), 78-83.

391. Ingram, D. B.; Linic, S., Water Splitting on Composite Plasmonic-Metal/Semiconductor Photoelectrodes: Evidence for Selective Plasmon-Induced Formation of Charge Carriers near the Semiconductor Surface. *Journal of the American Chemical Society* **2011**, *133*(14), 5202-5205.

392. Wu, F.; Hu, X.; Fan, J.; Liu, E.; Sun, T.; Kang, L.; Hou, W.; Zhu, C.; Liu, H., Photocatalytic Activity of Ag/Tio 2 Nanotube Arrays Enhanced by Surface Plasmon Resonance and Application in Hydrogen Evolution by Water Splitting. *Plasmonics* **2013**, *8* (2), 501-508.

393. Liu, E.; Kang, L.; Yang, Y.; Sun, T.; Hu, X.; Zhu, C.; Liu, H.; Wang, Q.; Li, X.; Fan, J., Plasmonic Ag Deposited Tio2 Nano-Sheet Film for Enhanced Photocatalytic Hydrogen Production by Water Splitting. *Nanotechnology* **2014**, *25* (16), 165401.

394. Ge, M.-Z.; Cao, C.-Y.; Li, S.-H.; Tang, Y.-X.; Wang, L.-N.; Qi, N.; Huang, J.-Y.; Zhang, K.-Q.; Al-Deyab, S.; Lai, Y.-K., In Situ Plasmonic Ag Nanoparticle Anchored Tio 2 Nanotube Arrays as Visible-Light-Driven Photocatalysts for Enhanced Water Splitting. *Nanoscale* **2016**, *8*(9), 5226-5234.

395. Lian, Z.; Wang, W.; Xiao, S.; Li, X.; Cui, Y.; Zhang, D.; Li, G.; Li, H., Plasmonic Silver Quantum Dots Coupled with Hierarchical Tio 2 Nanotube Arrays Photoelectrodes for Efficient Visible-Light Photoelectrocatalytic Hydrogen Evolution. *Scientific reports* **2015**, *5*(1), 1-10.

396. Chan, G. H.; Zhao, J.; Hicks, E. M.; Schatz, G. C.; Van Duyne, R. P., Plasmonic Properties of Copper Nanoparticles Fabricated by Nanosphere Lithography. *Nano letters* **2007**, *7*(7), 1947-1952.

397. Kum, J. M.; Park, Y. J.; Kim, H. J.; Cho, S. O., Plasmon-Enhanced Photocatalytic Hydrogen Production over Visible-Light Responsive Cu/Tio2. *Nanotechnology* **2015**, *26* (12), 125402.

398. McClellan, P., Manufacture and Uses of Ethylene Oxide and Ethylene Glycol. *Industrial & Engineering Chemistry* **1950**, *42*(12), 2402-2407.

399. Hader, R. N.; Wallace, R.; McKinney, R., Formaldehyde from Methanol. *Industrial & Engineering Chemistry* **1952**, *44*(7), 1508-1518.

400. Wachs, I. E.; Madix, R. J., The Oxidation of Methanol on a Silver (110) Catalyst. *Surface Science* **1978**, *76*(2), 531-558.

401. Medlin, J. W., Understanding and Controlling Reactivity of Unsaturated Oxygenates and Polyols on Metal Catalysts. *Acs Catalysis* **2011**, *1*(10), 1284-1297.

402. Claus, P., Selective Hydrogenation of A, B-Unsaturated Aldehydes and Other C= O and C= C Bonds Containing Compounds. *Topics in Catalysis* **1998**, *5*(1), 51-62.

403. Li, A. Y.; Kaushik, M.; Li, C.-J.; Moores, A., Microwave-Assisted Synthesis of Magnetic Carboxymethyl Cellulose-Embedded Ag-Fe3o4 Nanocatalysts for Selective Carbonyl Hydrogenation. *ACS Sustainable Chemistry & Engineering* **2016**, *4*(3), 965-973.

404. Lacheb, H.; Puzenat, E.; Houas, A.; Ksibi, M.; Elaloui, E.; Guillard, C.; Hermann, J., Photocatalytic Degradation of Various Types of Dyes (Alizarin S, Grocein Orange G, Methyl Red, Congo Red, Methylene Blue) in Water by Uv-Irradiated Titania. *Appl. Catal. B: Environ* **2002**, *39*, 75-90.

405. Wiley, B. J.; Im, S. H.; Li, Z.-Y.; McLellan, J.; Siekkinen, A.; Xia, Y., Maneuvering the Surface Plasmon Resonance of Silver Nanostructures through Shape-Controlled Synthesis. ACS Publications: 2006.

406. Linic, S.; Christopher, P., Overcoming Limitation in the Design of Selective Solid Catalysts by Manipulating Shape and Size of Catalytic Particles: Epoxidation Reactions on Silver. *ChemCatChem* **2010**, *2*(9), 1061-1063.

407. Zhang, X.; Ke, X.; Yao, J., Recent Development of Plasmon-Mediated Photocatalysts and Their Potential in Selectivity Regulation. *Journal of Materials Chemistry A* **2018**, *6*(5), 1941-1966.

408. da Silva, A. G.; Rodrigues, T. S.; Wang, J.; Yamada, L. K.; Alves, T. V.; Ornellas, F. R.; Ando, R. m. A.; Camargo, P. H., The Fault in Their Shapes: Investigating the Surface-Plasmon-Resonance-Mediated Catalytic Activities of Silver Quasi-Spheres, Cubes, Triangular Prisms, and Wires. *Langmuir* **2015**, *31* (37), 10272-10278.

409. Zhang, Q.; Wang, H., Facet-Dependent Catalytic Activities of Au Nanoparticles Enclosed by High-Index Facets. *ACS Catalysis* **2014**, *4*(11), 4027-4033.

