The Aqueous-based Synthesis of Functional

Nanoparticles for Advanced Energy Materials

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This thesis is dedicated to my grandfather Mohammad Ilyas (1933-2004)

Abstract

Catering to the rising demand for clean and affordable solar energy, this thesis explores aqueous solution synthesis and thin-film fabrication of two important photovoltaic semiconductors - TiO_2 and CZTS (Cu_2ZnSnS_4). Firstly, nanocrystals of TiO_2 were synthesized in a high-throughput production process in a continuous stirred-tank reactor (CSTR) using a dilute aqueous solution of $TiCl_4$ as the feed. The process was conducted at a range of TiCl₄ concentrations (0.1-1.0 M), temperatures (70-90 $^{\circ}$ C), and solution pH (2-6). Maintenance of relatively high solution pH 2-5 via continuous addition of NaOH prevented redissolution of the otherwise metastable anatase phase. Primary nanocrystals measuring ≈ 6 nm assembled into mesoporous aggregates with high surface area $\approx 200-250$ m^2/g were produced. On the other hand, when there was no external pH regulation and solution acidity was controlled only by the hydrolysis of TiCl₄, dissolution-precipitation processes were promoted leading to production of brookite and/or rutile. High $TiCl_4$ concentration (0.5-1.0 M) and consequently low solution pH led to synthesis of rutile, while at 0.1 M TiCl₄ a 90% brookite/ 10% rutile TiO₂ mixture was produced. The rutile particles took the shape of $\approx 1 \ \mu m$ spherical particles with the interior characterized by long 'fibrous' planes. On the other hand the brookite particles displayed a wide size range measuring 20-100 nm and the individual crystals appear to be mesoporous nanoplatelets. By controlling the supersaturation regime via tuning the pH and TiCl₄ concentration, selective precipitation of different phases was made possible at ambient conditions in an easily scalable process. The anatase nanocrystals showed promising results in photocatalysis and dye-sensitized solar cells (DSSCs); whereas the rutile particles showed excellent functionality as light scattering layers in DSSC photoanodes.

Once the TiO₂ particles were obtained, their assembly into DSSCs required dispersing the particles in the form of a screen-printable paste to fabricate photoanodes. Propylene glycol and polyethylene glycol (molecular weight: 20,000) replaced the toxic α -terpineol as the plasticizer and water-insoluble ethyl cellulose as the binder/pore-creating agent from the benchmark protocol that uses organic chemicals extensively. Propylene glycol was found to strongly influence mechanical stability of the paste and its adherence with the substrate while polyethylene glycol controlled the viscosity and acted as the pore-creating agent. Pore width of the sintered photoanodes was shown to be the most significant factor affecting DSSC efficiency. A direct correlation was found between paste viscosity, pore width and photovoltaic efficiency - all of which showed a parabolic dependence with increasing amount of polyethylene glycol.

Lastly, CZTS thin films were fabricated following a hydrothermal/spin-coating/annealing approach. Mixed ZnS and CuS precursors were synthesized by pumping cationic precursor solution of 0.2 M ZnCl, 0.4 M CuCl₂ into a solution of 0.8 M Na₂S and subjecting the resulting colloidal solution to hydrothermal treatment at 180 °C for 8 hours. Similar to TiO₂, deposition of CZTS thin films also requires homogeneous dispersion; in this case compact films without porosity were aimed for. To this end, the dried hydrothermal powder product of ZnS and CuS was dispersed in an aqueous solution of SnS₂ in $(NH_4)_2S$; SnS₂ served as the Sn source for CZTS, and also as a ligand to stabilize the solid particles in the suspension. It was observed that due to the excess sulphur contributed by the SnS₂, annealing at 500°C could be conducted in an argon atmosphere without the need for excess sulphur powder yielding Cu-poor/Zn-rich CZTS films as determined by Raman and other characterization methods. Annealing conducted at 600 °C and 2 hours still maintained the chemical stability of CZTS crystals since no secondary phases were observed.

Résumé

Pour répondre à la demande croissante d'énergie solaire propre et abordable, cette thèse explore la synthèse en solution aqueuse et fabrication de film mince de deux semiconducteurs photovoltaïques importants - TiO₂ et CZTS - Cu₂ZnSnS₄. Tout d'abord, les nanocristaux de TiO₂ ont été synthétisés dans un procédé de production à haut débit dans un réacteur continu à cuve agitée (CSTR) en utilisant une solution aqueuse diluée de TiCl₄ comme source. Le processus a été mené à avec une gamme de concentrations TiCl₄ (0,1-1,0 M), de températures (70-90 °C), et de solution pH (2-6). Une maintenance relativement élevée de la solution pH 2-5 par addition continue de NaOH a empêché la redissolution de la phase anatase métastable. Des nanocristaux primaires mesurant ≈ 6 nm et assemblés en agrégats mésoporeux avec une surface élevée $\approx 200-250 \text{ m}^2/\text{g}$ ont été produits. D'autre part, lorsqu'il n'y avait pas de régulation externe du pH et que l'acidité de la solution a été contrôlée uniquement par l'hydrolyse de TiCl₄, le processus dissolution-précipitation a été promu menant à la production de brookite et / ou rutile. Une haute concentration en TiCl₄ (0,5 à 1,0 M) et par conséquent une solution à faible pH a conduit à la synthèse de rutile, tandis qu'avec 0,1 M TiCl₄ un mélange 90% brookite / 10% rutile de TiO₂ a été produit. Les particules de rutile ont pris une forme sphérique de ≈ 1 um avec l'intérieur caractérisé par de long plan 'fibreux'. D'autre part, les particules de brookite affichent une large gamme de tailles mesurant de 20-100 nm et les cristaux individuels semblent être des nanoplaquettes mésoporeuses. En contrôlant le régime de sursaturation par le réglage du pH et de la concentration TiCl₄, une précipitation sélective des différentes phases a été rendue possible dans des conditions ambiantes dans un processus facilement extensible à une production à grande échelle. Les nanocristaux d'anatase ont montré des résultats prometteurs dans la photocatalyse et les cellules à pigment photosensible (DSSCs); tandis que les particules de rutile ont montré une excellente fonctionnalité en tant que couches de diffusion de la lumière dans les photoanodes de DSSC.

Une fois que les particules de TiO₂ ont été obtenues, leur assemblage en DSSC nécessite la dispersion des particules sous la forme d'une pâte d'écran imprimable pour fabriquer les photoanodes. Le propylène glycol et le polyéthylène glycol (poids moléculaire: 20 000) ont remplacé le toxique alpha-terpinéol comme plastifiant et l'éthyl cellulose insoluble dans l'eau en tant que liant / agent porogène par rapport au protocole de référence qui utilise abondamment des produits chimiques organiques. Le propylène-glycol influence fortement la stabilité mécanique de la pâte et son adhésion au substrat alors que le polyéthylène glycol contrôle la viscosité et a agi en tant qu'agent porogène. La largeur des pores du fritté photoanodes est le facteur plus important affectant l'efficacité des DSSC. Une corrélation directe a été trouvée entre la viscosité de la pâte, la largeur des pores et l'efficacité photovoltaïque – tous ont montré une dépendance parabolique avec l'augmentation de polyéthylène glycol.

Enfin, les films minces de CZTS ont été fabriqués suivant une approche hydrothermal / enrobage par rotation / recuit. Les précurseurs ZnS et CuS mixtes ont été synthétisés par le pompage d'une solution cationique de 0,2 M ZnCl, 0,4 M CuCl₂ dans une solution de 0,8 M de Na₂S et en soumettant la solution colloïdale résultante à un traitement à 180 °C pendant 8 heures. Semblable à TiO₂, le dépôt de films minces CZTS nécessite également une dispersion homogène; dans ce cas des films compacts sans porosité ont été visés. A cet effet, le produit en poudre séchée hydrothermique de ZnS et CuS a été dispersé dans une solution aqueuse de SnS₂ en (NH₄)₂S; le SnS₂ a servi de source de Sn dans le CZTS, et aussi comme ligand pour stabiliser les particules solides dans la suspension. Il a été observé qu'en raison de l'excès de soufre apporté par le SnS₂, un recuit à 500 °C peut être effectuée dans une atmosphère d'argon, sans la nécessité d'un ajout de poudre de soufre en excès donnant des films minces CZTS pauvre en Cu et riche en Zn, tel que déterminé par Raman et d'autres méthodes de caractérisation. Un

recuit réalisé à 600 °C pour 2 heures, maintient la stabilité chimique des cristaux CZTS puisqu'aucune phase secondaire n'a été observée.

Foreword

This thesis has been compiled using manuscript-based format, as prescribed by McGill University thesis preparation guidelines. The following research articles have been included as chapters 3,4,5, and 6 in this thesis respectively.

- Yasin, A., Guo, F., & Demopoulos, G.P. (2016). Continuous-reactor, pH-controlled synthesis of multifunctional mesoporous nanocrystalline anatase aggregates. Chemical Engineering Journal, 287, 398-409.
- Yasin, A., Guo, F., & Demopoulos, G.P. (2016). Aqueous, Screen-Printable Paste for Fabrication of Mesoporous Composite Anatase-Rutile TiO₂ Nanoparticle Thin Films for (Photo) electrochemical Devices. ACS Sustainable Chemistry & Engineering, 4(4), 2173-2181.
- Yasin, A., Guo, F., Sussman, M.J., Gauvin, R., & Demopoulos, G.P. (2016) Steadystate, scalable production of mesoporous rutile and brookite particles and their use in energy conversion and storage cells. Accepted by ChemNanoMat, DOI: 10.1002/cnma.201600185.
- Yasin, A., Gonfa, B., & Demopoulos, G.P. (2016) SnS₂ as the Sn source and ligand for all-aqueous deposition of light-absorbing CZTS (Cu₂ZnSnS₄) thin films. Ready to be submitted to Materials Letters.

Fuqiang Guo assisted in carrying out synthesis experiments. Micah J. Sussman provided cycling data of brookite in Li-ion batteries. Prof. Raynald Gauvin's microscope was used to take high resolution SEM images. Belete A. Gonfa synthesized SnS_2 following an established protocol from literature. All experimental work, analyses, and writing of the manuscripts were carried out by the author. Prof. Demopoulos provided overall guidance and supervision for the research work as well as writing of the manuscripts.

The accuracy of the contribution of authors is attested by the author's supervisor.

Professor George P. Demopoulos Mining and Materials Engineering McGill University Montreal, QC, Canada

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Chapter 1

Introduction

1.1 Motivation

Global energy consumption has been increasing at an annual average of 2.1% during the past decade. The share of renewables is growing yearly, but at a marginal pace; as of June 2015, only 3.0% energy consumption is contributed by renewable energy sources - these include the sum of biofuels, wind, hydroelectricity and solar technologies [1]. Their minuscule contribution to the global energy landscape emphasizes the fact that much development needs to be done to bring about widespread use of renewable energy technologies. The drive towards this paradigm shift evident by continued research and development efforts and promoting social awareness of 'alternative' energy sources to the traditional sources of oil, natural gas, and coal are no surprise anymore. Increasing concerns regarding the exhaustibility of the oil, gas and coal reserves, coupled with the heavy environmental cost their use incur in the form of greenhouse gases, destruction of the landscape, and oil-spills in the global waters and sand posing threat to local flora and fauna, underline the significance of green energy.

Solar energy is hailed as the champion of sustainable and clean sources of energy primarily due to its abundance – in one year the earth receives 3×10^{24} J of energy, about 10,000 times the current energy consumption demands [2]. However, the current cost of harvesting solar energy is at \$0.10-0.15/kWh (i.e. the payback cost of installation of

solar panels), relative to \$0.02-0.05/kWh for fossil fuels [3, 4]. Hence, the replacement of fossil fuels with solar panels can be accelerated if the solar energy technology is made cost-competitive.

1.1.1 Solar energy harvesting technologies

The direct conversion of solar light energy to electrical energy traces its roots back to the discovery of photovoltaic effect in 1839 in an electrolytic cell with platinum electrodes [5]. In 1953, Calvin Fuller, Gerald Pearson, and Daryl Chapin discovered the silicon solar cell. In 1958, photovoltaic technology was first used for space applications. In the 1970s oil embargo provided an incentive towards harvesting solar energy for terrestrial use, reinforced further by international awareness and push towards decreasing CO_2 emissions [6]. The advancement in solar technologies is roughly divided into three phases or 'generations'.

First generation: First generation solar cells are based on silicon wafers. Borrowing from the developed microelectronics industry, the first solar cells to emerge were based on high purity, single silicon crystal wafers. These were followed by manufacture of less costly, lower quality, multicrystalline silicon wafers to be used exclusively for photovoltaics [6, 7]. The highest efficiency for a monocrystalline silicon solar cell at 25.0% [8] is quite close to the Shockley–Queisser limit of 31% for single band-gap cells; at this stage this technology leaves little margin for efficiency improvement and/or cost reduction.

Second generation: Second generation solar cells, also called 'thin film' solar cells derive their nomenclature from the use of thin semiconductor films measuring $\approx 1 \ \mu m$ as the photovoltaic active material. This approach greatly reduces the amount of material required, and hence allows for other semiconductors, that are too expensive to be used as stand-alone wafers, to become potential candidates. Moreover, the basic unit for thin-film solar cells is a module, and not a single cell, making this technology commercially attractive. Semiconductors used for this technology include α -amorphous silicon, CIS (CuInSe₂), cadmium telluride (CdTe), CIGS (CuInGaSe₂), CZTS (Cu₂ZnSnS₄) etc [9].



Figure 1.1: NREL chart of best research cell efficiencies [8]

Third generation: Third generation photovoltaic technologies aim at circumventing the Shockley–Queisser limit imposed by cells employing single bandgap material, whilst using non-toxic and abundant materials to keep the costs in check. It is an umbrella term for a number of different solar cell technologies, such as tandem cells that employ multiple junctions, dye-sensitized solar cells, organic solar cells, and quantum dot solar cells.

Updated NREL chart of certified, best solar cells efficiencies for different types of solar cells are given in Figure 1.1.

Advanced solar energy technologies of second and third generation exploit the surface and functional properties of semiconductor nanomaterials. To make these systems competitive with fossil-fuel based energy sources, the cost of manufacturing and their environmental footprint has to be controlled.

DSSCs & TiO₂

Dye-sensitized solar cells (DSSCs) - a case of third generation solar cells - were invented by Brian O'Regan and Michael Grätzel in 1991 [10]. In a DSSC, the photoanode is comprised of a mesoporous (pore size 2-50 nm) TiO₂ film coated with dye molecules, on conductive glass. The counter electrode (cathode) is platinized conductive glass and the space is filled with an iodide based redox electrolyte. When light is incident on the photoanode electrons in the dye get excited and are transported through the TiO₂ to the external circuit. The redox electrolyte reduces the dye molecules, and receives electrons through the counter electrode. This cell is termed as a photoelectrochemical cell since it harvests solar energy as electric energy through redox reaction. The difference between the Fermi level of TiO₂ and redox potential of the electrolyte generates voltage [11].

The requirement of a mesoporous TiO_2 film fabricated with nanocrystalline TiO_2 particles is critical to DSSCs since it offers an enormous internal surface area for dye adsorption, increasing the light harvesting capability compared to a flat film deposited over equivalent dimensions. Secondly, it allows for the infiltration of the electrolyte and creates a junction of large surface area allowing for fast transport of charge carriers [11]. Therefore, the architecture of the TiO_2 photoanode has to be adequately engineered to be balanced between surface area and pore size to allow for large internal area and enough space to allow for infiltration of dye and electrolyte.

CZTS

 Cu_2ZnSnS_4 (CZTS) is a quaternary p-type semiconductor. The interest in CZTS stems from the photovoltaic performance of related p-type semiconductors - CIGS $Cu(In,Ga)(S,Se)_2$, CdTe, CIS (CuInS₂) - in thin film solar cells, and the fact that the aforementioned materials contain rare and expensive elements such as indium and gallium, or pose toxic threats as in the case of cadmium. As opposed to silicon, these semiconductors have direct band gaps and consequently high light absorption coefficients requiring much less material for equivalent light harvesting [12]. Although CZTS based solar cell has reached efficiencies of up to 8.4%, the highest-efficiency cells use flammable, toxic, and highly unstable chemical, hydrazine. Potential commercialization of CZTS-based solar cells demand its synthesis through safe, non-toxic, and low-cost processes opening new avenues for further research.