410. Heuer-Jungemann, A.; Feliu, N.; Bakaimi, I.; Hamaly, M.; Alkilany, A.; Chakraborty, I.; Masood, A.; Casula, M. F.; Kostopoulou, A.; Oh, E., The Role of Ligands in the Chemical Synthesis and Applications of Inorganic Nanoparticles. *Chemical reviews* **2019**, *119* (8), 4819-4880.

411. Im, S. H.; Lee, Y. T.; Wiley, B.; Xia, Y., Large-Scale Synthesis of Silver Nanocubes: The Role of Hcl in Promoting Cube Perfection and Monodispersity. *Angewandte Chemie International Edition* **2005**, *44*(14), 2154-2157.

412. Kirner, F.; Potapov, P.; Schultz, J.; Geppert, J.; Müller, M.; González-Rubio, G.; Sturm, S.; Lubk, A.; Sturm, E., Additive-Controlled Synthesis of Monodisperse Single Crystalline Gold Nanoparticles: Interplay of Shape and Surface Plasmon Resonance. *Journal of Materials Chemistry C*2020, *8*(31), 10844-10851.

413. Murphy, C. J.; Sau, T. K.; Gole, A. M.; Orendorff, C. J.; Gao, J.; Gou, L.; Hunyadi, S. E.; Li, T., Anisotropic Metal Nanoparticles: Synthesis, Assembly, and Optical Applications. *The Journal of Physical Chemistry* B2005, *109*(29), 13857-13870.

414. Sun, Y.; Mayers, B.; Herricks, T.; Xia, Y., Polyol Synthesis of Uniform Silver Nanowires: A Plausible Growth Mechanism and the Supporting Evidence. *Nano letters* **2003**, *3*(7), 955-960.

415. Xia, X.; Zeng, J.; Oetjen, L. K.; Li, Q.; Xia, Y., Quantitative Analysis of the Role Played by Poly (Vinylpyrrolidone) in Seed-Mediated Growth of Ag Nanocrystals. *Journal of the American Chemical Society* **2012**, *134*(3), 1793-1801.

416. Qi, X.; Balankura, T.; Zhou, Y.; Fichthorn, K. A., How Structure-Directing Agents Control Nanocrystal Shape: Polyvinylpyrrolidone-Mediated Growth of Ag Nanocubes. *Nano letters* **2015**, *15*(11), 7711-7717.

417. Chen, Z.; Chang, J. W.; Balasanthiran, C.; Milner, S. T.; Rioux, R. M., Anisotropic Growth of Silver Nanoparticles Is Kinetically Controlled by Polyvinylpyrrolidone Binding. *Journal of the American Chemical Society* **2019**, *141*(10), 4328-4337.

418. Sangaru, S. S.; Zhu, H.; Rosenfeld, D. C.; Samal, A. K.; Anjum, D.; Basset, J.-M., Surface Composition of Silver Nanocubes and Their Influence on Morphological Stabilization and Catalytic Performance in Ethylene Epoxidation. *ACS applied materials & interfaces* **2015**, *7* (51), 28576-28584.

419. Peng, S.; Okasinski, J. S.; Almer, J. D.; Ren, Y.; Wang, L.; Yang, W.; Sun, Y., Real-Time Probing of the Synthesis of Colloidal Silver Nanocubes with Time-Resolved High-Energy Synchrotron X-Ray Diffraction. *The Journal of Physical Chemistry* **C2012**, *116*(21), 11842-11847.

420. Han, L.; Wang, P.; Zhu, C.; Zhai, Y.; Dong, S., Facile Solvothermal Synthesis of Cube-Like Ag@ Agcl: A Highly Efficient Visible Light Photocatalyst. *Nanoscale* **2011**, *3*(7), 2931-2935.

421. Wang, P.; Huang, B.; Qin, X.; Zhang, X.; Dai, Y.; Wei, J.; Whangbo, M. H., Ag@ Agcl: A Highly Efficient and Stable Photocatalyst Active under Visible Light. *Angewandte Chemie International Edition* **2008**, *47*(41), 7931-7933.

422. Yang, Y.; Zhao, Y.; Yan, Y.; Wang, Y.; Guo, C.; Zhang, J., Preparation of Agcl Nanocubes and Their Application as Efficient Photoinitiators in the Polymerization of N-Isopropylacrylamide. *The Journal of Physical Chemistry* **B2015**, *119*(46), 14807-14813.

423. Nicoletti, O.; de La Peña, F.; Leary, R. K.; Holland, D. J.; Ducati, C.; Midgley, P. A., Three-Dimensional Imaging of Localized Surface Plasmon Resonances of Metal Nanoparticles. *Nature* **2013**, *502*(7469), 80-84.

424. Zhang, K.; Da, B.; Ding, Z., Effect of Asymmetric Morphology on Coupling Surface Plasmon Modes and Generalized Plasmon Ruler. *Ultramicroscopy* **2018**, *185*, 55-64.

425. Landry, M. J.; Gellé, A.; Meng, B. Y.; Barrett, C. J.; Moores, A., Surface-Plasmon-Mediated Hydrogenation of Carbonyls Catalyzed by Silver Nanocubes under Visible Light. *Acs Catalysis* **2017**, *7*(9), 6128-6133.

426. Ley, S. V., On Being Green: Can Flow Chemistry Help? *The Chemical Record* **2012**, *12*(4), 378-390.

427. Deadman, B. J.; Collins, S. G.; Maguire, A. R., Taming Hazardous Chemistry in Flow: The Continuous Processing of Diazo and Diazonium Compounds. *Chemistry–A European Journal* **2015**, *21*(6), 2298-2308.

428. Movsisyan, M.; Delbeke, E.; Berton, J.; Battilocchio, C.; Ley, S.; Stevens, C., Taming Hazardous Chemistry by Continuous Flow Technology. *Chemical Society Reviews* **2016**, *45* (18), 4892-4928.