In the solar technologies discussed above use of nanomaterials is vital.

1.1.2 Nanomaterials

Materials that have at least one dimension measuring between 1-100 nm are classified as nanomaterials. As the crystal size decreases, the surface area to volume ratio increases conferring higher chemical activity, lower melting points, and higher solubilities compared to their bulk counterparts. The particle size at the nanoscale also affects electronic band structure and thus optical and electronic properties of these materials [11], hence giving scientists more freedom to acutely engineer materials for photovoltaic applications.

A number of synthesis methods for semiconductor nanocrystals are in use. Of these, methods such as chemical vapor deposition (CVD), physical vapor deposition (PVD), molecular beam epitaxy (MBE), sputtering, etc. require specialized and expensive instrumentation to provide fine control over nanocrystal properties. To produce nanocrystals with a narrow distribution of properties and to enable acute control over properties, use of liquid phase synthesis routes is preferred. These are categorized as either aqueous (chemical precipitation, hydrothermal) or non-aqueous (sol-gel, solvothermal) depending on the nature of solvent, precursor, and other chemicals. Liquid phase methods yield colloidal suspensions which can be processed further through a variety of processes, for example, spin coating, dip coating, roll-to-roll casting inkjet printing [13]. While ample research is being dedicated towards environmentally benign, aqueous-based processes, the demonstrations are bench-scale and are not suitable for large volumes of production a prerequisite for commercialization and to derive benefits from economies of scale.

The research presented herein focusses on synthesis of TiO_2 nanocrystals for application in DSSCs, and CZTS thin films to be further assembled into solar cells.

1.2 Objectives

In view of the background provided, this research addresses scale-up of a nano-TiO₂ aqueous synthesis process, and further processing of the TiO₂ in an aqueous-based paste to deposit TiO₂ electrodes for application in DSSCs. The principles of aqueous synthesis of nanocrystals are extended to the synthesis of CZTS films. The aim of this research is to (1) design an aqueous, continuous, scalable, and green process for the production of nanocrystalline TiO₂ particles; (2) optimize the afore-mentioned process to select for the three TiO₂ phases, namely, anatase, brookite, and rutile; (3) develop and optimize an aqueous-based protocol for TiO₂ paste synthesis to be deposited as thin film photoanodes for use in DSSCs; and (4) synthesize CZTS thin films with a water-based process, followed by an investigation into annealing conditions to yield defect-free films for solar cells.

1.3 Thesis layout

This thesis has been organized in six chapters beyond this introductory chapter. Chapter 2 introduces the basics of DSSCs, and provides extensive survey of literature on properties and synthesis methods of nanocrystalline TiO₂ particles with emphasis on their relevance to DSSCs followed by literature review of screen-printable pastes for fabrication of TiO₂ photoanodes and ends with reviewing the progress made in CZTS thin-film fabrication for application in solar cells. Chapter 3 details the synthesis of anatase nanocrystals in a continued stirred tank reactor (CSTR); it probes the effects of changing process conditions and presents examples of applications of anatase. Chapter 4 focusses on the synthesis of rutile and brookite, and investigates the mechanism of phase formation and crystal growth ending with an investigation into application of rutile as light scattering particles in DSSCs. Chapter 5 documents the development of an aqueous-based, screen printable TiO₂ paste, correlating the effect of paste formulation, electrode characteristics and photovoltaic performance of resulting DSSCs. Chapter 6 presents the research undertaken to fabricate CZTS thin films following a hydrothermal/spin-coating approach and effect of annealing conditions on morphology and elemental composition of the films.

Lastly, Chapter 7 summarizes the conclusions presented in Chapter 3-6, and reports the claims to original contributions to knowledge.

1.4 References

- [1] BP. BP Statistical Review of World Energy June 2015. Tech. rep. BP p.l.c., 2015.
- [2] M. Grätzel. "Photoelectrochemical cells". In: *Nature* 414.6861 (2001), pp. 338–344.
- [3] N. S. Lewis and D. G. Nocera. "Powering the planet: Chemical challenges in solar energy utilization". In: *Proceedings of the National Academy of Sciences* 103.43 (2006), pp. 15729–15735.
- [4] N. S. Lewis. "Research opportunities to advance solar energy utilization". In: Science 351.6271 (2016), aad1920.
- [5] A. W. Copeland, O. D. Black, and A. Garrett. "The Photovoltaic Effect." In: *Chemical Reviews* 31.1 (1942), pp. 177–226.
- [6] M. A. Green. "Photovoltaics: technology overview". In: *Energy Policy* 28.14 (2000), pp. 989–998.
- M. A. Green. "Crystalline and thin-film silicon solar cells: state of the art and future potential". In: Solar Energy 74.3 (2003), pp. 181–192.
- [8] NREL. Best Research-Cell Efficiencies. 2015. URL: http://www.nrel.gov/ncpv/.
- [9] M. Green. "Recent developments in photovoltaics". In: Solar Energy 76.1 (2004), pp. 3–8.
- [10] B. O'Regan and M. Grätzel. "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films". In: *Nature* 353.6346 (1991), pp. 737–740.
- [11] X. Chen, C. Li, M. Gratzel, R. Kostecki, and S. S. Mao. "Nanomaterials for renewable energy production and storage". In: *Chemical Society Reviews* 41 (23 2012), pp. 7909–7937.

- [12] J. Scragg. "Copper Zinc Tin Sulfide Thin Film for Photovoltaics". PhD thesis. University of Bath, 2011.
- J. Chang and E. R. Waclawik. "Colloidal semiconductor nanocrystals: controlled synthesis and surface chemistry in organic media". In: *RSC Advances* 4 (45 2014), pp. 23505–23527.

Chapter 2

Literature review

2.1 Overview

This section provides introductory information and a survey of research studies undertaken previously pertinent to the research presented in this thesis. It starts with an introduction to dye-sensitized solar cells (DSSCs), followed by nanocrystalline TiO₂ phases, properties and synthesis with particular emphasis on solution synthesis. Afterwards the properties of TiO₂ thin films are discussed in relation to their application in DSSCs and a survey of the paste formulations used to form TiO₂ thin films is presented. Finally Cu₂ZnSnS₄ (CZTS) nanocrystals are discussed briefly with respect to their applications in photovoltaics.

2.2 TiO₂ based dye-sensitized solar cells (DSSCs)

Dye-sensitized solar cells (DSSCs) were pioneered by Brian O'Regan and Michael Grätzel, and reported in their historic publication in *Nature* in 1991 [1]. DSSCs belong to the third generation of solar cells, driven by *low-cost*, *low-efficiency* mantra. Like other cell types included in this category, such as organic-based or quantum dots based solar cells, these solar technologies do not require expensive equipment and stringent manufacturing protocols; at the same time, the efficiencies generated are much less than silicon or thin-film based solar cells.



Figure 2.1: Schematic displaying basic structure of a DSSC cell

A schematic of DSSCs is shown in Figure 2.1. A DSSC consists of a closed assembly of a photoanode, counter-electrode (cathode) and an electrolyte filling the space between the two electrodes. Both electrodes are built upon conductive glass (generally fluorine-doped tin oxide - FTO glass) and connected to an external circuit. The photoanode is composed of a thin layer ($\approx 12 \mu m$) of large surface area, mesoporous, n-type semiconductor, typically TiO₂, deposited onto the glass. Organometallic dye molecules with high absorption in the visible-light range are chemisorbed on the TiO₂ particles. Furthermore, the porous film is penetrated by a hole transport material, or electrolyte, typically I^-/I_3^- redox couple, forming a large, continuous junction between p- and n- type materials. Platinized glass serves as the counter-electrode with the layer of platinum acting as a catalyst for the redox reactions of the electrolyte [1, 2].

Figure 2.2 shows a schematic illustrating the operation of a DSSC. When light is irradiated onto the photoanode, the electrons in the dye molecules absorb the photons and get excited (1). The excited electrons are injected into the conduction band of the TiO₂ film (2) and are transported through the TiO₂ network to the conductive glass (3) from where they travel to the external load - hence the term "dye-sensitized" solar cell. The oxidized dye molecules are reduced by the redox electrolyte, whereby the I⁻ gets oxidized to I_3^- (5) which in turn is regenerated to I⁻ by the electrons arriving at the platinized counter-electrode through the external load (4). The voltage of the cell is determined by the difference in the Fermi level of the semiconductor, i.e. TiO₂ under



Figure 2.2: Illustration of working principle of a DSSC cell [3]

irradiation and Nernst potential of the redox electrolyte [1, 2].

DSSCs mimic photosynthesis insofar the functions of light absorption, and charge generation and transport are separate, as opposed to silicon-based, and thin-film devices. It is also referred to as a photoelectrochemical cell since light-to-electric energy conversion is achieved through a series of chemical redox reactions [1]. However, the cell itself does not undergo any significant permanent chemical transformation. The distinctive feature of DSSCs is that they do not require the incident light to be perpendicular to photoanode surface; this ability to function under diffuse light conditions makes them suitable for cloudy weathers, and dispenses away with the requirement of having an associated tracking system.

The following section expands further into the three critical constituents of a DSSC - photoanode, counter-electrode, and the hole-transport material or electrolyte.

2.2.1 DSSC components - photoanode, counter-electrode, electrolyte

As explained previously, the photoanode has two active components: n-type semiconductor, and sensitizing dye. It is to be noted that the fabrication of TiO_2 thin film on the photoanode is the primary focus of this investigation, and will be discussed in detail later.

Light sensitive dye: The most commonly used light sensitizing dyes are based on Ruthenium (II) polypyridyl complexes in the form of [*cis*-(dithiocyanato)-Ru-bis(2,2'bipyridine-4,4'-dicarboxylate)] (N3), or its doubly protonated tetrabutyl ammonium salt (N719) [4], and black dye. The molecular structure and absorption spectrum of N719 is given in Figure 2.3; the absorption in the visible light range (450-600 nm) and near IR region (920 nm) are due to the Ru-ligand charge transfer transition. Compared against the Ru-containing dye, sensitization with an indoline-based dye, D205, produced comparable J_{sc} but lower V_{oc} and fill-factor, lowering the overall conversion efficiency [5]. In recent years, use of perovskites as the light absorbing material has revolutionized the photovoltaic efficiencies of sensitized solar cells [6].

Electrolyte: The DSSCs employ liquid electrolytes, the most common of which is I^-/I_3^- dissolved in acetonitrile [1]. The durability of DSSCs is affected by the loss of liquid electrolytes via leakage and/or evaporation. To remedy this problem, use of gel-based [7] and solid-state electrolytes [8] has been probed extensively.

Counter-electrode: The counter electrode serves as a catalyst for the electrolyte reduction. Relative to platinum, carbon nanotubes counter-electrodes show lower catalytic activity [9, 10]. CoS deposited on flexible PEN substrates shows equivalent overall photovoltaic efficiency but offers a cost advantage due to the lower cost of cobalt over platinum [11].

2.2.2 DSSC photovoltaic performance characterization

Testing DSSCs under natural sunlight conditions for photovoltaic performance is not always practical and poses the problem of comparing devices fabricated and tested in different parts of the globe. Hence, calibrated solar simulators generally equipped with a Xenon lamp are used to simulate sunlight conditions indoors. Recently there has been a strong drive in the photovoltaic research community to standardize protocols for device measurements to produce results comparable across literature, and more importantly discourage practices that enable publication of inflated measurements [13]


Figure 2.3: Absorption spectrum of N719 with the inset showing the N719 molecular structure [12]

A DSSC is illuminated under simulated Air Mass 1.5G sunlight of 100 mW/cm² intensity by a calibrated light source. Under these conditions, step-wise bias voltage is applied as seen in Figure 2.4 (a) where T_d represents the delay time between each voltage application, and photocurrent measurements are taken at T_m . The voltage (V) and current (I) values are plotted as I-V or J-V curves; J represents the current density per surface area of the cell, as shown in Figure 2.4 (b). Some important parameters deduced from J-V curves are:

Open-circuit voltage, V_{oc} : The maximum potential difference that can be produced by the cell (at J=0). Theoretically, it represents the difference between the Nernst potential of the electrolyte and Fermi-level of the TiO₂ semiconductor.

Short-circuit current density, J_{sc} : The maximum current density that can flow between the electrodes (at V=0).

Fill-factor, FF: The ratio of maximum achievable power of the cell to the maximum theoretical power.

$$FF = \frac{P_{max}}{V_{oc} \times J_{sc}} \tag{2.1}$$

Where



Figure 2.4: (a) Step-wise applied photovoltage (b) J-V curve

$$P_{max} = V_{max} \times J_{max} \tag{2.2}$$

Conversion efficiency, η : The overall light-to-current conversion efficiency denoted by the ratio of maximum achievable power to the incident light irradiation power.

$$\eta = \frac{FF \times V_{oc} \times J_{sc}}{P_{light}} \times 100$$
(2.3)

[14, 15]

2.2.3 DSSC photoelectrochemical characterization

Voltage decay (OCVD)

Open Circuit Voltage Decay (OCVD) is used to investigate the kinetics of recombination in DSSCs. A DSSC is allowed to reach a quasi-equilibrium state under illumination followed by switching off the illumination and monitoring the rate of decay in V_{oc} under relaxation in dark. The electron lifetime, τ_n is determined using Equation 2.4 [16]:

$$\tau_n = \frac{K_B T}{e} \left(\frac{dV_{oc}}{dt}\right)^{-1} \tag{2.4}$$

Where, K_B is the Boltzmann constant (m²kgs⁻¹K⁻¹), T is the temperature (K), and e is the electron charge (C).

Electrochemical impedance spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is used to study the kinetics of electrochemical and photoelectrochemical process in DSSCs. A DSSC is modelled as an equivalent electrical circuit as shown in Figure 2.5 to stimulate the experiment. Tiny AC voltage amplitudes are applied to the device to exert small perturbations and the current response is recorded. The impedance response is presented as a Nyquist plot shown in Figure 2.6. An arc in the Nyquist plot corresponds to presence of electrochemical interfaces. The high frequency arc on the left represents charge transfer processes at the counter electrode and FTO/TiO_2 interface, the middle arc corresponds to charge transfer processes across the TiO₂ film/dye/electrolyte interface and chemical capacitance, and the low frequency arc on the right represents the ionic diffusion in the electrolyte [17–19]. A software is needed to extract the individual values of the parameters shown in Figure 2.5 to study the ionic and electronic processes occurring.

The topic of interest for this research is the TiO_2 photoanode - TiO_2 nanoparticle synthesis and subsequent fabrication into photoanodes. Related literature review follows.

2.3 Nanocrystalline titanium dioxide (TiO₂)

 TiO_2 is preferred as the photoanodic semiconductor due to its stability under irradiation [21], non-toxicity, and abundance. In addition to photovoltaics, nanocrystalline TiO_2 is used in a variety of applications such as lithium ion batteries [22], gas and humidity sensors [23], thin film capacitors [24], chromatography [25], photocatalysts [26], and optical wave-guides [27].



Figure 2.5: Transmission line model for DSSC: R_s is the series resistance including sheet resistance of the FTO glass and contact resistances of the cell; r_{ct} is the chargetransfer resistance to recombination across the TiO₂ film/dye/electrolyte interface; C_{μ} is the chemical capacitance of the TiO₂ film; r_t is the charge transport resistance within the TiO₂ film; Z_d represents Nernst diffusion of ions in the electrolyte; R_{Pt} and C_{Pt} are the charge-transfer resistance and double-layer capacitance at the counter-electrode; R_{TCO} and C_{TCO} represent the charge-transfer resistance and double-layer capacitance at the electrolyte/TiO₂ interface; R_{CO} and C_{CO} represent the charge-transfer resistance and double-layer capacitance at the glass/TiO₂ interface; and L represents the TiO₂ film thickness [18].



Figure 2.6: Schematic of a typical Nyquist plot produced from EIS [20]

2.3.1 TiO₂ phases & properties

Phases

Titanium (IV) dioxide (TiO₂), also referred to as titania has molar mass 79.87 g/mol. The most common natural and synthetic polymorphs of TiO₂ are anatase and rutile, followed by brookite. A number of other phases measurable at the nanoscale also exist in nature, for example, TiO₂(B), baddeleyte, fluorite, spinel, hollandite, columbite, OI, pyrite, and ramsdellite. These phases are usually grouped as 'high-pressure' phases as they can be obtained by high pressure transformation of anatase or rutile. Another phase, namely lepidocrocite has a tendency to form single 2-D sheets. Recently, the search for a low-bandgap TiO₂ structure has sparked interest in the less-common polymorphs [4]. Since the common phases of anatase, rutile and brookite are widely studied, the focus of this thesis is their properties and applications.