429. Plutschack, M. B.; Pieber, B. u.; Gilmore, K.; Seeberger, P. H., The Hitchhiker's Guide to Flow Chemistry. *Chemical reviews* **2017**, *117*(18), 11796-11893.

430. Wegner, J.; Ceylan, S.; Kirschning, A., Flow Chemistry–a Key Enabling Technology for (Multistep) Organic Synthesis. *Advanced Synthesis & Catalysis* **2012**, *354*(1), 17-57.

431. Gérardy, R.; Emmanuel, N.; Toupy, T.; Kassin, V. E.; Tshibalonza, N. N.; Schmitz, M.; Monbaliu, J. C. M., Continuous Flow Organic Chemistry: Successes and Pitfalls at the Interface with Current Societal Challenges. *European Journal of Organic Chemistry* **2018**, *2018*(20-21), 2301-2351.

432. Rehm, T. H., Flow Photochemistry as a Tool in Organic Synthesis. *Chemistry (Weinheim an der Bergstrasse, Germany)* **2020**, *26*(71), 16952.

433. Baxendale, I. R., The Integration of Flow Reactors into Synthetic Organic Chemistry. *Journal of Chemical Technology & Biotechnology* **2013**, *88*(4), 519-552.

434. Porta, R.; Benaglia, M.; Puglisi, A., Flow Chemistry: Recent Developments in the Synthesis of Pharmaceutical Products. *Organic Process Research & Development* **2016**, *20* (1), 2-25.

435. Pastre, J. C.; Browne, D. L.; Ley, S. V., Flow Chemistry Syntheses of Natural Products. *Chemical Society Reviews* **2013**, *42*(23), 8849-8869.

436. Bogdan, A. R.; Dombrowski, A. W., Emerging Trends in Flow Chemistry and Applications to the Pharmaceutical Industry. *Journal of medicinal chemistry* **2019**, *62*(14), 6422-6468.

437. Kockmann, N.; Gottsponer, M.; Zimmermann, B.; Roberge, D. M., Enabling Continuous-Flow Chemistry in Microstructured Devices for Pharmaceutical and Fine-Chemical Production. *Chemistry–A European Journal* **2008**, *14*(25), 7470-7477.

438. Vaccaro, L.; Lanari, D.; Marrocchi, A.; Strappaveccia, G., Flow Approaches Towards Sustainability. *Green Chemistry* **2014**, *16*(8), 3680-3704.

439. Sambiagio, C.; Noël, T., Flow Photochemistry: Shine Some Light on Those Tubes! *Trends in Chemistry* **2020**, *2*(2), 92-106.

440. Newman, S. G.; Jensen, K. F., The Role of Flow in Green Chemistry and Engineering. *Green chemistry* **2013**, *15*(6), 1456-1472.

441. Brzozowski, M.; O'Brien, M.; Ley, S. V.; Polyzos, A., Flow Chemistry: Intelligent Processing of Gas-Liquid Transformations Using a Tube-in-Tube Reactor. *Accounts of chemical research* **2015**, *48*(2), 349-362.

442. Ravelli, D.; Dondi, D.; Fagnoni, M.; Albini, A., Photocatalysis. A Multi-Faceted Concept for Green Chemistry. *Chem. Soc. Rev.* **2009**, *38*(7), 1999-2011.

443. Luo, J.; Zhang, S.; Sun, M.; Yang, L.; Luo, S.; Crittenden, J. C., A Critical Review on Energy Conversion and Environmental Remediation of Photocatalysts with Remodeling Crystal Lattice, Surface, and Interface. *ACS Nano* **2019**, *13*(9), 9811-9840.

444. Li, J.; Wu, N., Semiconductor-Based Photocatalysts and Photoelectrochemical Cells for Solar Fuel Generation: A Review. *Catal. Sci. Technol.* **2015**, *5*(3), 1360-1384.

445. McCullagh, C.; Skillen, N.; Adams, M.; Robertson, P. K., Photocatalytic Reactors for Environmental Remediation: A Review. *J. Chem. Technol. Biotechnol.* **2011**, *86* (8), 1002-1017.

446. König, B., Photocatalysis in Organic Synthesis–Past, Present, and Future. *Eur. J. Org. Chem.* **2017**, *2017*(15), 1979-1981.

447. Michelin, C.; Hoffmann, N., Photocatalysis Applied to Organic Synthesis–a Green Chemistry Approach. *Curr. Opin. Green Sustain. Chem.* **2018**, *10*, 40-45.

448. Ong, C. B.; Ng, L. Y.; Mohammad, A. W., A Review of Zno Nanoparticles as Solar Photocatalysts: Synthesis, Mechanisms and Applications. *Renew. Sust. Energy Rev.* **2018**, *81*, 536-551.

449. Wang, X.; Blechert, S.; Antonietti, M., Polymeric Graphitic Carbon Nitride for Heterogeneous Photocatalysis. *ACS Catal.* **2012**, *2*(8), 1596-1606.

450. Cao, S.; Low, J.; Yu, J.; Jaroniec, M., Polymeric Photocatalysts Based on Graphitic Carbon Nitride. *Adv. Mater.* **2015**, *27*(13), 2150-2176.

451. Wang, J.-L.; Wang, C.; Lin, W., Metal–Organic Frameworks for Light Harvesting and Photocatalysis. *ACS Catal.* **2012**, *2*(12), 2630-2640.

452. Wang, J.-L.; Wang, C.; deKrafft, K. E.; Lin, W., Cross-Linked Polymers with Exceptionally High Ru (Bipy) 32+ Loadings for Efficient Heterogeneous Photocatalysis. *ACS Catal.* **2012**, *2*(3), 417-424.

453. Ravelli, D.; Protti, S.; Neri, P.; Fagnoni, M.; Albini, A., Photochemical Technologies Assessed: The Case of Rose Oxide. *Green Chem.* **2011**, *13*(7), 1876-1884.

454. Prier, C. K.; Rankic, D. A.; MacMillan, D. W., Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113*(7), 5322-5363.

455. Twilton, J.; Zhang, P.; Shaw, M. H.; Evans, R. W.; MacMillan, D. W., The Merger of Transition Metal and Photocatalysis. *Nat. Rev. Chem.* **2017**, *1*(7), 1-19.

456. Kuramochi, Y.; Ishitani, O.; Ishida, H., Reaction Mechanisms of Catalytic Photochemical Co2 Reduction Using Re (I) and Ru (Ii) Complexes. *Coord. Chem. Rev.* **2018**, *373*, 333-356.

457. Deponti, E.; Natali, M., Photocatalytic Hydrogen Evolution with Ruthenium Polypyridine Sensitizers: Unveiling the Key Factors to Improve Efficiencies. *Dalton Trans.* **2016**, *45*(22), 9136-9147.

458. Lehn, J.-M.; Ziessel, R., Photochemical Reduction of Carbon Dioxide to Formate Catalyzed by 2, 2t́-Bipyridine-or 1, 10-Phenanthroline-Ruthenium (Ii) Complexes. *J. Organomet. Chem.* **1990**, *382*(1-2), 157-173.

459. Luo, Q.; Mao, R.; Zhu, Y.; Wang, Y., Photoredox-Catalyzed Generation of Sulfamyl Radicals: Sulfonamidation of Enol Silyl Ether with Chlorosulfonamide. *J. Org. Chem.* **2019**, *84*(21), 13897-13907.

460. Sumino, S.; Uno, M.; Fukuyama, T.; Ryu, I.; Matsuura, M.; Yamamoto, A.; Kishikawa, Y., Photoredox-Catalyzed Hydrodifluoroalkylation of Alkenes Using Difluorohaloalkyl Compounds and a Hantzsch Ester. *J. Org. Chem.* **2017**, *82*(10), 5469-5474.

461. Chandrasekhar, D.; Borra, S.; Nanubolu, J. B.; Maurya, R. A., Visible Light Driven Photocascade Catalysis: Ru (Bpy) 3 (Pf6) 2/Tbhp-Mediated Synthesis of Fused B-Carbolines in Batch and Flow Microreactors. *Org. Lett.* **2016**, *18*(12), 2974-2977.

462. Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P. I.; von Zelewsky, A. v., Ru (Ii) Polypyridine Complexes: Photophysics, Photochemistry, Eletrochemistry, and Chemiluminescence. *Coord. Chem. Rev.* **1988**, *84*, 85-277.

463. Cerfontaine, S.; Wehlin, S. A.; Elias, B.; Troian-Gautier, L., Photostable Polynuclear Ruthenium (Ii) Photosensitizers Competent for Dehalogenation Photoredox Catalysis at 590 Nm. *J. Am. Chem. Soc.* **2020**, *142*(12), 5549-5555.

464. Montagnon, T.; Tofi, M.; Vassilikogiannakis, G., Using Singlet Oxygen to Synthesize Polyoxygenated Natural Products from Furans. *Accounts of chemical research* **2008**, *41*(8), 1001-1011.

465. Astruc, D.; Lu, F.; Aranzaes, J. R., Nanoparticles as Recyclable Catalysts: The Frontier between Homogeneous and Heterogeneous Catalysis. *Angew. Chem. Int. Ed.* **2005**, *44*(48), 7852-7872.

466. Tambosco, B.; Segura, K.; Seyrig, C.; Cabrera, D.; Port, M.; Ferroud, C.; Amara, Z., Outer-Sphere Effects in Visible-Light Photochemical Oxidations with Immobilized and Recyclable Ruthenium Bipyridyl Salts. *ACS Catal.* **2018**, *8*(5), 4383-4389.

467. Fabry, D. C.; Ronge, M. A.; Rueping, M., Immobilization and Continuous Recycling of Photoredox Catalysts in Ionic Liquids for Applications in Batch Reactions and Flow Systems: Catalytic Alkene Isomerization by Using Visible Light. *Chemistry – A European Journal* **2015**, *21*(14), 5350-5354.

468. Sheehan, F. Element Scarcity – Euchems Periodic Table. <u>https://www.euchems.eu/euchems-periodic-table/</u> (accessed Feb. 5 2021).

469. Teixeira, R. I.; de Lucas, N. C.; Garden, S. J.; Lanterna, A. E.; Scaiano, J. C., Glass Wool Supported Ruthenium Complexes: Versatile, Recyclable Heterogeneous Photoredox Catalysts. *Catal. Sci. Technol.* **2020**, *10*(5), 1273-1280.

470. Li, J.-F.; Li, C.-Y.; Aroca, R. F., Plasmon-Enhanced Fluorescence Spectroscopy. *Chem. Soc. Rev.* **2017**, *46*(13), 3962-3979.

471. Turner, A. P., Biosensors: Sense and Sensibility. *Chem. Soc. Rev.* **2013**, *42* (8), 3184-3196.

472. Ueno, K.; Oshikiri, T.; Sun, Q.; Shi, X.; Misawa, H., Solid-State Plasmonic Solar Cells. *Chem. Rev.* **2017**, *118*(6), 2955-2993.

473. Li, N.; Zhao, P.; Astruc, D., Anisotropic Gold Nanoparticles: Synthesis, Properties, Applications, and Toxicity. *Angew. Chem. Int. Ed.* **2014**, *53*(7), 1756-1789.

474. Lang, X.; Chen, X.; Zhao, J., Heterogeneous Visible Light Photocatalysis for Selective Organic Transformations. *Chem. Soc. Rev.* **2014**, *43*(1), 473-486.