The basic repeating unit in TiO_2 crystals is a distorted TiO_6 octahedron whereby a titanium atom is surrounded by six oxygen atoms (O_2^{-}) . The varied stacking order of octahedra leads to different three-dimensional crystal structures of rutile, anatase, and brookite as shown in Figure 2.7. The unit cells of rutile and anatase are tetragonal. The angle between the Ti and O at the apices is longer (102.3°) than the angles along the equatorial plane (92.6°) ; this 'distortion' in the octahedra is higher in anatase than rutile (Figure 2.7). A rutile unit cell has 6 atoms; the octahedra share edges in the cdirection forming long chains - the octahedra in the chains share corners in the *ab* plane with orientation of each chain alternating by 90°. Thus in the rutile structure, each octahedron has ten neighboring octahedra, two of them sharing edges and the other eight sharing corners. In anatase, each unit cell has 12 atoms; each octahedron shares four edges with neighboring octahedra forming zigzag chains in the a and b directions; the chains are linked together via corner sharing. In both anatase and brookite structures, each octahedron has eight neighboring octahedra, four of them sharing edges and the other four sharing corners. Brookite has 8 formula units in an orthorhombic unit cell sharing three edges. Brookite has 6 different Ti-O bond lengths and 12 different O-Ti-O



Figure 2.7: Bulk crystal structures of TiO_2 (a) rutile (b) anatase (c) brookite [28]

bond angles, making brookite crystal structure more complicated than the former two. In all three structures each O atom is coordinated to 3 Ti atoms [28–30]. The three bulk crystal structures are shown in Figure 2.7. Brookite is the rarest of the three commonly found minerals, and it is difficult to synthesize in the laboratory - hence a thorough understanding of its properties and subsequent applications is less extensive than anatase and rutile [28].

Thermodynamic stability

At ambient conditions macrocrystalline rutile is thermodynamically more stable relative to anatase and brookite. When subjected to high-temperature treatment, (as dry or wet media) anatase and brookite will irreversibly transform to rutile. Zhang and Banfield [31] studied thermal phase transformations on nanometric anatase and brookite and concluded that thermodynamic stability is dependant on particle size, such that for crystals of equal sizes, anatase, brookite, and rutile are stable for particle size < 11 nm, between 11 nm and 35 nm, and size > 35 nm, respectively. Transformation of anatase and brookite to rutile becomes rapid above 850 K since enthalpy of rutile decreases above this temperature. Zhang and Banfield observed the thermal transformation sequence to be $A \rightarrow B \rightarrow R$, but cautioned that at 623 K transformation between brookite and anatase is reversible and the direction is determined by enthalpy of anatase and brookite particles for the given particle sizes. On the other hand, Ranade *et al.* [32] propose the dependency of



Figure 2.8: Phase stability of titania as a function of surface area [32]

transformation sequence on the crossover between surface enthalpies of bulk nanotitania (as seen in Figure 2.8) as opposed to Zhang and Banfield who determined enthalpy starting from the particle sizes. Kandiel *et al.* reported direct $A \rightarrow R$ transformation at 600 °C, and direct $B \rightarrow R$ transformation at 700 °C [33]. Transformation from anatase to rutile is governed by interface (< 873 K) and/or surface nucleation phenomenon (893-1273 K) [31]. Therefore, it is postulated that rate of transformation is greater for smaller particles due to an increased in the number of contact sites for nucleation to occur [33].

The variable crystal structures of the polymorphs impart difference in properties, some of which are reviewed here.

Optical properties

Optical properties of a material are characterized primarily by its band-gap. Band-gap is the energy difference between the valence band, or the highest occupied density of states and the conduction band, or the lowest occupied density of states. Density of states is the distribution of states available for electron occupancy at different energy levels. Both rutile and brookite have a direct $\gamma \rightarrow \gamma$ transition, hence these are direct-band gap materials. On the other hand, anatase has an indirect $0.88\gamma \rightarrow M$ transition. The

	Rutile	Anatase	Brookite
Band-gap	3.0	3.19-3.39	3.0-3.4
(eV)			
Refractive	2.3-2.75	2.1-2.6	-
index			

Table 2.1: Bandgap and refractive indices found in literature [37–43]

valence band is formed of filled 2p orbitals of O_2^- while the conduction band is formed of empty 3d belonging to Ti₄⁺ [34]. Band-gap values of the three polymorphs reported in literature are listed in Table 2.1. The values between 3-3.4 eV indicate natural TiO₂ is only responsive in the UV region of the electromagnetic spectrum [35]. For particles at the nanoscale, band-gap increases as the particles become smaller due to quantumconfinement effects - this implication has been exploited fully with research into quantum dots [36]. Anatase shows the highest band-gap among the three polymorphs and hence is used as active semiconductor in DSSCs. On the other hand, rutile acts as light scattering particles to assist in light reflectance within the film due to its bigger size and higher refractive index (2.75) vs. anatase (2.52) [37].

2.3.2 TiO₂ synthesis

The widespread use of nanocrystalline materials in advanced technologies drove the development of a variety of synthesis processes. A brief overview of the most popular technologies employed is given below.

Flame synthesis

In flame synthesis titanium alkoxide or halide vapors are oxidized by an oxygen-methane flame, forming agglomerated TiO₂ particles. The benchmark photocatalytic and photovoltaic Degussa P25 variety of TiO₂ - composed of $\approx 85\%$ anatase and $\approx 15\%$ rutile - is synthesized following this procedure. In another variation, termed as flame spray pyrolysis (FSP), instead of using gaseous precursors, liquid droplets are sprayed into the flame; thus a broader variety of precursors can be utilized [44]. In yet another variation, liquid sols are deposited on the substrates which are inserted into the post-flame region to obtain crystals [45]. Flame synthesis is conducted in flame reactors, furnace reactors, plasma furnace reactors, laser and sputtering reactors, etc. The advantages of this process include direct process and no-moving parts machinery [46]. However, high temperatures ≈ 900 °C are required to vaporize the precursors.

Physical/chemical vapor deposition (PVD/CVD)

In physical/chemical vapor deposition (PVD/CVD) methods precursors diluted in gaseous states condense on a substrate to form solid thin films. CVD involves chemical reaction on the substrate surface. The processes require vacuum and high temperatures to achieve vaporization of precursors and in case of CVD also to drive the chemical reaction. The disadvantages of these processes include expensive equipment, vacuum and high temperatures [47].

Sol-gel synthesis

'Sol' is a colloidal suspension prepared by hydrolysis of titanium alkoxide or salt precursor in an organic solvent in the presence of small amount of water; addition of acid to the sol catalyzes polymerization to form a three dimensional Ti-O network called 'gel'. The gel is a continuous polymeric network surrounded by a continuous liquid phase [48]. The gel is dried to yield dry TiO₂ nanoparticles, or subjected to hydrothermal treatment and/or aging before drying for phase selective crystallization. The gel can also be processed to deposit thin films without drying which are calcined at desired temperatures later on. The most common precursor for sol-gel is titanium isopropoxide, $Ti(OCH(CH_3)_2)_4$ [49]. In another configuration, called the Pechini sol-gel process, a hydrocarboxylic acid, such as citric acid is used as a chelating agent to bind with Ti ions via two carboxyl groups and one hydroxyl group. A glycol is then added to form an organic ester. Heat-driven condensation and polymerization form gel [50]. Sol-gel synthesis is controlled by varying titanium precursor, organic additives, solution pH, hydrothermal/aging conditions, drying method, calcination temperature [51, 52].

Hydrothermal/solvothermal synthesis

In solvothermal synthesis Ti-alkoxide precursors are dissolved in organic solvents and a little amount of water is added for hydrolysis. The mixture is subjected to thermal treatment in autoclaves at elevated temperatures ($\approx 180-250$ °C) and times to induce crystallization [53, 54]. Hydrothermal synthesis follows a similar principle but uses only water as the solvent. Similar to sol-gel synthesis, the final product characteristics of TiO₂ can be manipulated by changing operating conditions.

Aqueous synthesis

Aqueous synthesis processes are based on forced hydrolysis of inorganic Ti salts in water to precipitate TiO_2 ; they are distinguished from sol-gel and solvothermal synthesis methods in that they only contain water-soluble chemicals. The hydrolysis of Ti precursor is often coupled with hydrothermal treatment to obtain the desired TiO_2 phases.

A significant part of this thesis is dedicated towards hydrolysis of $TiCl_4$, hence the principles of precipitation in a homogeneous, aqueous solution, hydrolysis of $TiCl_4$ and mechanism of crystallization into various TiO_2 phases is explained first, followed by a survey of literature on aqueous synthesis processes.

Forced hydrolysis

In general, precipitation of metal oxides from aqueous solutions can be achieved via addition of enough quantities of a base. However, precipitation conducted in this manner is so rapid that it is hard to obtain particles with uniform properties. The alternative approach is 'forced hydrolysis' whereby the first step is formation of metal hydroxides or oxyhydroxides, and in the second step these hydroxides are dehydrated or deprotonated to yield (hydrous) oxides [55]. Kinetic control of the formation of the intermediate species by controlling the solution conditions are leveraged to selectively synthesize different phases and to control other properties such as size, crystallinity etc.

In order to understand precipitation in aqueous solutions saturation is a fundamental concept. Saturation of a solute in a solution, S is defined as the ratio of the activity of solute in initial solution to the activity of the solute in equilibrium with solid (α/α_{eq}) ; generally it is taken to be the ratio of the respective concentrations (C/C_{eq}) . For precipitation reactions involving a chemical reaction, such as is the case with TiO₂, S is inversely proportional to the solubility product, K_{sp} , of the compound. When S>1, the solution is supersaturated and the compound will tend to precipitate out of the solution in solid form to reduce S. Thus, supersaturation provides the driving force for precipitation. It is also to be noted that K_{sp} is a function of various parameters such as temperature and pressure so the degree of supersaturation can be controlled via changing any of these parameters in addition to the amount of solute [56].

The formation of a solid compound in a solution is explained by the phenomenon of nucleation, growth and aggregation.

Homogeneous nucleation, growth & aggregation: In a supersaturated solution molecules join together to form clusters or embryos with 10-1000 molecules/cluster. Figure 2.9 presents a thermodynamic picture of this process. ΔG represents the free energy barrier that must be overcome for a crystal to form. The red curve represents the overall change in free energy such that

$$\Delta G = \Delta G_{volume} - \Delta G_{surface} \tag{2.5}$$

Where

$$\Delta G_{volume} = -n\Delta\mu \tag{2.6}$$

$$\Delta G_{surface} = 6\alpha n^{2/3} \tag{2.7}$$

When the size of the embryos is less than n^* , the change in the free energy associated with change in volume (ΔG_{volume}) is not large enough to overcome the change in the free energy associated with a change in surface area ($\Delta G_{surface}$), hence the change in free energy is positive and such embryos will not stabilize. However, when the size of the embryo (n) is greater than a critical size (n^{*}) further growth of the formed embryo results in decrease of ΔG ; hence such embryos or nuclei, as they are commonly referred to, are stabilized and grow in the solution. n^{*} represents the size of nucleus where the probability of growth and decay are equal and represents the critical size [56, 57].



Figure 2.9: Change in free energy during nucleation [57]

In aqueous solutions growth of particles occurs via aggregation, or attachment of molecules to nuclei. Nucleation and growth can be affected by changing factors such as the concentration of the colloid in the solution, shear forces acting on the solution, and ionic strength of the solution.

Figure 2.10 presents the famous LaMer diagram which explains the formation of monodispersed particles by separating the processes of particle nucleation and particle growth. In stage I no precipitation occurs since the concentration of solute (the hydrated metal cation) is too low and the solution is undersaturated. As the concentration builds up and eventually reaches the critical solute concentration, C^*_{min} , the solution enters a stage of supersaturation, and nucleation begins. In stage II, solute concentration increases for a short time and then decreases due to nucleation. When the concentration reaches C^*_{min} again nucleation stops and growth of nuclei begins. In stage III concentration decreases continuously until it reaches C_s , the equilibrium solution saturation at the given conditions.



Figure 2.10: LaMer's model for monodispersed particle formation [58]

Crystals, including TiO₂ often exist as multiple polymorphs. A number of such polymorphs are able to crystallize in a given system. As described, the driving force for crystallization is the decrease in free energy of the system. The attainment of the thermodynamic state with the lowest possible energy is however offset by the kinetic tendency of the system to relieve the supersaturation as soon as possible. Therefore, it is possible for a polymorph to crystallize in a phase that does not represent the lowest possible energy state, but the state which can be achieved quickly; its transformation to the most stable or the lowest energy state can happen later [59].

This classical nucleation theory relies on bulk energies to explain microscopic phenomena and in doing so it does not consider the intricacies of atomic arrangements in crystal structures. What follows is a survey of literature on precipitation of the three polymorphs of TiO_2 - anatase, brookite, and rutile - from perspective of crystal structures.

Aqueous synthesis of TiO₂

When TiCl₄ is slowly added to water at temperatures close to melting point of water abrupt hydrolysis and formation of TiO₂ is suppressed that would happen otherwise. Instead Ti ions exists as a coordinated octahedral species surrounded by OH^-/OH_2 complexes whereby the exact stoichiometry of the complex(es) is a function of solution conditions (initial Ti concentration, temperature, pH, additive ions, etc). For example, in solutions of TiCl₄ it is surmised that the complexed ion takes the form $Ti(OH)_aCl_b(OH_2)_c]^{(4-a+b)+}$ where a+b+c=6 and a and b are a functions of acidity and Cl^- concentration. Cécile Charbonneau compiled the possible forms of the complexes in a solution with Cl^- ions (reproduced as Figure 2.11) [60]. Links between neighboring octahedra are formed via olation reactions whereby dehydration occurs between -OH and -H₂O ligands along equatorial or apical edges [61]. The form of the complexed Ti ion in aqueous solutions governs these dehydration reactions and thus what phases are formed.

Yanqing *et al.* [62] proposed that species of the $[Ti(OH)_2(OH_2)_4]^{2+}$ form can lead to different structures because these species can undergo condensation along equatorial and apical edges, as are present in brookite and anatase crystals, whereas the species $[TiO(OH)_5]^{2+}$ can only share equatorial edges and hence form linear chains specific of rutile crystal (Figure 2.12). However, this explanation ignores the possibility that Cl⁻ ions might act as ligands.

Another way of explaining the formation of different phases from complexed Ti ions is by considering the fact that one edge-shared bond requires one dehydration reaction whereas one corner-shared bond requires two simultaneous dehydration reactions to occur. Under high pH conditions there is an excess of -OH ligands favoring edge-shared bonds and hence anatase and/or brookite crystallization. Whereas under low pH conditions corner-sharing bonds are favoring leading to rutile synthesis [63, 64].

Charbonneau and co-workers pioneered a simple method by conducting forced hydrolysis of TiCl₄ in 200 mL water at 80 °C and produced 4-5 nm anatase nanoparticles with 0.1 M TiCl₄ in 30 minutes [65], and \approx 300 nm rutile particles with 0.5 M TiCl₄ in 2 hours [66]. Reyes-Coronado *et al.* [38] explored the effect of HCl concentration on phase formation. They postulated that under 3 M HCl Ti(IV) exists as [Ti(OH)₂Cl(OH₂)₃]⁺. With more availability of Cl⁻ ions with increasing HCl concentration the complexed ion has more Cl⁻ ligands and evolves into [Ti(OH)₂Cl₄]²⁻. The former is an asymmetric chloro-complex which leads to formation of brookite while the latter serves as the monomer for the more symmetric rutile crystals. Such strong dependence of brookite/rutile formation on Cl⁻/Ti(IV) concentration is also reported by Cassaignon *et al.* who claimed that



Figure 2.11: Ti-Cl- H_2O species present in aqueous systems [60]

brookite is obtained under $17 < [Cl^-]/[Ti(IV)] < 34$ [67]. Cassaignon *et al.* further explored the effect on phase selectivity in presence of nitric acid. They observed that anatase is the first phase to appear after 24 hour of thermolysis and that after a week, rutile is the main phase in the presence of ≈ 1 M HNO₃, while for HNO₃ ≥ 3 M brookite is stabilized. TiO₂ exhibits low solubility in nitric acid discouraging dissolution-recrystallization and hence the transformation to rutile.