475. Gellé, A.; Moores, A., Plasmonic Nanoparticles: Photocatalysts with a Bright Future. *Current Opinion in Green and Sustainable Chemistry* **2018**.

476. Gellé, A.; Jin, T.; de la Garza, L.; Price, G. D.; Besteiro, L. V.; Moores, A., Applications of Plasmon-Enhanced Nanocatalysis to Organic Transformations. *Chemical Reviews* **2019**.

477. Scaiano, J. C.; Stamplecoskie, K., Can Surface Plasmon Fields Provide a New Way to Photosensitize Organic Photoreactions? From Designer Nanoparticles to Custom Applications. *J. Phys. Chem. Let.* **2013**, *4*(7), 1177-1187.

478. Giannini, V.; Fernández-Domínguez, A. I.; Heck, S. C.; Maier, S. A., Plasmonic Nanoantennas: Fundamentals and Their Use in Controlling the Radiative Properties of Nanoemitters. *Chem. Rev.* **2011**, *111*(6), 3888-3912.

479. Schuller, J. A.; Barnard, E. S.; Cai, W.; Jun, Y. C.; White, J. S.; Brongersma, M. L., Plasmonics for Extreme Light Concentration and Manipulation. *Nat. Mater.* **2010**, *9*, 193.

480. Barnes, W. L.; Dereux, A.; Ebbesen, T. W., Surface Plasmon Subwavelength Optics. *Nature* **2003**, *424*(6950), 824-830.

481. Kinkhabwala, A.; Yu, Z.; Fan, S.; Avlasevich, Y.; Müllen, K.; Moerner, W., Large Single-Molecule Fluorescence Enhancements Produced by a Bowtie Nanoantenna. *Nat. Photonics* **2009**, *3*(11), 654-657.

482. Wertz, E.; Isaacoff, B. P.; Flynn, J. D.; Biteen, J. S., Single-Molecule Super-Resolution Microscopy Reveals How Light Couples to a Plasmonic Nanoantenna on the Nanometer Scale. *Nano Lett.* **2015**, *15*(4), 2662-2670.

483. Darvill, D.; Centeno, A.; Xie, F., Plasmonic Fluorescence Enhancement by Metal Nanostructures: Shaping the Future of Bionanotechnology. *Phys. Chem. Chem. Phys* **2013**, *15*(38), 15709-15726.

484. Deng, W.; Goldys, E. M., Plasmonic Approach to Enhanced Fluorescence for Applications in Biotechnology and the Life Sciences. *Langmuir* **2012**, *28*(27), 10152-10163. 485. Deng, W.; Xie, F.; Baltar, H. T.; Goldys, E. M., Metal-Enhanced Fluorescence in the Life Sciences: Here, Now and Beyond. *Phys. Chem. Chem. Phys* **2013**, *15* (38), 15695-15708.

486. Anker, J.; Hall, P.; Lyandres, O.; Shah, N.; Zhao, J.; Van Duyne, R., Biosensing with Plasmonic Nanosensors. *Nat. Mater.* **2008**, *7*, 442-453.

487. Willets, K. A.; Van Duyne, R. P., Localized Surface Plasmon Resonance Spectroscopy and Sensing. *Annu. Rev. Phys. Chem.* **2007**, *58*, 267-297.

488. Banholzer, M. J.; Millstone, J. E.; Qin, L.; Mirkin, C. A., Rationally Designed Nanostructures for Surface-Enhanced Raman Spectroscopy. *Chem. Soc. Rev.* **2008**, *37*(5), 885-897.

489. Robatjazi, H.; Zhao, H.; Swearer, D. F.; Hogan, N. J.; Zhou, L.; Alabastri, A.; McClain, M. J.; Nordlander, P.; Halas, N. J., Plasmon-Induced Selective Carbon Dioxide Conversion on Earth-Abundant Aluminum-Cuprous Oxide Antenna-Reactor Nanoparticles. *Nat Commun* **2017**, *8*(1), 27.

490. Li, K.; Hogan, N. J.; Kale, M. J.; Halas, N. J.; Nordlander, P.; Christopher, P., Balancing near-Field Enhancement, Absorption, and Scattering for Effective Antenna-Reactor Plasmonic Photocatalysis. *Nano Lett.* **2017**, *17*(6), 3710-3717.

491. Drexhage, K. H.; Kuhn, H.; Schäfer, F. P., Variation of the Fluorescence Decay Time of a Molecule in Front of a Mirror. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*(2), 329-329.

492. Aslan, K.; Gryczynski, I.; Malicka, J.; Matveeva, E.; Lakowicz, J. R.; Geddes, C. D., Metal-Enhanced Fluorescence: An Emerging Tool in Biotechnology. *Curr. Opin. Biotechnol.* **2005**, *16*(1), 55-62.

493. Lakowicz, J. R., Radiative Decay Engineering: Biophysical and Biomedical Applications. *Anal. Biochem.* **2001**, *298*(1), 1-24.

494. Lakowicz, J. R.; Ray, K.; Chowdhury, M.; Szmacinski, H.; Fu, Y.; Zhang, J.; Nowaczyk, K., Plasmon-Controlled Fluorescence: A New Paradigm in Fluorescence Spectroscopy. *Analyst* **2008**, *133*(10), 1308-1346.

495. Zhang, J.; Fu, Y.; Chowdhury, M. H.; Lakowicz, J. R., Single-Molecule Studies on Fluorescently Labeled Silver Particles: Effects of Particle Size. *J. Phys. Chem. C* **2008**, *112* (1), 18-26.

496. Macia, N.; Kabanov, V.; Heyne, B., Rationalizing the Plasmonic Contributions to the Enhancement of Singlet Oxygen Production. *J. Phys. Chem.* C**2020**, *124*(6), 3768-3777.