As is mentioned previously, brookite is the most difficult material to synthesize without residual anatase and/or rutile - most studies report brookite is prepared under 'intermediate' pH conditions. Jiao *et al.* [68] suggested that brookite synthesis occurs in presence of a strong base such as NaOH, catalyzed by the interaction of Na⁺ ions. Thus they employed NaCl as an additive during hydrothermal treatment of titanate and observed pure brookite at 0.5 M NaCl after hydrothermal treatment of 72 hours at 180 °C. On the other hand Li *et al.* [40] synthesized brookite particles measuring \approx 154 nm using dilute solution of TiCl₃ in the presence of urea at 70 °C.

Sulfate ions (SO_4^{2-}) show an affinity for the positive Ti(IV) ions and has been observed



Figure 2.12: (a) Possible crystallization pathway for rutile starting with octahedral cation $[TiO(OH_2)_5]^{2+}$ (b) Possible crystallization pathway for anatase or brookite starting with octahedral cation $[Ti(OH_2(OH_2)_4]^{2+}$ [62]

to catalyze anatase crystallization pathway. The adsorption of SO_4^{2-} ions on TiO₂ also prevents agglomeration [64, 69–71]. However, in another study using 1 M Ti(SO₄)₂ and 2 M NaOH solution, and adjusting the pH through addition of H₂SO₄ or NaOH, it was found that for pH 10-11.35 pure brookite could be produced without any anatase, while pure anatase was produced at pH 5. The authors in this case did not consider the possible role of Na⁺ and/or SO₄²⁻ ions [72].

Finally, some studies aim to synthesize crystalline TiO_2 , particularly anatase, with certain crystal planes exposed in favor of increased reactivity [73–76]; while another popular area deals with composite and/or doped structures [77–79] but these are outside the scope of the present study.

2.4 TiO₂ film in DSSC photoanode

Nano-TiO₂ properties and synthesis have been discussed previously in sections 2.3.1, and 2.3.2. Once the TiO₂ nanoparticles are obtained, whether in form of dry powder or colloidal suspension, the next step is fabrication of mesoporous films onto transparent conductive glass to serve as the photoanode in DSSCs [80]. A typical procedure entails deposition of the TiO₂ nanoparticles on the conductive substrate, usually fluorine-doped tin oxide (FTO) glass, followed by sintering at elevated temperatures (450 - 500°C) to achieve sintering/necking of individual particles and evaporate/decompose the paste components [81, 82].

Formation of a TiO₂ compact layer on the FTO substrate before deposition of TiO₂ nanoparticles, and afterwards on the sintered TiO₂ film is a common practice. The former acts as a barrier between the substrate and electrolyte to prevent short circuit. The latter also contributes to improved photovoltaic performance although the exact reason is unclear [83]. Photoanode films are desired to have high surface area, high porosity (50-60%), less roughness, good necking between the particles, good adhesion to glass substrate, be crack-free, and have average thickness between 8-12 μ m [2, 21, 82, 84].

Large surface area is paramount to DSSC efficiency and the principle of achieving

a high surface area, >100 m²/g via use of sintered nanoparticles is the distinguishing characteristic of DSSCs. Films with TiO₂ nanoparticles measuring 20-25 nm are deemed suitable to possess high enough surface area for effective dye loading. Anatase is the phase of choice due to small particle size (inferring high surface area for dye adsorption), and high bandgap. The commercial Dyesol 18NRT has anatase particles \approx 20 nm in size. However, the scale of the particles renders the film transparent to light and hence light scattering is introduced to harvest a higher percentage of photons. Rutile particles, on account of high refractive index and larger size are incorporated for this purpose. Light scattering is introduced by either having the light scattering particles embedded within the film, or by introducing a separate layer deposited atop the transparent film. In a highly common architecture, layers of anatase are overlaid with layers of rutile particles, so the photons transmitted through the transparent anatase are reflected by the rutile particles back into the film increasing the chances of adsorption. The larger scattering particles are not good candidates as the active particles due to low surface area leading to low dye adsorption.

The optimum thickness of transparent and scattering layers is 12 μ m and 5-7 μ m respectively. Thin films have lower light scattering and suffer from leakage of electrons to the triiodide electrolyte. However, beyond the optimum thickness, electrons have a longer path length and hence they suffer from high series resistance. High charge transfer resistance and limitations in the permeation of the dye and electrolyte throughout the films have the effect of decreasing V_{oc} [82, 85, 86].

Presence of large aggregates leads to non-uniform and/or cracked films increasing recombination between photoinduced electrons and the triiodide electrolyte and thus decreases DSSC efficiency [87]. Extended cracks lead to low shunt resistance and thus reduced photocurrent [82]. In order to fabricate crack-free films with large surface area, Miranda and Chianese [88] used colloids with bimodal distribution of particles, measuring 5 nm and 50-100 nm, and found the efficiency to increase up to 70% compared to cells assembled with a narrow range of particles.

Raj et al. [15] researched the photovoltaic properties of three different TiO_2 particle

size based DSSCs - 9 nm, 20 nm, and 400 nm; they found 9 nm particles to yield the highest efficiency, attributed to improved photoelectron injection due to higher dye loading. On the other hand, the 400 nm based cells yielded the highest open-circuit voltage, due to reduced electron path length leading to less recombinations.

Distribution of TiO₂ nanoparticle size can also influence interconnection between particles and particles and substrate [89]. Lee *et al.* [90] fabricated one-layer hybrid photoanodes with anatase nanoparticles and rutile particles with 'sea urchin'-like morphology measuring 5-6 μ m in thickness and obtained 7.04%.

Hore *et al.* [91] introduced TiO_2 spherical voids measuring 200 nm by dispersing carboxyl stabilized polystyrene spheres in TiO_2 colloidal paste. They exhibited that the hollow spheres acted as light scattering centres leading to increased short-circuit current and hence efficiency compared against films without spherical voids, or with solid spherical scattering centres. In a similar approach of exploiting voids in the film, Li et al. [92] synthesized anatase hollow spheres measuring 1-1.4 μ m using a solvothermal method followed by their deposition as TiO_2 film. The resulting films yielded 11% - higher photovoltaic efficiency than the benchmark Dyesol-18NRT, owing to its light scattering capability. In another study Yu et al. [93] studied the presence of both solid nanoparticles (P25) and hollow spheres in different permutations. They concluded that hollow spheres deposited atop solid nanoparticles yielded the highest efficiency since it exploited the scattering abilities of the hollow spheres and the robust electron path connectivity of the underlying TiO_2 particles. In yet another design the photoanode comprises of a layer of titanate nanobelts covering two layers of 5-20 nm TiO_2 particles where the nanobelts act as a barrier to transmitted light and reflect it back, thus improving the device photovoltaic performance [94].

Cheng and co-workers synthesized sub-micron sized, mesoporous anatase beads and conducted a variety of studies on their functionality in the photoanode. In one study [83], three different bead diameters - 320, 550, and 830 nm - were used in individual working electrodes (no separate scattering layer) and it was observed that the highest bead diameter generated the highest photovoltaic efficiency at 9%, owing to high open-circuit voltage. The smallest bead constituting photoanodes possess the highest dye loading, yet the highest short circuit current is observed for medium-sized beads. The dominating behaviour in these photoanodes is the electron diffusion in the TiO_2 film which is highest for the largest beads on account of least number of contact points between neighboring beads. In a second study [95] they used the beads measuring 830 nm as scattering layer over transparent anatase layer. This layer serves the dual purpose of acting as scattering particles due to their large size, as well as offering large surface area for dye adsorption attributed by the porosity of the beads. Moreover, photons can enter the bead layer and be scattered within and enable electron excitation, resulting in a relative increase in photovoltage and photocurrent.

2.4.1 Sintering

Sintering of nanoparticles is critical as it ensures electromechanical bonding, improves crystallinity, and decreases the surface area to maximize electron diffusion length [89]. Sintering rate has to be slow to allow for crack-free films [19].

Zhao *et al.* analyzed the EIS performance of films annealed at temperatures in the range 350 - 600 °C and concluded that sintering at 500 °C yields the highest efficiency. The authors present the case that annealing decreases the density of surface states, and hence decreases the acceptance of photoinjected electrons by the dye/electrolyte species, ultimately increasing the photovoltaic efficiency. On the other hand annealing at 600 °C is believed to lead to collapse of the microstructure giving rise to new surface states and hence increasing the frequency of interfacial recombination [96].

Thermal treatment at low temperatures $\approx 150^{\circ}$ C is not enough to eliminate organic constituents and their residual limits electron diffusion through the cells adversely affecting light-to-current efficiency [19]. Research studies have also attempted at achieving appropriate paste viscosity (see Section 2.4.4) by exploiting acid-base chemistry to avoid high temperature sintering and enable film printing on polymer substrates. Park *et al.* [81] added ammonium hydroxide NH₄OH solution to TiO₂ colloidal solution prepared with titanium tetraisopropoxide and acetic acid, in order to regulate the viscosity. Presence of positively charged ammonium, and negatively charged acetate ions caused flocculation of TiO_2 particles, and hence an increase in viscosity. However, the photovoltaic efficiency of the assembled DSSCs was 2.55%, due to insufficient necking between TiO_2 particles. We erasinghe *et al.* [97] controlled the viscosity of ethanolic suspension of P25 powder by adding HCl which reduces the electrical double layer on TiO_2 particles. Low temperature sintering (150°C) is not enough to achieve interparticle necking; films treated this way are only connected via Ti-O-Ti bridges formed by dehydration of surface hydroxyl groups [19].

2.4.2 Effect of porosity and surface area

 TiO_2 photoanode films must have a high surface area to allow sites for dye adsorption, and big pores for adequate permeation of dye and electrolyte. Higher porosity or large pore size entails less TiO₂ per unit volume decreasing the surface area available for dye adsorption and lowering photogenerated current. Hence surface area and porosity have to be balanced to optimize solar cell efficiency. Barbé et al. [98] reported that for films with similar surface area, in films with smaller pores ≈ 4 nm, the solar efficiency decreased upon full illumination of the cell - faster dye oxidation could not be replenished by the electrolyte due to slow diffusion in the smaller pores, whereas there was no adverse effect in films with larger pores. Hence, sintering of the films at higher temperatures (> 400)°C) is imperative to decrease the number of small pores. However, in the same study the authors also reported that films with too much porosity suffer from a lack of high current generation due to less dye adsorption as expected. Hsiao et al. [99] made two pastes, one with PEG to act as the dispersant, and one without. They showed that the paste with PEG yielded sintered films with higher surface area, 81.6 m^2/g vs. 68.07 m^2/g . The resultant DSSCs had similar V_{oc} and FF, but the former had 32.3% higher J_{sc} , leading to a higher efficiency at 6.23 % vs. 4.66%. Zhao *et al.* [100] showed that at the optimum porosity, high charge transfer and low TiO₂/electrolyte interfacial recombination are observed. They also demonstrated that charge transfer characteristics of films with porosity higher than the optimum are similar to films with no porosity.

2.4.3 TiO₂ photoanode fabrication via screen printing

Photovoltaic performance of DSSCs is strongly dependent on the optical and electronic properties, and the surface morphology and microstructure of the TiO_2 films [82]. This is determined by the nature of the particles, as well as the process of film fabrication. A number of techniques are in use, such as doctor blading [101], screen printing [85], electrophoretic deposition [102], roll-to-roll manufacture [103], spray pyrolysis [104], and spin coating [105].

Similar to synthesis of nanosize TiO_2 as discussed earlier, large-scale economic printing of TiO_2 photoanodes is also crucial for commercial applications. Screen printing is one such industrially preferable, and reproducible method of homogeneous film deposition with the ability to cover large areas and control film thickness [80, 82].

Screen printing requires the TiO_2 nanocrystals to be dispersed homogeneously in a viscous paste with 10-20% TiO_2 loading to allow for deposition of thick films. The paste is deposited on glass substrate through a screen of the desired mesh size by the motion of a squeegee. The angle, speed, and pressure of the squeegee can be manipulated to change the film properties. The photovoltaic performance of the DSSCs is a function of the screen-printing parameters as well as the chemical constituents of the paste formulation.

2.4.4 Paste formulation

The paste formulation for screen printing is designed to be shear-thinning whereby the paste viscosity decreases under application of pressure during screen printing. Moreover, the paste should level after printing so as not to leave the screen imprint and form a uniform film.

The essential components in a paste formulation are acid, rheological agent, and binder dissolved in an organic solvent. The acid, such as acetic acid, when added to the paste is adsorbed on the surface of TiO_2 nanoparticles and prevents aggregation through electrostatic repulsion between neighboring particles. Without the addition of acid, TiO_2 forms bigger aggregates which undergo large shrinkage upon sintering and cause large cracks and peeling-off of the films [85]. Rheological agent is added to regulate the viscosity of the paste; α -terpineol by far is the most common rheological agent as it also contributes towards long-term stability of the paste [85, 89]. The binder, for example, ethyl cellulose or polyethylene glycol (PEG), provides a continuous phase holding everything together. It affects viscosity during sintering and provides mechanical stability to the printed films. Upon sintering, the binder evaporates away leaving pores, and hence directly impacts the microstructure, surface area, and pore distribution of films [21, 82, 87, 89, 99]. While less binder amount results in small pores and less surface area available for dye adsorption, and leads to cracks due to reduced strength, films with excess binder tend to collapse during sintering. Therefore optimized proportion of binder in the paste is necessary for good DSSC efficiency [82, 89]. Chemical bonds between TiO₂ particles and between TiO₂ and the SnO₂ glass substrate during sintering are formed by dehydration of surface hydroxyl groups (-OH); therefore it is essential that the particles either have adsorbed hydroxyl groups by virtue of the synthesis process or addition of water during paste making [85].

The first report of screen printing TiO₂ paste [106] employed ethanolic solution of ethyl cellulose, α -terpineol, and nitric acid, dissolved in ethanol, to print film with final thickness of 18 μ m, and remains the most commonly used protocol for paste fabrication. However, research has been conducted on other compatible functional organic chemicals too. Xu *et al.* [87] employed Triton-X to provide steric and electrostatic repulsion between titania, and acetylacetone as the dispersant, dissolved in ethanol. Tasić *et al.* [21] used stearic acid, PEG MW 1K-20K as binder, PEG MW: 200 as plasticizer, α -terpineol and isopropanol as solvent and found that average particle size of sintered particles decreased with an increase in PEG molecular weight. Fan *et al.* [82] employed both PEG MW: 20000 and ethyl cellulose to increase viscosity and induce porosity, 4hydroxy-benzoic acid and acetylacetone to prevent aggregation of TiO₂ nanoparticles and to improve mechanical stability of the films, and terpineol as dispersant. Ma *et al.* [80] fabricated a P25 paste with only PEG 600 and ethanol. A number of researchers employ an integrated approach towards the process, adding the necessary constituents during colloidal synthesis. For example, Krašovec *et al.* [107] followed the Pechini sol-gel method to form colloidal titania and added commercial TiO₂ to obtain viscosity suitable for doctor blading. Calderon-Moreno *et al.* [108] used tetraethyl-orthotitanate Ti(OC₂H₅)₄, ethanol, water, and nitric acid as precursors for sol-gel and researched the effect of adding PEG of variable molecular weight - 6000, 20 000, and 35 000 to the colloidal solution. The films incorporating MW: 6000, and 20,000 possessed pores with diameters around 20-80 nm and 100-400 nm respectively, whereas 35 000 MW film had cracked areas with irregular voids. The diameter of PEG 35,000 compared to the film thickness causes pressure build-up in cavities left by PEG 35,000 during sintering. Therefore, PEG 20,000 is the most commonly used PEG for TiO₂ pastes in DSSCs applications. In PEG, MW: 600, 1000, and 2000 the polymer chain lengths are too small to form a stable polymeric template [21, 82].

Literature survey of paste formulations quickly reveals that they intensively incorporate organic constituents and solvents. Water based pastes, although environmentally preferable, are deemed unsuitable for screen printing because the water based paste is repelled by the hydrophobic glass substrate, and high surface tension of water induces cracking into the films during sintering [80]. For the same reason, ethanol is deemed a suitable solvent due to low surface tension which yields smooth and compact films upon sintering [87].