497. Macia, N.; Bresoli-Obach, R.; Nonell, S.; Heyne, B., Hybrid Silver Nanocubes for Improved Plasmon-Enhanced Singlet Oxygen Production and Inactivation of Bacteria. *J. Am. Chem. Soc.* **2018**, *141*(1), 684-692.

498. Mendoza, C.; Désert, A.; Chateau, D.; Monnereau, C.; Khrouz, L.; Lerouge, F.; Andraud, C.; Monbaliu, J.-C. M.; Parola, S.; Heinrichs, B., Au Nanobipyramids@ Msio 2 Core-Shell Nanoparticles for Plasmon-Enhanced Singlet Oxygen Photooxygenations in Segmented Flow Microreactors. *Nanoscale Advances* **2020**, *2*(11), 5280-5287.

499. Yin, N.; Liu, Y.; Liu, L.; Lei, J.; Jiang, T.; Wang, H.; Zhu, L.; Xu, X., Fluorescence Enhancement of Ru(Bpy)32+ by Core–Shell Ag@Sio2 Nanocomposites. *J. Alloys Compd.* **2013**, *581*, 6-10.

500. Tovmachenko, O. G.; Graf, C.; van den Heuvel, D. J.; van Blaaderen, A.; Gerritsen, H. C., Fluorescence Enhancement by Metal-Core/Silica-Shell Nanoparticles. *Adv. Mater.* **2006**, *18*(1), 91-95.

501. Cheng, D.; Xu, Q.-H., Separation Distance Dependent Fluorescence Enhancement of Fluorescein Isothiocyanate by Silver Nanoparticles. *Chem. Commun.* **2007**, (3), 248-250.

502. Bardhan, R.; Grady, N. K.; Cole, J. R.; Joshi, A.; Halas, N. J., Fluorescence Enhancement by Au Nanostructures: Nanoshells and Nanorods. *ACS Nano* **2009**, *3* (3), 744-752.

503. An, X.; Stelter, D.; Keyes, T.; Reinhard, B. M., Plasmonic Photocatalysis of Urea Oxidation and Visible-Light Fuel Cells. *Chem* **2019**, *5*(8), 2228-2242.

504. Chen, Y.; Munechika, K.; Ginger, D. S., Dependence of Fluorescence Intensity on the Spectral Overlap between Fluorophores and Plasmon Resonant Single Silver Nanoparticles. *Nano Lett.* **2007**, *7*(3), 690-696.

505. Linic, S.; Chavez, S.; Elias, R., Flow and Extraction of Energy and Charge Carriers in Hybrid Plasmonic Nanostructures. *Nat. Mater.* **2021**, 1-9.

506. Blanchard, V.; Asbai, Z.; Cottet, K.; Boissonnat, G.; Port, M.; Amara, Z., Continuous Flow Photo-Oxidations Using Supported Photocatalysts on Silica. *Org. Proc. Res. Dev.* **2020**, *24*(5), 822-826.

507. Wu, C.; Mosher, B. P.; Lyons, K.; Zeng, T., Reducing Ability and Mechanism for Polyvinylpyrrolidone (Pvp) in Silver Nanoparticles Synthesis. *J. Nanosci. Nanotechnol.* **2010**, *10*(4), 2342-2347.

508. Kobayashi, Y.; Katakami, H.; Mine, E.; Nagao, D.; Konno, M.; Liz-Marzán, L. M., Silica Coating of Silver Nanoparticles Using a Modified Stöber Method. *J. Colloid Interface Sci.* **2005**, *283*(2), 392-396.

509. Matsui, K.; Momose, F., Luminescence Properties of Tris (2, 2 '-Bipyridine) Ruthenium (Ii) in Sol- Gel Systems of Sio2. *Chem. Mater.* **1997**, *9*(11), 2588-2591.

510. Innocenzi, P.; Kozuka, H.; Yoko, T., Fluorescence Properties of the Ru (Bpy) 32+ Complex Incorporated in Sol– Gel-Derived Silica Coating Films. *J. Phys. Chem. B* **1997**, *101* (13), 2285-2291.

511. Macia, N.; Kabanov, V.; Côté-Cyr, M.; Heyne, B., Roles of near and Far Fields in Plasmon-Enhanced Singlet Oxygen Production. *J. Phys. Chem. Let.* **2019**, *10* (13), 3654-3660.

512. Szmacinski, H.; Lakowicz, J. R.; Catchmark, J. M.; Eid, K.; Anderson, J. P.; Middendorf, L., Correlation between Scattering Properties of Silver Particle Arrays and Fluorescence Enhancement. *Appl. Spectrosc.* **2008**, *62*(7), 733-738.

513. Liz-Marzán, L. M., Tailoring Surface Plasmons through the Morphology and Assembly of Metal Nanoparticles. *Langmuir* **2006**, *22*(1), 32-41.

514. Wertz, E. A.; Isaacoff, B. P.; Biteen, J. S., Wavelength-Dependent Super-Resolution Images of Dye Molecules Coupled to Plasmonic Nanotriangles. *ACS Photonics* **2016**, *3*(10), 1733-1740.

515. Abadeer, N. S.; Brennan, M. R.; Wilson, W. L.; Murphy, C. J., Distance and Plasmon Wavelength Dependent Fluorescence of Molecules Bound to Silica-Coated Gold Nanorods. *ACS Nano* **2014**, *8*(8), 8392-8406.

516. Hu, B.; Cao, X.; Nahan, K.; Caruso, J.; Tang, H.; Zhang, P., Surface Plasmon-Photosensitizer Resonance Coupling: An Enhanced Singlet Oxygen Production Platform for Broad-Spectrum Photodynamic Inactivation of Bacteria. *J. Mater. Chem. B***2014**, *2*(40), 7073-7081.