2.5 CZTS

 Cu_2ZnSnS_4 - commonly referred to as CZTS - is a quaternary semiconductor. Aside from its photovoltaic properties, it is preferable over materials currently employed in large-scale photovoltaic devices, such as cadmium telluride (CdTe), copper indium selenium (CIS), copper indium gallium selenium (CIGS), gallium arsenide (GaAs), by virtue of the presence of earth abundant materials as opposed to indium and tellurium, and excludes non-toxic elements such as cadmium and arsenic. Moreover, due to similarities between optical and electronic properties of CZTS and CIGS knowledge and expertise of CIGS



Figure 2.13: Crystal structures of (a) stannite, and (b) kesterite [111]

based solar technology can be used [109].

2.5.1 CZTS crystal structure

 Cu_2ZnSnS_4 is I₂-II-IV-VI₄ compound derived from the structure of $CuInS_2$ (I-III-VI₂) via replacement of In with Zn and Sn. CZTS crystals can take two stable forms, stannite and kesterite presented in Figure 2.13 [110]. The main difference between the two crystal structures is that in the kesterite structure cation layers of CuSn and CuZn alternate while in the stannite structure, ZnSn layers alternate with Cu_2 layers [111]. CZTS kesterite phase is of interest as light absorbing material in photovoltaics.

2.5.2 CZTS properties

CZTS is a p-type semiconductor with direct bandgap between 1.4-1.6 eV [112–114]. The bandgap value can be tuned by varying the elemental stoichiometry of the thin films. Malerba *et al.* [115] observed that the bandgap energy has almost no dependence on zinc amount while as the [Sn]/[Cu] ratio is increased in CZTS thin films from 1.11 to 1.14, the band-gap energy shows an abrupt increase from 1.48 eV to 1.63 eV. In addition,

CZTS films have absorption coefficients of 10^4 - 10^5 [112, 113]. The suitable bandgap and high absorption coefficient make the theoretical conversion efficiency of CZTS solar cells at 32.2% [116] making it a desirable material for thin film solar cells.

2.5.3 CZTS in photovoltaics

CZTS has demonstrated a variety of functional roles in photovoltaics. CZTS nanoparticles have been adsorbed on TiO₂ as alternative to organometallic light sensitizers in DSSCs [117, 118]. CZTS nanosheet and nanoparticle structures have been deposited on FTO glass to serve as counter-electrode in DSSCs [119, 120]. However, as mentioned previously, the most extensive research has been conducted on use of CZTS thin films in 2nd generation solar cell architecture as a replacement to CIGS. It is also a very common practice to increase V_{oc} by introducing selenium to yield films of $Cu_2ZnSn(S_{1-x},Se_x)_4$ form with $S/(S+Se) \approx 0.4$ since the addition of selenium lowers the bandgap. However environmental concerns discourage the use of selenium [121, 122].

Experiments have shown CZTS thin films with the stoichiometry $Cu/(Zn+Sn) \approx 0.8$, and $Zn/Sn \approx 1.22$ to yield high efficiency solar cells. Cu-poor composition prevents formation of $Cu_{2-x}S$ and CuSnS phases and also compensates for Sn loss that occurs during annealing (discussed later in Section 2.5.4) [115, 123]. Moreover, Cu-poor composition enhances the formation of Cu vacancies, which gives rise to shallow acceptors in CZTS and simultaneously Zn-rich composition suppresses the substitution of Cu in Zn sites, which results in relatively deep acceptors [124].

2.5.4 CZTS synthesis

CZTS thin film fabrication is a two-step process: firstly, elemental precursors or CZTS nanoparticles are deposited on substrate at low temperatures (< 200 °C), followed by annealing at elevated temperatures (500-600 °C) aimed at nucleation or grain growth of nanoparticles, and densification of the film to reduce defects and voids [125]. Being a quaternary semiconductor, synthesis of CZTS poses the challenge of appearance of secondary and tertiary compounds including, but not limited to CuS, Cu₂S, ZnS, SnS₂,

and Cu_2SnS_3 . A second major concern is posed by decomposition of CZTS yielding SnS and S_2 which are volatile at high temperatures. Thus, under vacuum the volatile species can be removed from the CZTS film disturbing the starting elemental stoichiometry. Hence, it is common practice to conduct annealing in the presence of excess sulphur powder or gases such as H_2S [126, 127] - the process is termed as 'sulfurization'.

The first step of elemental deposition is done either using vacuum-based, or solutionbased approaches. The former include techniques such as pulse-layer deposition [128], sputtering [129], and thermal evaporation [130]. However all these methods require expensive and specialized equipment forcing researchers to exploit the soft chemistry route offered by solution based methods.

Solution-based methods

CZTSSe (Cu₂ZnSn(S,Se)₄) synthesis via use of hydrazine as a solvent has yielded by far the highest photovoltaic efficiency at 12.6% [131]. In one study, the precursors including Cu₂S-S (Cu₂S powder and elemental sulfur), SnSe₂-Se (SnSe₂ powder and elemental selenium), and metallic zinc powder were dissolved in hydrazine. Since the copper and tin species are soluble in hydrazine, they readily form a complex Cu₂Sn(Se,S)₃, which then reacts with Zn(Se,S) to form Cu₂SnZn(Se,S)₄. Such straightforward pathway bypasses the formation of secondary phases, as encountered in other synthesis methods [125]. However, hydrazine is a highly toxic and explosive chemical requiring extreme caution in handling and storage, hence necessitating further research in solution-based methods to bypass its use.

Camara *et al.* [132] implemented a straight-forward approach by subjecting an aqueous solution of $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$, ZnCl_2 , $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ and $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ to hydrothermal treatment at 230 °C for 24 hours to synthesize CZTS nanoparticles, and fabricated thin films via spin-coating. Successive ionic layer adsorption-reaction - SILAR - is a solution deposition method whereby the desired substrate is immersed in separate anionic and cationic solutions successively for a number of cycles. This method allows thickness to be controlled down to 1 nm and results in uniform deposition of thin sulfide layers. Kahraman et al. [123] used CuCl₂, SnCl₂ and Na₂S \cdot 9 H₂O solutions to fabricate Cu₂SnS₃ layers, alternatively stacked with ZnS layers deposited with $ZnCl_2$ and $Na_2S \cdot 9H_2O$ layers. The films were annealed at 500 °C for 2 hours in the presence of elemental sulfur. Wangperaong et al. [133] deposited SnS_x films in a chemical bath, followed by ZnS deposition. After heat treatment the substrates were placed in an aqueous bath containing Cu⁺ ions. Diffusion of the sulfides is achieved through sulfurization treatment. Furthermore KCN treatment was conducted to dissolve excess $Cu_{2-x}S$. Wang et al. [134] used acetate salts of copper and zinc, tin chloride, and thioacetamide as the precursors and ammonia to maintain neutral pH in a hydrothermal treatment conducted at 200 $^{\circ}\mathrm{C}$ for 24 hours. They observed that affinity of ammonia towards Cu^{2+} and Zn^{2+} and its effect on release of S_2^- ions from thioacetamide suppresses growth of CZTS nanoparticles as well as discourages aggregation resulting in average particle size of 12 nm without the use of organic surfactants or hydrazine. Emrani et al. [135] subjected films to annealing temperatures 500-600 °C and measured the bandgap to increase from 1.5 eV at 550 °C to 1.59 eV at 525 °C. They concluded that annealing at 550°C yields the best photovoltaic performance with 5.75% efficiency. While films annealed at lower temperatures suffer from poor compactness and presence of voids, at higher temperatures the films are too rough giving rise to recombination centres.

Another solution based technique is electrochemical deposition of CZTS thin films. The copper, zinc, and tin metals are electrodeposited in subsequent layers followed by sulfurization. Another one-step way is to co-deposit all the elements from an electrolytic solution, although it is difficult to synthesize uniform and crystalline films with this method [136]. Lastly, in spray pyrolysis aqueous solution precursors are sprayed on a hot substrate. By carefully controlling the sputtering rate and substrate temperature, sulfurization can be bypassed [137].

2.6 References

- B. O'Regan and M. Grätzel. "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films". In: *Nature* 353.6346 (1991), pp. 737–740.
- [2] M. Grätzel. "Photoelectrochemical cells". In: Nature 414.6861 (2001), pp. 338–344.
- [3] NREL. Best Research-Cell Efficiencies. 2015. URL: http://www.nrel.gov/ncpv/.
- [4] F. De Angelis, S. Fantacci, E. Mosconi, M. K. Nazeeruddin, and M. Grätzel.
 "Absorption spectra and excited state energy levels of the N719 dye on TiO₂ in dye-sensitized solar cell models". In: *The Journal of Physical Chemistry C* 115.17 (2011), pp. 8825–8831.
- [5] J. Archana, M. Navaneethan, and Y. Hayakawa. "Solvothermal growth of high surface area mesoporous anatase TiO₂ nanospheres and investigation of dyesensitized solar cell properties". In: *Journal of Power Sources* 242 (2013), pp. 803– 810.
- [6] H. J. Snaith. "Perovskites: the emergence of a new era for low-cost, high-efficiency solar cells". In: *The Journal of Physical Chemistry Letters* 4.21 (2013), pp. 3623–3630.
- H.-L. Hsu, C.-F. Tien, and J. Leu. "Effect of pore size/distribution in TiO₂ films on agarose gel electrolyte-based dye-sensitized solar cells". In: *Journal of Solid State Electrochemistry* 18.6 (2014), pp. 1665–1671.
- [8] S. Li, L. Qiu, C. Shi, X. Chen, and F. Yan. "Water-resistant, solid-state, dyesensitized solar cells based on hydrophobic organic ionic plastic crystal electrolytes". In: Advanced Materials 26.8 (2014), pp. 1266–1271.
- [9] H. Choi, H. Kim, S. Hwang, W. Choi, and M. Jeon. "Dye-sensitized solar cells using graphene-based carbon nano composite as counter electrode". In: *Solar Energy Materials and Solar Cells* 95.1 (2011), pp. 323–325.

- [10] H. Anwar, A. E. George, and I. G. Hill. "Vertically-aligned carbon nanotube counter electrodes for dye-sensitized solar cells". In: *Solar Energy* 88 (2013), pp. 129–136.
- [11] M. Wang, A. M. Anghel, B. Marsan, N.-L. Cevey Ha, N. Pootrakulchote, S. M. Zakeeruddin, and M. Grätzel. "CoS supersedes Pt as efficient electrocatalyst for triiodide reduction in dye-sensitized solar cells". In: *Journal of the American Chemical Society* 131.44 (2009), pp. 15976–15977.
- [12] Z.-S. Wang, H. Kawauchi, T. Kashima, and H. Arakawa. "Significant influence of TiO₂ photoelectrode morphology on the energy conversion efficiency of N719 dye-sensitized solar cell". In: *Coordination Chemistry Reviews* 248.13 (2004), pp. 1381–1389.
- [13] H. J. Snaith. "How should you measure your excitonic solar cells?" In: Energy & Environmental Science 5.4 (2012), pp. 6513–6520.
- [14] X. Yang, M. Yanagida, and L. Han. "Reliable evaluation of dye-sensitized solar cells". In: *Energy & Environmental Science* 6.1 (2013), pp. 54–66.
- C. J. Raj, S.-K. Kim, K.-H. Yu, and H.-J. Kim. "Photo-electrochemical properties of variously-sized titanium dioxide nanoparticle-based dye-sensitized solar cells". In: *Materials Science in Semiconductor Processing* 26 (2014), pp. 354–359.
- [16] A. Zaban, M. Greenshtein, and J. Bisquert. "Determination of the electron lifetime in nanocrystalline dye solar cells by open-circuit voltage decay measurements". In: *ChemPhysChem* 4.8 (2003), pp. 859–864.
- [17] Q. Wang, J.-E. Moser, and M. Grätzel. "Electrochemical impedance spectroscopic analysis of dye-sensitized solar cells". In: *The Journal of Physical Chemistry B* 109.31 (2005), pp. 14945–14953.
- Q. Wang, S. Ito, M. Grätzel, F. Fabregat-Santiago, I. Mora-Sero, J. Bisquert,
 T. Bessho, and H. Imai. "Characteristics of high efficiency dye-sensitized solar cells". In: *The Journal of Physical Chemistry B* 110.50 (2006), pp. 25210–25221.

- [19] J. H. Yune, I. Karatchevtseva, G. Triani, K. Wagner, and D. Officer. "A study of TiO₂ binder-free paste prepared for low temperature dye-sensitized solar cells". In: Journal of Materials Research 28.03 (2013), pp. 488–496.
- [20] N. P. Benehkohal. "Innovations in Electrophoretic Deposition of Nanotitania-based Photoanodes for Use in Dye-sensitized Solar Cells". PhD thesis. McGill University, 2013.
- [21] N. Tasić, Z. Branković, Z. Marinković-Stanojević, and G. Branković. "Effect of binder molecular weight on morphology of TiO₂ films prepared by tape casting and their photovoltaic performance". In: Science of Sintering 44.3 (2012), pp. 365–372.
- [22] M. Sussman, N. Brodusch, R. Gauvin, and G. Demopoulos. "Binder-free fabrication of nanotitania/carbon lithium-ion intercalation electrodes". In: *Journal of The Electrochemical Society* 160.5 (2013), A3100–A3107.
- [23] V. Galstyan, E. Comini, G. Faglia, and G. Sberveglieri. "TiO₂ nanotubes: recent advances in synthesis and gas sensing properties". In: *Sensors* 13.11 (2013), pp. 14813–14838.
- [24] A. Kahouli, C. Marichy, A. Sylvestre, and N. Pinna. "Anomalous CV response correlated to relaxation processes in TiO₂ thin film based-metal-insulator-metal capacitor: Effect of titanium and oxygen defects". In: *Journal of Applied Physics* 117.15 (2015), p. 154101.
- [25] I. Fukuda, Y. Hirabayashi-Ishioka, I. Sakikawa, T. Ota, M. Yokoyama, T. Uchiumi, and A. Morita. "Optimization of enrichment conditions on TiO₂ chromatography using glycerol as an additive reagent for effective phosphoproteomic analysis". In: *Journal of Proteome Research* 12.12 (2013), pp. 5587–5597.
- [26] J. Henych, V. Stengl, M. Kormunda, A. Mattsson, and L. Osterlund. "Role of bismuth in nano-structured doped TiO₂ photocatalyst prepared by environmentally benign soft synthesis". In: *Journal of Materials Science* 49.9 (2014), pp. 3560–3571.

- Y. Enami, B. Yuan, M. Tanaka, J. Luo, and A.-Y. Jen. "Electro-optic polymer/TiO₂ multilayer slot waveguide modulators". In: *Applied Physics Letters* 101.12 (2012), p. 123509.
- [28] A. Beltran, L. Gracia, and J. Andres. "Density functional theory study of the brookite surfaces and phase transitions between natural titania polymorphs". In: *The Journal of Physical Chemistry B* 110.46 (2006), pp. 23417–23423.
- [29] U. Diebold. "The surface science of titanium dioxide". In: Surface Science Reports 48.5 (2003), pp. 53–229.
- [30] S.-D. Mo and W. Ching. "Electronic and optical properties of three phases of titanium dioxide: Rutile, anatase, and brookite". In: *Physical Review B* 51.19 (1995), p. 13023.
- [31] H. Zhang and J. F. Banfield. "Understanding polymorphic phase transformation behavior during growth of nanocrystalline aggregates: insights from TiO₂". In: *The Journal of Physical Chemistry B* 104.15 (2000), pp. 3481–3487.
- [32] M. Ranade, A. Navrotsky, H. Zhang, J. Banfield, S. Elder, A. Zaban, P. Borse,
 S. Kulkarni, G. Doran, and H. Whitfield. "Energetics of nanocrystalline TiO₂". In: Proceedings of the National Academy of Sciences 99.suppl 2 (2002), pp. 6476–6481.
- [33] T. A. Kandiel, L. Robben, A. Alkaim, and D. Bahnemann. "Brookite versus anatase TiO₂ photocatalysts: phase transformations and photocatalytic activities". In: *Photochemical & Photobiological Sciences* 12.4 (2013), pp. 602–609.
- [34] M. Kapilashrami, Y. Zhang, Y.-S. Liu, A. Hagfeldt, and J. Guo. "Probing the optical property and electronic structure of TiO₂ nanomaterials for renewable energy applications". In: *Chemical Reviews* 114.19 (2014), pp. 9662–9707.
- [35] M. Landmann, E. Rauls, and W. Schmidt. "The electronic structure and optical response of rutile, anatase and brookite TiO₂". In: *Journal of Physics: Condensed Matter* 24.19 (2012), p. 195503.