517. Kedem, O.; Wohlleben, W.; Rubinstein, I., Distance-Dependent Fluorescence of Tris (Bipyridine) Ruthenium (Ii) on Supported Plasmonic Gold Nanoparticle Ensembles. *Nanoscale* **2014**, *6* (24), 15134-15143.

518. Terra, J. C.; Desgranges, A.; Monnereau, C.; Sanchez, E. H.; De Toro, J. A.; Amara, Z.; Moores, A., Photocatalysis Meets Magnetism: Designing Magnetically Recoverable Supports for Visible-Light Photocatalysis. *ACS Appl. Mater. Inter.* **2020**, *12* (22), 24895-24904.

519. Banholzer, M. J.; Harris, N.; Millstone, J. E.; Schatz, G. C.; Mirkin, C. A., Abnormally Large Plasmonic Shifts in Silica-Protected Gold Triangular Nanoprisms. *J. Phys. Chem. C* **2010**, *114*(16), 7521-7526.

520. Rodríguez-Fernández, J.; Pastoriza-Santos, I.; Perez-Juste, J.; García de Abajo, F. J.; Liz-Marzan, L. M., The Effect of Silica Coating on the Optical Response of Sub-Micrometer Gold Spheres. *J. Phys. Chem.* C**2007**, *111*(36), 13361-13366.

521. Pastoriza-Santos, I.; Gomez, D.; Pérez-Juste, J.; Liz-Marzán, L. M.; Mulvaney, P., Optical Properties of Metal Nanoparticle Coated Silica Spheres: A Simple Effective Medium Approach. *Phys. Chem. Chem. Phys* **2004**, *6* (21), 5056-5060.

522. Aslam, U.; Chavez, S.; Linic, S., Controlling Energy Flow in Multimetallic Nanostructures for Plasmonic Catalysis. *Nat. Nanotechnol.* **2017**, *12*(10), 1000-1005.

523. Chavez, S.; Rao, V. G.; Linic, S., Unearthing the Factors Governing Site Specific Rates of Electronic Excitations in Multicomponent Plasmonic Systems and Catalysts. *Faraday Discuss.* **2019**, *214*, 441-453.

524. Cole-Hamilton, D. J.; Tooze, R. P., *Catalyst Separation, Recovery and Recycling: Chemistry and Process Design*. Springer Science & Business Media: 2006; Vol. 30.

525. Vankayala, R.; Sagadevan, A.; Vijayaraghavan, P.; Kuo, C.-L.; Hwang, K. C., Metal Nanoparticles Sensitize the Formation of Singlet Oxygen. *Angew. Chem. Int. Ed.* **2011**, *50* (45), 10640-10644.

526. Toftegaard, R.; Arnbjerg, J.; Daasbjerg, K.; Ogilby, P. R.; Dmitriev, A.; Sutherland, D. S.; Poulsen, L., Metal-Enhanced 1270 Nm Singlet Oxygen Phosphorescence. *Angew. Chem. Int. Ed.* **2008**, *47*(32), 6025-6027.

527. Huang, Y. F.; Zhang, M.; Zhao, L. B.; Feng, J. M.; Wu, D. Y.; Ren, B.; Tian, Z. Q., Activation of Oxygen on Gold and Silver Nanoparticles Assisted by Surface Plasmon Resonances. *Angew. Chem. Int. Ed.* **2014**, *53*(9), 2353-2357.

528. Reineck, P.; Gómez, D.; Ng, S. H.; Karg, M.; Bell, T.; Mulvaney, P.; Bach, U., Distance and Wavelength Dependent Quenching of Molecular Fluorescence by Au@ Sio2 Core-Shell Nanoparticles. *ACS Nano* **2013**, *7*(8), 6636-6648.

529. Wu, Y.; Li, G.; Camden, J. P., Probing Nanoparticle Plasmons with Electron Energy Loss Spectroscopy. *Chem. Rev.* **2017**, *118*(6), 2994-3031.

530. Kociak, M.; Stéphan, O., Mapping Plasmons at the Nanometer Scale in an Electron Microscope. *Chem. Soc. Rev.* **2014**, *43*(11), 3865-3883.

531. Brodusch, N.; Demers, H.; Gellé, A.; Moores, A.; Gauvin, R., Electron Energy-Loss Spectroscopy (Eels) with a Cold-Field Emission Scanning Electron Microscope at Low Accelerating Voltage in Transmission Mode. *Ultramicroscopy* **2019**, *203*, 21-36.

532. Bicket, I. C.; Bellido, E. P.; McRae, D. M.; Lagugné-Labarthet, F.; Botton, G. A., Carving Plasmon Modes in Silver Sierpinski Fractals. *ACS Photonics* **2019**, *6*(11), 2974-2984.

533. Wang, W.; Yang, Q.; Fan, F.; Xu, H.; Wang, Z. L., Light Propagation in Curved Silver Nanowire Plasmonic Waveguides. *Nano letters* **2011**, *11*(4), 1603-1608.

534. Koh, A. L.; Bao, K.; Khan, I.; Smith, W. E.; Kothleitner, G.; Nordlander, P.; Maier, S. A.; McComb, D. W., Electron Energy-Loss Spectroscopy (Eels) of Surface Plasmons in Single Silver Nanoparticles and Dimers: Influence of Beam Damage and Mapping of Dark Modes. *ACS Nano* **2009**, *3*(10), 3015-3022.

535. Hohenester, U., Simulating Electron Energy Loss Spectroscopy with the Mnpbem Toolbox. *Comput. Phys. Commun.* **2014**, *185*(3), 1177-1187.

536. De Abajo, F. G.; Howie, A., Retarded Field Calculation of Electron Energy Loss in Inhomogeneous Dielectrics. *Physical Review B* **2002**, *65* (11), 115418.