- [36] N. Satoh, T. Nakashima, K. Kamikura, and K. Yamamoto. "Quantum size effect in TiO₂ nanoparticles prepared by finely controlled metal assembly on dendrimer templates". In: *Nature Nanotechnology* 3.2 (2008), pp. 106–111.
- [37] P. Zhao, P. Cheng, B. Wang, S. Yao, P. Sun, F. Liu, J. Zheng, G. Lu, et al. "Bilayered photoanode from rutile TiO₂ nanorods and hierarchical anatase TiO₂ hollow spheres: a candidate for enhanced efficiency dye sensitized solar cells". In: *RSC Advances* 4 (2014), pp. 64737–64743.
- [38] D. Reyes-Coronado, G. Rodriguez-Gattorno, M. Espinosa-Pesqueira, C. Cab, R. De Coss, and G. Oskam. "Phase-pure TiO₂ nanoparticles: anatase, brookite and rutile". In: *Nanotechnology* 19.14 (2008), p. 145605.
- [39] D. C. Cronemeyer. "Electrical and optical properties of rutile single crystals". In: *Physical Review* 87.5 (1952), p. 876.
- [40] J.-G. Li, C. Tang, D. Li, H. Haneda, and T. Ishigaki. "Monodispersed spherical particles of brookite-type TiO₂: synthesis, characterization, and photocatalytic property". In: *Journal of the American Ceramic Society* 87.7 (2004), pp. 1358– 1361.
- [41] M. Koelsch, S. Cassaignon, J. Guillemoles, and J. Jolivet. "Comparison of optical and electrochemical properties of anatase and brookite TiO₂ synthesized by the sol–gel method". In: *Thin Solid Films* 403 (2002), pp. 312–319.
- [42] T. Nishide, M. Sato, and H. Hara. "Crystal structure and optical property of TiO₂ gels and films prepared from Ti-edta complexes as titania precursors". In: *Journal of Materials Science* 35.2 (2000), pp. 465–469.
- [43] J. L. H. Chau, Y.-M. Lin, A.-K. Li, W.-F. Su, K.-S. Chang, S. L.-C. Hsu, and T.-L. Li. "Transparent high refractive index nanocomposite thin films". In: *Materials Letters* 61.14 (2007), pp. 2908–2910.
- [44] W. Y. Teoh, L. Mädler, D. Beydoun, S. E. Pratsinis, and R. Amal. "Direct (one-step) synthesis of TiO₂ and Pt/TiO₂ nanoparticles for photocatalytic miner-

alisation of sucrose". In: *Chemical Engineering Science* 60.21 (2005), pp. 5852–5861.

- [45] N. Sobti, A. Bensouici, F. Coloma, C. Untiedt, and S. Achour. "Structural and photoelectrochemical properties of porous TiO₂ nanofibers decorated with Fe₂O₃ by sol-flame". In: *Journal of Nanoparticle Research* 16.8 (2014), pp. 1–10.
- [46] H. K. Kammler, L. M\u00e4dler, and S. E. Pratsinis. "Flame synthesis of nanoparticles".
 In: Chemical Engineering & Technology 24.6 (2001), pp. 583–596.
- [47] X. Chen and S. S. Mao. "Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications". In: *Chemical Reviews* 107.7 (2007), pp. 2891– 2959.
- [48] X. Wang, Z. Li, J. Shi, and Y. Yu. "One-dimensional titanium dioxide nanomaterials: nanowires, nanorods, and nanobelts". In: *Chemical Reviews* 114.19 (2014), pp. 9346–9384.
- [49] M. S. Ghamsari, S. Radiman, M. A. A. Hamid, S. Mahshid, and S. Rahmani.
 "Room temperature synthesis of highly crystalline TiO₂ nanoparticles". In: *Materials Letters* 92 (2013), pp. 287–290.
- [50] M. Drev, U. O. Krašovec, M. Hočevar, M. Berginc, M. K. Maček, and M. Topič. "Pechini based titanium sol as a matrix in TiO₂ pastes for dye-sensitized solar cell application". In: *Journal of Sol-Gel Science and Technology* 59.2 (2011), pp. 245– 251.
- [51] M. Behnajady, H. Eskandarloo, N. Modirshahla, and M. Shokri. "Investigation of the effect of sol–gel synthesis variables on structural and photocatalytic properties of TiO₂ nanoparticles". In: *Desalination* 278.1 (2011), pp. 10–17.
- [52] N. Renuka, A. Praveen, and K. Aravindakshan. "Synthesis and characterisation of mesoporous anatase TiO₂ with highly crystalline framework". In: *Materials Letters* 91 (2013), pp. 118–120.

- [53] Y. Ma, G. Ji, B. Ding, and J. Y. Lee. "Facile solvothermal synthesis of anatase TiO₂ microspheres with adjustable mesoporosity for the reversible storage of lithium ions". In: *Journal of Materials Chemistry* 22.46 (2012), pp. 24380–24385.
- [54] G.-B. Shan and G. P. Demopoulos. "The synthesis of aqueous-dispersible anatase TiO₂ nanoplatelets". In: *Nanotechnology* 21.2 (2010), p. 025604.
- [55] Fine particles: synthesis, characterization, and mechanisms of growth. Marcel Dekker, Inc., 2000.
- [56] G. Demopoulos. "Aqueous precipitation and crystallization for the production of particulate solids with desired properties". In: *Hydrometallurgy* 96.3 (2009), pp. 199–214.
- [57] P. G. Vekilov. "Nucleation". In: Crystal Growth & Design 10.12 (2010), pp. 5007– 5019.
- [58] T. Sugimoto. "Preparation of monodispersed colloidal particles". In: Advances in Colloid and Interface Science 28 (1987), pp. 65–108.
- [59] J. Bernstein, R. J. Davey, and J.-O. Henck. "Concomitant polymorphs". In: Angewandte Chemie International Edition 38.23 (1999), pp. 3440–3461.
- [60] C. Charbonneau. "Aqueous Solution Synthesis of Nanocrystalline TiO₂ Powders: Kinetics, Characterization and Application to Fabrication of Dye-Sensitized Solar Cell Photoanodes". PhD thesis. McGill University, 2011.
- [61] A. Di Paola, G. Cufalo, M. Addamo, M. Bellardita, R. Campostrini, M. Ischia, R. Ceccato, and L. Palmisano. "Photocatalytic activity of nanocrystalline TiO₂ (brookite, rutile and brookite-based) powders prepared by thermohydrolysis of TiCl₄ in aqueous chloride solutions". In: *Colloids and Surfaces A: Physicochemical* and Engineering Aspects 317.1 (2008), pp. 366–376.
- [62] Z. Yanqing, S. Erwei, C. Zhizhan, L. Wenjun, and H. Xingfang. "Influence of solution concentration on the hydrothermal preparation of titania crystallites". In: Journal of Materials Chemistry 11.5 (2001), pp. 1547–1551.

- [63] H. Cheng, J. Ma, Z. Zhao, and L. Qi. "Hydrothermal preparation of uniform nanosize rutile and anatase particles". In: *Chemistry of Materials* 7.4 (1995), pp. 663–671.
- [64] J.-G. Li, T. Ishigaki, and X. Sun. "Anatase, brookite, and rutile nanocrystals via redox reactions under mild hydrothermal conditions: phase-selective synthesis and physicochemical properties". In: *The Journal of Physical Chemistry C* 111.13 (2007), pp. 4969–4976.
- [65] C. Charbonneau, K. Lee, G. Shan, M. Gomez, R. Gauvin, and G. Demopoulos. "Preparation and DSSC performance of mesoporous film photoanodes based on aqueous-synthesized anatase nanocrystallites". In: *Electrochemical and Solid-State Letters* 13.8 (2010), H257–H260.
- [66] C. Charbonneau, R. Gauvin, and G. Demopoulos. "Nucleation and growth of self-assembled nanofibre-structured rutile (TiO₂) particles via controlled forced hydrolysis of titanium tetrachloride solution". In: Journal of Crystal Growth 312.1 (2009), pp. 86–94.
- [67] S. Cassaignon, M. Koelsch, and J.-P. Jolivet. "Selective synthesis of brookite, anatase and rutile nanoparticles: thermolysis of TiCl₄ in aqueous nitric acid". In: *Journal of Materials Science* 42.16 (2007), pp. 6689–6695.
- [68] Y. Jiao, B. Zhao, F. Chen, and J. Zhang. "Insight into the crystal lattice formation of brookite in aqueous ammonia media: the electrolyte effect". In: *CrystEngComm* 13.12 (2011), pp. 4167–4173.
- [69] D. Dambournet, I. Belharouak, and K. Amine. "Tailored preparation methods of TiO₂ anatase, rutile, brookite: mechanism of formation and electrochemical properties". In: *Chemistry of Materials* 22.3 (2010), pp. 1173–1179.
- [70] Y. Zheng, E. Shi, S. Cui, W. Li, and X. Hu. "Hydrothermal Preparation of Nanosized Brookite Powders". In: *Communications of the American Ceramic Society* (2000).
- [71] S. Ngamta, N. Boonprakob, N. Wetchakun, K. Ounnunkad, S. Phanichphant, and B. Inceesungvorn. "A facile synthesis of nanocrystalline anatase TiO₂ from TiOSO₄ aqueous solution". In: *Materials Letters* 105 (2013), pp. 76–79.
- [72] X. Lü, D. Mao, X. Wei, H. Zhang, J. Xie, and W. Wei. "Tunable synthesis of enhanced photodegradation activity of brookite/anatase mixed-phase titanium dioxide". In: *Journal of Materials Research* 28.03 (2013), pp. 400–404.
- [73] H. Xu, P. Reunchan, S. Ouyang, H. Tong, N. Umezawa, T. Kako, and J. Ye.
 "Anatase TiO₂ single crystals exposed with high-reactive {111} facets toward efficient H₂ evolution". In: *Chemistry of Materials* 25.3 (2013), pp. 405–411.
- [74] J. Yu, J. Low, W. Xiao, P. Zhou, and M. Jaroniec. "Enhanced photocatalytic CO₂-reduction activity of anatase TiO₂ by coexposed {001} and {101} facets".
 In: Journal of the American Chemical Society 136.25 (2014), pp. 8839–8842.
- [75] H. Lin, L. Li, M. Zhao, X. Huang, X. Chen, G. Li, and R. Yu. "Synthesis of high-quality brookite TiO2 single-crystalline nanosheets with specific facets exposed: Tuning catalysts from inert to highly reactive". In: *Journal of the American Chemical Society* 134.20 (2012), pp. 8328–8331.
- [76] Y. Ohno, K. Tomita, Y. Komatsubara, T. Taniguchi, K.-i. Katsumata, N. Matsushita, T. Kogure, and K. Okada. "Pseudo-cube shaped brookite (TiO₂) nanocrystals synthesized by an oleate-modified hydrothermal growth method". In: Crystal Growth & Design 11.11 (2011), pp. 4831–4836.
- [77] Q. Huang, S. Tian, D. Zeng, X. Wang, W. Song, Y. Li, W. Xiao, and C. Xie. "Enhanced photocatalytic activity of chemically bonded TiO₂/graphene composites based on the effective interfacial charge transfer through the C–Ti bond". In: ACS Catalysis 3.7 (2013), pp. 1477–1485.
- [78] H.-J. Hwang and H.-S. Kim. "TiO₂/silver/carbon nanotube nanocomposite working electrodes for high-performance dye-sensitized solar cells". In: *Journal of Composite Materials* (2013), p. 0021998313490215.

- [79] G. Liu, H. G. Yang, X. Wang, L. Cheng, J. Pan, G. Q. Lu, and H.-M. Cheng.
 "Visible light responsive nitrogen doped anatase TiO₂ sheets with dominant {001} facets derived from TiN". In: *Journal of the American Chemical Society* 131.36 (2009), pp. 12868–12869.
- [80] T. Ma, T. Kida, M. Akiyama, K. Inoue, S. Tsunematsu, K. Yao, H. Noma, and E. Abe. "Preparation and properties of nanostructured TiO₂ electrode by a polymer organic-medium screen-printing technique". In: *Electrochemistry Communications* 5.4 (2003), pp. 369–372.
- [81] N.-G. Park, K. M. Kim, M. G. Kang, K. S. Ryu, S. H. Chang, and Y.-J. Shin. "Chemical sintering of nanoparticles: A methodology for low-temperature fabrication of dye-sensitized TiO₂ films". In: *Advanced Materials* 17.19 (2005), pp. 2349– 2353.
- [82] K. Fan, M. Liu, T. Peng, L. Ma, and K. Dai. "Effects of paste components on the properties of screen-printed porous TiO₂ film for dye-sensitized solar cells". In: *Renewable Energy* 35.2 (2010), pp. 555–561.
- [83] Y. Chen, F. Huang, D. Chen, L. Cao, X. L. Zhang, R. A. Caruso, and Y.-B. Cheng.
 "Effect of mesoporous TiO₂ bead diameter in working electrodes on the efficiency of dye-sensitized solar cells". In: *ChemSusChem* 4.10 (2011), pp. 1498–1503.
- [84] A. S. Nair, R. Jose, Y. Shengyuan, and S. Ramakrishna. "A simple recipe for an efficient TiO₂ nanofiber-based dye-sensitized solar cell". In: *Journal of Colloid* and Interface Science 353.1 (2011), pp. 39–45.
- [85] S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Pechy, and M. Grätzel.
 "Fabrication of screen-printing pastes from TiO₂ powders for dye-sensitised solar cells". In: *Progress in Photovoltaics: Research and Applications* 15.7 (2007), pp. 603–612.
- [86] W.-G. Yang, F.-R. Wan, Q.-W. Chen, J.-J. Li, and D.-S. Xu. "Controlling synthesis of well-crystallized mesoporous TiO₂ microspheres with ultrahigh surface area for

high-performance dye-sensitized solar cells". In: *Journal of Materials Chemistry* 20.14 (2010), pp. 2870–2876.

- [87] S. Xu, C.-h. Zhou, Y. Yang, H. Hu, B. Sebo, B.-l. Chen, Q.-d. Tai, and X. Zhao.
 "Effects of ethanol on optimizing porous films of dye-sensitized solar cells". In: Energy & Fuels 25.3 (2011), pp. 1168–1172.
- [88] L. Miranda and A. Chianese. "Optimal effect of TiO₂ particles size on the current - potential behaviour of dye sensitized TiO₂ solar cells". In: *Chemical Engineering Transactions* (2009).
- [89] S. K. Dhungel and J. G. Park. "Optimization of paste formulation for TiO₂ nanoparticles with wide range of size distribution for its application in dye sensitized solar cells". In: *Renewable Energy* 35.12 (2010), pp. 2776–2780.
- [90] K. E. Lee, C. Charbonneau, and G. P. Demopoulos. "Thin single screen-printed bifunctional titania layer photoanodes for high performing DSSCs via a novel hybrid paste formulation and process". In: *Journal of Materials Research* 28.03 (2013), pp. 480–487.
- [91] S. Hore, P. Nitz, C. Vetter, C. Prahl, M. Niggemann, and R. Kern. "Scattering spherical voids in nanocrystalline TiO₂-enhancement of efficiency in dye-sensitized solar cells". In: *Chemical Communications* 15 (2005), pp. 2011–2013.
- [92] Z.-Q. Li, W.-C. Chen, F.-L. Guo, L.-E. Mo, L.-H. Hu, and S.-Y. Dai. "Mesoporous TiO₂ yolk-shell microspheres for eye-sensitized solar cells with a high efficiency exceeding 11%". In: *Scientific Reports* 5 (2015).
- [93] J. Yu, Q. Li, and Z. Shu. "Dye-sensitized solar cells based on double-layered TiO₂ composite films and enhanced photovoltaic performance". In: *Electrochimica Acta* 56.18 (2011), pp. 6293–6298.
- [94] J. Fan, Z. Li, W. Zhou, Y. Miao, Y. Zhang, J. Hu, and G. Shao. "Dye-sensitized solar cells based on TiO₂ nanoparticles/nanobelts double-layered film with improved photovoltaic performance". In: *Applied Surface Science* 319 (2014), pp. 75–82.

- [95] F. Huang, D. Chen, X. L. Zhang, R. A. Caruso, and Y.-B. Cheng. "Dual-function scattering layer of submicrometer-sized mesoporous TiO₂ beads for high-efficiency dye-sensitized solar cells". In: *Advanced Functional Materials* 20.8 (2010), pp. 1301– 1305.
- [96] D. Zhao, T. Peng, L. Lu, P. Cai, P. Jiang, and Z. Bian. "Effect of annealing temperature on the photoelectrochemical properties of dye-sensitized solar cells made with mesoporous TiO₂ nanoparticles". In: *The Journal of Physical Chemistry* C 112.22 (2008), pp. 8486–8494.
- [97] H. Weerasinghe, P. Sirimanne, G. Franks, G. Simon, and Y. Cheng. "Low temperature chemically sintered nano-crystalline TiO₂ electrodes for flexible dye-sensitized solar cells". In: *Journal of Photochemistry and Photobiology A: Chemistry* 213.1 (2010), pp. 30–36.
- C. J. Barbé, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, and M. Grätzel. "Nanocrystalline titanium oxide electrodes for photovoltaic applications".
 In: Journal of the American Ceramic Society 80.12 (1997), pp. 3157–3171.
- [99] H.-A. Hsiao, C.-C. Leu, C.-H. Yang, T.-L. Wang, and Y.-T. Shieh. "Binderaddition effect in TiO₂ nanoparticles on dye-sensitized solar cells evidenced by spectroscopic techniques". In: *Electrochimica Acta* 111 (2013), pp. 784–790.
- [100] X. G. Zhao, J.-Y. Park, E. M. Jin, and H.-B. Gu. "Tuning the interfacial area and porosity of TiO₂ film for enhanced light harvesting in DSSC". In: *Journal of The Electrochemical Society* 162.1 (2015), E1–E6.
- [101] J. Liu, A. Wei, Y. Zhao, K. Lin, and F. Luo. "Dye-sensitized solar cells based on ZnO nanoflowers and TiO₂ nanoparticles composite photoanodes". In: *Journal of Materials Science: Materials in Electronics* 25.2 (2014), pp. 1122–1126.
- [102] N. P. Benehkohal and G. Demopoulos. "Green preparation of TiO₂-ZnO nanocomposite photoanodes by aqueous electrophoretic deposition". In: *Journal of The Electrochemical Society* 159.5 (2012), B602–B610.

- [103] K.-H. Shin, J.-H. Ahn, H.-K. Kang, and Y. S. Eom. System and method for producing flexible dye-sensitized solar cells by a roll-to-roll printing process. US Patent 8,658,455. Feb. 2014.
- [104] C. Dwivedi, V. Dutta, A. K. Chandiran, M. K. Nazeeruddin, and M. Grätzel. "Anatase TiO₂ hollow microspheres fabricated by continuous spray pyrolysis as a scattering layer in dye-sensitised solar cells". In: *Energy Procedia* 33 (2013), pp. 223–227.
- [105] H. Chang, C.-H. Chen, M.-J. Kao, S.-H. Chien, and C.-Y. Chou. "Photoelectrode thin film of dye-sensitized solar cell fabricated by anodizing method and spin coating and electrochemical impedance properties of DSSC". In: *Applied Surface Science* 275 (2013), pp. 252–257.
- [106] M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, et al. "Engineering of efficient panchromatic sensitizers for nanocrystalline TiO₂-based solar cells". In: *Journal of the American Chemical Society* 123.8 (2001), pp. 1613–1624.
- [107] U. O. Krašovec, M. Berginc, M. Hočevar, and M. Topič. "Unique TiO₂ paste for high efficiency dye-sensitized solar cells". In: Solar Energy Materials and Solar Cells 93.3 (2009), pp. 379–381.
- [108] J. Calderon-Moreno, S. Preda, L. Predoana, M. Zaharescu, M. Anastasescu,
 M. Nicolescu, M. Stoica, H. Stroescu, M. Gartner, O. Buiu, et al. "Effect of polyethylene glycol on porous transparent TiO₂ films prepared by sol-gel method".
 In: *Ceramics International* 40.1 (2014), pp. 2209–2220.
- [109] T. J. Huang, X. Yin, G. Qi, and H. Gong. "CZTS-based materials and interfaces and their effects on the performance of thin film solar cells". In: *physica status solidi (RRL)-Rapid Research Letters* 8.09 (2014), pp. 735–762.
- [110] X. Song, X. Ji, M. Li, W. Lin, X. Luo, and H. Zhang. "A review on development prospect of CZTS based thin film solar cells". In: *International Journal of Photoenergy* 2014 (2014).

- [111] S. Schorr. "The crystal structure of kesterite type compounds: A neutron and X-ray diffraction study". In: Solar Energy Materials and Solar Cells 95.6 (2011), pp. 1482–1488.
- [112] A. Khalkar, K.-S. Lim, S.-M. Yu, S. P. Patole, and J.-B. Yoo. "Effect of growth parameters and annealing atmosphere on the properties of Cu₂ZnSnS₄ thin films deposited by cosputtering". In: *International Journal of Photoenergy* 2013 (2013).
- [113] J. Henry, K. Mohanraj, and G. Sivakumar. "Electrical and optical properties of CZTS thin films prepared by SILAR method". In: *Journal of Asian Ceramic Societies* 4.1 (2016), pp. 81–84.
- [114] S. Pawar, A. Moholkar, I. Kim, S. Shin, J. Moon, J. Rhee, and J. Kim. "Effect of laser incident energy on the structural, morphological and optical properties of Cu₂ZnSnS₄ (CZTS) thin films". In: *Current Applied Physics* 10.2 (2010), pp. 565– 569.
- [115] C. Malerba, F. Biccari, C. L. A. Ricardo, M. Valentini, R. Chierchia, M. Müller, A. Santoni, E. Esposito, P. Mangiapane, P. Scardi, et al. "CZTS stoichiometry effects on the band gap energy". In: *Journal of Alloys and Compounds* 582 (2014), pp. 528–534.
- [116] Q. Guo, H. W. Hillhouse, and R. Agrawal. "Synthesis of Cu₂ZnSnS₄ nanocrystal ink and its use for solar cells". In: *Journal of the American Chemical Society* 131.33 (2009), pp. 11672–11673.
- [117] Y. Wang, C. Li, X. Yin, H. Wang, and H. Gong. "Cu₂ZnSnS₄ (CZTS) application in TiO₂ solar cell as dye". In: ECS Journal of Solid State Science and Technology 2.7 (2013), Q95–Q98.
- [118] Z. Wang and G. P. Demopoulos. "Growth of Cu₂ZnSnS₄ nanocrystallites on TiO₂ nanorod arrays as novel extremely thin absorber solar cell structure via the successive-ion-layer-adsorption-reaction method". In: ACS Applied Materials & Interfaces 7.41 (2015), pp. 22888–22897.

- [119] K. Mokurala, A. Kamble, P. Bhargava, and S. Mallick. "Fabrication of dye sensitized solar cells with cost-effective quaternary sulfide counter electrode". In: *Power Electronics, Drives and Energy Systems (PEDES), 2014 IEEE International Conference on.* IEEE. 2014, pp. 1–4.
- [120] S. Chen, A. Xu, J. Tao, H. Tao, Y. Shen, L. Zhu, J. Jiang, T. Wang, and L. Pan. "In-situ and green method to prepare Pt-free Cu₂ZnSnS₄ (CZTS) counter electrodes for efficient and low cost dye-sensitized solar cells". In: ACS Sustainable Chemistry & Engineering 3.11 (2015), pp. 2652–2659.
- [121] B. Shin, O. Gunawan, Y. Zhu, N. A. Bojarczuk, S. J. Chey, and S. Guha. "Thin film solar cell with 8.4% power conversion efficiency using an earth-abundant Cu₂ZnSnS₄ absorber". In: *Progress in Photovoltaics: Research and Applications* 21.1 (2013), pp. 72–76.
- [122] K. Woo, Y. Kim, W. Yang, K. Kim, I. Kim, Y. Oh, J. Y. Kim, and J. Moon. "Band-gap-graded $Cu_2ZnSn(S_{1-x},Se_x)_4$ solar cells fabricated by an ethanol-based, particulate precursor ink route". In: *Scientific Reports* 3 (2013), p. 3069.
- [123] S. Kahraman, S. Çetinkaya, H. Çetinkara, and H. Güder. "A comparative study of Cu₂ZnSnS₄ thin films growth by successive ionic layer adsorption-reaction and sol-gel methods". In: *Thin Solid Films* 550 (2014), pp. 36–39.
- [124] S. G. Lee, J. Kim, H. S. Woo, Y. Jo, A. Inamdar, S. Pawar, H. S. Kim, W. Jung, and H. S. Im. "Structural, morphological, compositional, and optical properties of single step electrodeposited Cu₂ZnSnS₄ (CZTS) thin films for solar cell application". In: *Current Applied Physics* 14.3 (2014), pp. 254–258.
- [125] W.-C. Hsu, B. Bob, W. Yang, C.-H. Chung, and Y. Yang. "Reaction pathways for the formation of Cu₂ZnSn(Se,S)₄ absorber materials from liquid-phase hydrazinebased precursor inks". In: *Energy & Environmental Science* 5.9 (2012), pp. 8564– 8571.

- [126] K. Tanaka, Y. Fukui, N. Moritake, and H. Uchiki. "Chemical composition dependence of morphological and optical properties of Cu₂ZnSnS₄ thin films deposited by sol-gel sulfurization and Cu₂ZnSnS₄ thin film solar cell efficiency". In: Solar Energy Materials and Solar Cells 95.3 (2011), pp. 838–842.
- [127] J. Scragg. "Copper Zinc Tin Sulfide Thin Film for Photovoltaics". PhD thesis. University of Bath, 2011.
- [128] A. Moholkar, S. Shinde, A. Babar, K.-U. Sim, Y.-b. Kwon, K. Rajpure, P. Patil, C. Bhosale, and J. Kim. "Development of CZTS thin films solar cells by pulsed laser deposition: influence of pulse repetition rate". In: *Solar Energy* 85.7 (2011), pp. 1354–1363.
- [129] T. Tanaka, T. Nagatomo, D. Kawasaki, M. Nishio, Q. Guo, A. Wakahara, A. Yoshida, and H. Ogawa. "Preparation of Cu₂ZnSnS₄ thin films by hybrid sputtering". In: *Journal of Physics and Chemistry of Solids* 66.11 (2005), pp. 1978–1981.
- [130] B.-A. Schubert, B. Marsen, S. Cinque, T. Unold, R. Klenk, S. Schorr, and H.-W. Schock. "Cu₂ZnSnS₄ thin film solar cells by fast coevaporation". In: *Progress in Photovoltaics: Research and Applications* 19.1 (2011), pp. 93–96.
- [131] W. Wang, M. T. Winkler, O. Gunawan, T. Gokmen, T. K. Todorov, Y. Zhu, and D. B. Mitzi. "Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency". In: Advanced Energy Materials 4.7 (2014).
- [132] S. M. Camara, L. Wang, and X. Zhang. "Easy hydrothermal preparation of Cu₂ZnSnS₄ (CZTS) nanoparticles for solar cell application". In: *Nanotechnology* 24.49 (2013), p. 495401.
- [133] A. Wangperawong, J. King, S. Herron, B. Tran, K. Pangan-Okimoto, and S. Bent.
 "Aqueous bath process for deposition of Cu₂ZnSnS₄ photovoltaic absorbers". In: *Thin Solid Films* 519.8 (2011), pp. 2488–2492.

- [134] J. Wang, P. Zhang, X. Song, and L. Gao. "Surfactant-free hydrothermal synthesis of Cu₂ZnSnS₄ (CZTS) nanocrystals with photocatalytic properties". In: *RSC Advances* 4.53 (2014), pp. 27805–27810.
- [135] A. Emrani, P. Vasekar, and C. R. Westgate. "Effects of sulfurization temperature on CZTS thin film solar cell performances". In: *Solar Energy* 98 (2013), pp. 335– 340.
- [136] M. I. Khalil, R. Bernasconi, and L. Magagnin. "CZTS layers for solar cells by an electrodeposition-annealing route". In: *Electrochimica Acta* 145 (2014), pp. 154– 158.
- [137] S. Bhosale, M. Suryawanshi, M. Gaikwad, P. Bhosale, J. Kim, and A. Moholkar. "Influence of growth temperatures on the properties of photoactive CZTS thin films using a spray pyrolysis technique". In: *Materials Letters* 129 (2014), pp. 153–155.

Chapter 3

Continuous-reactor, pH-controlled synthesis of multifunctional mesoporous nanocrystalline anatase aggregates

The primary motivation of this thesis is to develop a scalable, green, aqueous process for TiO₂ synthesis for use in solar cells. For polymorphic materials like TiO₂, it is very important to define process parameters for the controlled synthesis of a single or multiple phases. In solution synthesis operating conditions (temperature, pressure, concentration, pH, additives etc.) are exploited to affect product properties such as phase, size, and morphology. This chapter focusses on synthesis of metastable anatase form of TiO₂ in an aqueous solution in a continuous stirred tank reactor. The research presented herein has been published in: Yasin, A., Guo, F. & Demopoulos, G.P., *Continuousreactor, pH-controlled synthesis of multifunctional mesoporous nanocrystalline anatase aggregates*, Chemical Engineering Journal, 2016, 287, pp.398-409. Appendix A describes the Supporting Information.

3.1 Abstract

Anatase is an important functional nanomaterial in a wide variety of applications. Despite a breadth of research on novel synthesis methods, there is a lack of studies geared towards developing scalable processes for nanoscale anatase crystalline materials. In this study, anatase secondary nanoparticles are produced in a continuous stirred-tank reactor (CSTR) through forced hydrolysis of pre-diluted aqueous TiCl₄ solution by controlling pH. The steady-state supersaturation regime of the CSTR process is shown to be inducive to the formation of phase-pure nanocrystalline anatase aggregates in the order of $\approx 500-1000$ nm possessing a very high surface area $\approx 200-250 \ m^2/g$. The aggregates made of ≈ 6 nm individual primary nanocrystallites are mesoporous – a highly desirable property in building photocatalytic and thin film electrode (Li-ion and solar) devices with enhanced interfacial functionalities. The new process was tested at a range of conditions, 70–90 °C, 0.1–0.5 M TiCl₄, pH 2–5, and 30–60 min. pH control was vital in stabilizing the metastable anatase nanocrystallites and promoting their aggregation that facilitates their handling and application. The process achieves >98% steady-state conversion of $TiCl_{4(aq)}$ to nanoanatase without the use of toxic organic chemicals constituting a cost-effective and green alternative to commonly used sol-gel or hydrothermal technologies.

3.2 Introduction

Nano-titania (TiO₂) exists in three common crystallographic phases: anatase, brookite and rutile. Rutile is thermodynamically the most stable in macrocrystalline form, whereas anatase and brookite in nature exist as nanoscale structures, which upon coarsening transform to rutile [1, 2]. The three polymorphs find applications in a variety of fields owing to their functionalities rendered by their specific crystal structures. Anatase due to its high band gap, surface area and intercalation capacity is used in photovoltaics [3], photocatalysis [4], lithium-ion batteries [5], gas sensors [6]. Although a variety of nano-TiO₂ synthesis processes have been proposed, from an industrial standpoint, most of them are not suitable for large-scale production at low manufacturing cost and low environmental impact.

Nano-Ti O_2 is produced via processes such as hydrothermal [7], sol-gel /solvothermal [8], flame synthesis [9], physical/chemical vapor deposition (PVD/CVD), and sonochemical [10] or microemulsion reactions [11]. Among these, solution synthesis methods offer the best control over nanocrystal product properties with sol-gel and hydrothermal technologies being the most successful in this regard [12]. In sol-gel method, a colloidal suspension is formed by mixing Ti(IV)-organic precursor, such as titanium(IV) tetraisopropoxide, in water; acid-catalyzed polymerization leads to gel formation which is then subjected to (hydro)thermal treatment at elevated temperatures to induce crystallization [12–16]. In hydrothermal synthesis, titanium hydroxide intermediates precipitated from Ti(IV) salt or alkoxide solution using a base like ammonia are subjected to thermal treatment at high temperature (\approx 120-300 °C) in autoclaves to induce transformation of amorphous titania to the desired crystalline phase [17–19]. The aforementioned processes enable control over the final product characteristics of size, shape, phase proportions etc. but their application is limited to small volume production. In addition, necessity of hydrothermal treatment incurs high capital and operating costs, and poses a challenge of process scaling-up for high-volume production to meet the global demand for clean environmental and energy (photovoltaic and storage) technologies, not to mention the environmentally questionable reliance on hazardous organic chemicals.