537. Anker, J.; Hall, P.; Lyandres, O.; Shah, N.; Zhao, J.; Van Duyne, R., Biosensing with Plasmonic Nanosensors. *J. Nanosci. Nanotechnol.*, 308-319.

538. Yeh, A. T.; Shank, C. V.; McCusker, J. K., Ultrafast Electron Localization Dynamics Following Photo-Induced Charge Transfer. *Science* **2000**, *289*(5481), 935-938.

539. Redmond, R. W.; Gamlin, J. N., A Compilation of Singlet Oxygen Yields from Biologically Relevant Molecules. *Photochemistry and photobiology* **1999**, *70*(4), 391-475. 540. Neckers, D., Rose Bengal. *Journal of Photochemistry and Photobiology A: Chemistry* **1989**, *47*(1), 1-29.

541. Yaraki, M. T.; Hu, F.; Rezaei, S. D.; Liu, B.; Tan, Y. N., Metal-Enhancement Study of Dual Functional Photosensitizers with Aggregation-Induced Emission and Singlet Oxygen Generation. *Nanoscale Advances* **2020**, *2*(7), 2859-2869.

542. Dragan, A. I.; Geddes, C. D., Metal-Enhanced Fluorescence: The Role of Quantum Yield, Q0, in Enhanced Fluorescence. *Applied Physics Letters* **2012**, *100*(9), 093115.

543. Cortie, M. B.; McDonagh, A. M., Synthesis and Optical Properties of Hybrid and Alloy Plasmonic Nanoparticles. *Chemical Reviews* **2011**, *111*(6), 3713-3735.

544. Wang, L.; Wang, Z.; Li, L.; Zhang, J.; Liu, J.; Hu, J.; Wu, X.; Weng, Z.; Chu, X.; Li, J.; Qiao, Z., Magnetic–Plasmonic Ni@Au Core–Shell Nanoparticle Arrays and Their Sers Properties. *RSC Advances* **2020**, *10*(5), 2661-2669.

545. Lim, J.; Majetich, S. A., Composite Magnetic–Plasmonic Nanoparticles for Biomedicine: Manipulation and Imaging. *Nano Today* **2013**, *8*(1), 98-113.

546. She, H.; Chen, Y.; Chen, X.; Zhang, K.; Wang, Z.; Peng, D.-L., Structure, Optical and Magnetic Properties of Ni@Au and Au@Ni Nanoparticles Synthesized Via Non-Aqueous Approaches. *Journal of Materials Chemistry* **2012**, *22*(6), 2757-2765.

547. Song, H.-M.; Wei, Q.; Ong, Q. K.; Wei, A., Plasmon-Resonant Nanoparticles and Nanostars with Magnetic Cores: Synthesis and Magnetomotive Imaging. *ACS Nano* **2010**, *4*(9), 5163-5173.

548. Ravichandran, M.; Oza, G.; Velumani, S.; Ramirez, J. T.; Garcia-Sierra, F.; Andrade, N. B.; Vera, A.; Leija, L.; Garza-Navarro, M. A., Plasmonic/Magnetic Multifunctional Nanoplatform for Cancer Theranostics. *Scientific Reports* **2016**, *6*(1), 34874.

549. Souza, J. B.; Varanda, L. C., Magneto-Plasmonic Au-Coated Co Nanoparticles Synthesized Via Hot-Injection Method. *Nanotechnology* **2018**, *29*(6), 065604.

550. Levin, C. S.; Hofmann, C.; Ali, T. A.; Kelly, A. T.; Morosan, E.; Nordlander, P.; Whitmire, K. H.; Halas, N. J., Magnetic–Plasmonic Core–Shell Nanoparticles. *ACS Nano* **2009**, *3*(6), 1379-1388.

551. Zhao, T.; Sun, R.; Yu, S.; Zhang, Z.; Zhou, L.; Huang, H.; Du, R., Size-Controlled Preparation of Silver Nanoparticles by a Modified Polyol Method. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2010**, *366* (1-3), 197-202.

552. Hohenester, U.; Trügler, A., Mnpbem - a Matlab Toolbox for the Simulation of Plasmonic Nanoparticles. *Computer Physics Communications* **2012**, *183*(2), 370-381.

553. Palik, E. D., *Handbook of Optical Constants of Solids*. Academic press: 1998; Vol. 3.

554. Hayashi, H.; Hiraoka, N., Accurate Measurements of Dielectric and Optical Functions of Liquid Water and Liquid Benzene in the Vuv Region (1–100 Ev) Using Small-Angle Inelastic X-Ray Scattering. *The Journal of Physical Chemistry* **B2015**, *119*(17), 5609-5623.

555. Moutzouris, K.; Papamichael, M.; Betsis, S. C.; Stavrakas, I.; Hloupis, G.; Triantis, D., Refractive, Dispersive and Thermo-Optic Properties of Twelve Organic Solvents in the Visible and near-Infrared. *Applied Physics B***2014**, *116*(3), 617-622.

556. Virtanen, P.; Gommers, R.; Oliphant, T. E.; Haberland, M.; Reddy, T.; Cournapeau, D.; Burovski, E.; Peterson, P.; Weckesser, W.; Bright, J., Scipy 1.0: Fundamental Algorithms for Scientific Computing in Python. *Nature methods* **2020**, *17*(3), 261-272.

557. Zhao, T.; Sun, R.; Yu, S.; Zhang, Z.; Zhou, L.; Huang, H.; Du, R., Size-Controlled Preparation of Silver Nanoparticles by a Modified Polyol Method. *Colloids Surf. A Physicochem. Eng.* **2010**, *366* (1-3), 197-202

Shining light on plasmonic silver nanoparticles for catalysis

by

Alexandra Marie Flora Gellé

Centre for Green Chemistry and Catalysis, Department of Chemistry McGill University, Montréal, QC, Canada April, 2021