Considering the drawbacks of sol-gel/hydrothermal processes, research has been conducted to develop aqueous solution synthesis processes particularly due to their inherent reduced environmental impact [20]. Inorganic Ti salts such as TiCl₃ [21], TiCl₄ [22], or TiOSO₄ [23], are used as precursors. Temperature, concentration, pH and reaction times are manipulated to obtain the desired phase(s) [24]. Similar to sol-gel, these processes involve sequential steps [25] making them difficult to scale-up; use of additives [21, 25]; or hydrothermal treatment to induce crystallization [25], all of which increase process complexity and cost.

In view of the above limitations when it comes to high volume, commercial production of crystalline nanoanatase, efforts have been directed towards continuous synthesis methods.

These include different approaches. Thus in a method developed by Kawasaki et al., anatase nanocrystallites (13–30 nm) were produced continuously in a supercritical reactor operating at 400 °C by fast reactive mixing of titanium sulfate $Ti(SO_4)_2$ solution with KOH base [26]. By contrast, Malinger *et al.* opted to utilize pre-precipitated amorphous TiO_2 slurry in water as feed to a plug-flow hydrothermal reactor operating between 120 -220 °C [27]. In this way the amorphous TiO_2 was converted to anatase nanoparticles in the range of 7–13 nm. Yet in a contrasting approach very recently Mohammadi et al. described the continuous synthesis of amorphous TiO_2 particles via the sol-gel route in a spinning disc reactor at 50 °C, which are subsequently calcined at 400 °C to obtain crystalline anatase [28]. Despite these significant advances the need remains for a continuous process capable of direct production of anatase nanocrystallites without having to resort to organic solvents or costly hydrothermal reactors. In this work we attempt to address this need by proposing direct synthesis of anatase nanocrystallites from aqueous Ti(IV) chloride solution in a CSTR (continuous-stirred tank reactor) at near-ambient conditions. Moreover, the present work provides a compelling case for the scalable synthesis of nanomaterials in CSTRs, which thanks to their inherent steady-state regime allow for crystallinity and size control of metastable phases as is anatase.

Previous research in our laboratory [29] led to the development of an aqueous batch process for the synthesis of nanocrystalline anatase via forced hydrolysis without organic additives or pH regulation. The process required instantaneous heating of pre-diluted (0.2 M) TiCl₄ solution from <10 °C to 80 °C to avoid pre-mature formation of amorphous TiO₂ during the heat up period that interfered with homogeneous nucleation of crystalline anatase nanoparticles. The process reached \approx 90% precipitation in 30 minutes and was quenched immediately to prevent transformation of anatase to rutile [23]. The synthesis was carried out in a 200 mL beaker making it a low-yield process, yet it offered a facile, environmentally friendly, single-step way of synthesizing high surface area, and functional anatase nanocrystals [30, 31] at near-ambient conditions. However, anatase was not obtained when the hydrolysis of TiCl₄ was carried out in a CSTR. This limitation is overcome in the present work by controlling pH in the range 1pH<6. By maintaining a</pre> steady-state precipitation regime over that pH range the homogeneously formed anatase nanocrystallites are organized in easily recoverable mesoporous aggregates, which are phase-pure without signs of partial conversion to brookite or rutile as observed with other processes. The novel anatase nanocrystalline aggregates are extensively characterized and their formation/physical characteristics are correlated to key process parameters: pH (2 to 5), temperature (70 – 90 °C), and TiCl₄ feed concentration (0.1 – 0.5 M). Further, the newly synthesized nanoanatase material is shown to be excellent candidate in photocatalytic and solar energy conversion and storage applications. Overall the CSTRbased system offers a scalable, simple and green alternative to the sol-gel and hydrothermal synthesis routes without making use of Ti(IV) alkoxides nor employing post treatment to induce crystallization yet producing highly performing anatase nanomaterials.

3.3 Experimental

3.3.1 Synthesis

Titanium tetrachloride stock solution preparation

Titanium tetrachloride TiCl₄ (ReagentPlus[®], 99.9% trace metals basis, Sigma-Aldrich) was used as the titanium source. 190 mL deionized water was frozen to ice in a plastic bottle. 55 mL TiCl₄ was added drop-wise to the ice bottle kept in a liquid nitrogen container. As the addition progressed the ice melted due to heat released upon aqueous dilution of TiCl₄. The final solution was clear and was kept refrigerated. The Ti(IV) concentration was determined using ICP-AES; the TiCl₄ concentration was further adjusted to 2M and resultant solution was used as stock solution.

Continued stirred tank reactor (CSTR) and procedure

A 2 L Applikon[®] jacketed reactor was used as the CSTR. The head plate of the reactor was equipped with two tubes, one for the outlet, one for inlet; three baffles; a shaft with a three-blade marine impeller; and a tube for thermocouple. Masterflex[®] norprene tubing

(ID: 4.8 mm) was used to deliver the inlet and outlet solutions using peristaltic pumps. Silicone oil pumped through the jacket via a heat bath/circulator was used to maintain solution temperature inside the reactor. An accompanying controller unit monitored agitation, and pH control via continuous addition of NaOH (19 M) (Fisher Scientific, 50% w/w solution in water.) Figure A.1 shows the schematic of the reaction vessel. The oil bath was heated to 90 °C. 1 L of 0.01 M TiCl₄, prepared by diluting the 2 M TiCl₄ stock solution with cold (3 °C) deionized water, was added to the reactor and agitated at 800 rpm. The pH of the reactor solution was maintained at 3 through continuous addition of NaOH. Once this receiving solution had reached 80 °C, the operation was put into continuous mode; $TiCl_4$ aqueous solution of the desired concentration (0.1 - 0.5 M) was fed to the reactor continuously. The flow rates of the inlet and the outlet streams were adjusted to a residence time of 30 minutes (33 mL/min). The temperature of the oil bath was increased to 100 °C in order to maintain the solution temperature at 80 °C. The inlet solution was kept cold using an ice-water bath (≈ 0 °C) to avoid premature hydrolytic precipitation of amorphous TiO_2 [25]. The white colloidal solution from the outlet solution was quenched using an ice-water bath in order to stop the reaction and prevent further changes to particle properties. The obtained colloidal TiO₂ suspension was centrifuged and washed alternatively with deionized water twice, and a final wash with ethanol, to separate the TiO₂ anatase product in wet cake ("gel") form. The wet cake was dried overnight in an oven at 80 °C, and manually ground to yield white powder for characterization and further use in applications. Further details about the procedure are given in Section A.1.

3.3.2 Characterization

Extent of reaction was determined by collecting samples from the outlet stream at regular intervals throughout the operation. The aggregate particles were allowed to settle down and the supernatant was analyzed via Inductive Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) performed using Thermo Jarrel Ash Trace Scan Machine to measure the Ti concentration. For phase identification, X-ray diffraction (XRD) was performed on a Bruker D8 Discovery X-Ray Diffractometer equipped with a copper target λ (CuK α 1) = 1.5406 Å. The diffractometer operated at 40 kV and 40 mA. Scanning took place between 20° and 70° (2 θ) with 0.005° step/second. Background subtraction and smoothing were performed on EVA software. The XRD patterns were compared against JCPDS reference data of anatase (JCPDS # 00-021-1272). Crystallite size was determined using Scherrer equation [7]:

$$D_{hkl} = k\lambda/\beta cos\theta \tag{3.1}$$

 D_{hkl} is crystal size in nm, k is 0.89, λ is wavelength of Cu radiation (0.1549 nm), β is FWHM (Full Width at Half Maximum) corresponding to (hkl) plane in radians, and θ is the Bragg angle corresponding to (hkl) plane in radians. BET (Brunauer-Emmett-Teller) surface area analysis was performed on a Micromeritics TriStar 3000 apparatus. 200 mg of powder sample was degassed with nitrogen gas at 70 °C for 10 hours. A multiple point specific surface area type of analysis was carried out. Field Emission Gun-Transmission Electron Microscopy (FEG-TEM) was performed on a Philips CM-200 microscope operated with an accelerating voltage of 200 kV. SEM images were taken on Hitachi SU-8230. FT-IR (Fourier Transform Infrared Spectroscopy) was conducted on Perkin Elmer Spectrum 400 FT Mid-IR and Far-IR Spectrometer to determine the presence of adsorbed and structural -OH groups on the dry TiO₂ powders. FTIR spectra were collected over 400-4000 $\rm cm^{-1}$ with a 0.5 $\rm cm^{-1}$ resolution. Thermogravimetric Analysis (TGA) was performed on TA Instruments Q500 TGA. The powder samples were heated up to 600 °C at 10 °C/minute in a N_2 environment. XPS (X-ray photoelectron spectroscopy) was conducted on Thermo Scientific K-Alpha XPS System from 0-1350 eV in 1 eV steps. The TiO₂ powder was etched with Ar^+ ion bombardment with energy of 2 keV for 30s to remove any carbon-based contaminants. Optical band-gap was determined through UV-Vis diffuse reflectance spectroscopy performed on Evolution 300 UV-visible Spectrometer with a scanning wavelength from 200 to 620 nm. A mirror was used for calibration.

3.3.3 Functional property evaluation

Photocatalytic activity measurements

The photocatalytic activity of the as-synthesized anatase aggregates was evaluated by monitoring the degradation of methyl orange with time. In a typical test 50 mL of 10 mg/L aqueous methyl orange solution was added to a 100 mL beaker along with 50 mg of dry anatase powder. The beaker was placed on a stirrer plate in a closed chamber equipped with a UV light source (Sankyo Denki[®] UV range: 280 - 360 nm, peak at 306 nm, UV output: 3 W). The solution was stirred in the dark for 60 min to reach adsorption-desorption equilibrium. It was then irradiated with UV light source and stirred for another 60 minutes. 5 mL of irradiated solution was taken every 15 minutes, centrifuged and subjected to UV-vis absorption measurements [32]. UV-vis spectroscopy was conducted to collect absorption spectra of methyl orange samples between 205-600 nm in order to quantify the photocatalytic degradation activity. Deionized water was used as a blank. The degradation efficiency was calculated by analyzing the methyl orange absorption peak at 464 nm using the following equation [32]:

$$\%D = \frac{A_o - A_t}{A_o} \times 100 \tag{3.2}$$

Where A_o is the absorption peak after the solution has reached adsorption-desorption equilibrium and before irradiation.

Photoanode measurements

The synthesized anatase was incorporated as the semiconductor component of the photoanode in dye-sensitized solar cells. Briefly, dried anatase powder was combined with rutile (synthesis discussed in Chapter 4) and P25 in the ratio 40%A/40%R/20%P25 [31] to manufacture a screen printable paste following a standard protocol [33]. The powders were ground and dispersed in ethanol with acetic acid, ethyl-cellulose, α -terpineol, as the dispersant, binder and rheological agent respectively. The mixture was concentrated in a rotary evaporator to evaporate the excess ethanol yielding pastes with 20 wt% TiO₂

content. The paste was printed on fluorine doped tin oxide (FTO) glass substrate with a screen-printer (Atma Champ Ent. Corp., Taiwan). 1-3 TiO₂ layers were printed to obtain variable thickness photoanodes. The photoanodes were sintered at 450 °C for 30 minutes, treated in a bath of 50 mM TiCl₄ for 30 minutes and sintered again at 450 °C for 30 minutes. The photoanodes were immersed in 52 mM N719 dye solution for 24 hours. Counter electrodes were prepared by platinizing FTO glass. The photoanode and counter electrode were sandwiched together with a thermoplastic sealant. An I^-/I_3^- based electrolyte was injected through holes pierced in the counter electrode, subsequently sealed with the plastic sealant and glass. Photovoltaic measurements were conducted under AM 1.5 conditions using a solar cell I-V curve testing system (PV Measurements, Inc., Colorado).

3.3.4 Li-ion battery measurements

As described in detail elsewhere [34, 35] the synthesized anatase nanocrystallites were assembled into two kinds of electrodes. Firstly [34], following the standard method of electrode fabrication for Li-ion batteries, anatase nanocrystalline aggregates were mixed with acetylene black carbon, and poly(vinylidene) fluoride in 80/10/10 ratio in 1-methyl 2-pyrrolidone solvent, doctor bladed on aluminum foil and dried at 120 °C [34]. In another method [35], 90 wt% anatase and 10 wt% carbon were diluted to a colloidal suspension with anhydrous ethanol, then made into paste using α -terpineol and ethyl cellulose by evaporating the excess ethanol. The resulting paste was doctor-bladed onto an aluminum foil substrate, and dried at 80 °C overnight before annealing/sintering at 450 °C following a specific heating profile. More details can be found in the indicated reference [35]. In both cases, lithium foil was used as the counter electrode and 1M LiPF6 in EC:DMC:DEC(2:2:1) solution as electrolyte. Galvanostatic cycling was carried out between 3 V (charge limit) and 1 V (discharge limit) at 1 C rate (current kept constant at 168 mAg⁻¹).

3.4 Results & Discussion

3.4.1 Start-up and steady-state attainment: nucleation

In our previous batch reactor-based synthesis of anatase work [29], a 200 mL solution of 0.2M TiCl₄ was stirred at 80 °C for 30 minutes and produced nanocrystalline TiO₂ with 90% anatase content as per hydrolysis reaction 3.3.

$$TiCl_{4(aq)} + 2H_2O \rightarrow TiO_{2(s)} + 4HCl_{(aq)}$$

$$(3.3)$$

However, when this reaction was carried out in a 1L capacity CSTR, it led to the formation of brookite and rutile TiO₂ phases rather than anatase TiO₂ phase (Chapter 4). The problem was traced to the low pH ≈ 0.25 of the steady-state solution arising from the continuous generation of HCl from the hydrolysis reaction 3.3. By exploring different operating conditions it was found that maintaining a solution pH >1 was necessary to synthesize the anatase phase. To this end, CSTR tests with combinations of pH, temperature, and TiCl₄ feed concentration among other conditions were conducted to determine the operating limits for anatase synthesis, elucidate the underlying nucleation mechanism and establish process parameter effects on nanoparticle characteristics.

For the start-up operation, the concentration of the receiving solution was set to 0.01M $TiCl_4$ so as to be closer to the expected steady state Ti(IV) concentration for 0.1M $TiCl_4$ feed, assuming a 90% extent of reaction from batch synthesis [29]. The receiving solution concentration was then kept at 0.01M $TiCl_4$ so as not to change multiple variables between tests. As mentioned previously, NaOH was continuously added to maintain the solution pH constant; as a result the generated HCl (see reaction 3.3) converts to NaCl. This means that for a 0.1 M $TiCl_4$ feed solution the nominal concentration of produced NaCl is 0.4 M. It took one hour for the receiving solution to reach 80 °C, after which the reactor was put into continuous mode. The process was considered to have reached a steady state when the concentration of Ti(IV) in the outlet stream reached a constant value.

The receiving solution of $TiCl_4$ was colorless when added to the reactor. As the first

few NaOH drops entered the solution, local white cloud formation was observed which dissipated promptly in the agitated solution. The solution turned from transparent to opaque due to TiO_2 precipitation as the temperature increased from 0 °C to 80 °C.

Figure 3.1 shows Ti(IV) and Na⁺ concentrations in the outlet stream with time during continuous operation. The time when the pump was started is taken as the initial time; hence the lag between when the pump was started and when the first sample was collected from the outlet tube. The first sample (0.336 mM) represents Ti(IV) solution concentration of the 0.01 M Ti(IV) receiving solution. Similarly, image given in Figure 3.2(a) is of the initial nuclei formed in the solution prior to the start of the continuous operation. A few crystal planes can be seen within the mostly amorphous precipitate, suggesting that while crystallization had begun, it was still in the very early stage when the continuous reactor operation started. After the feed is pumped into the reactor the concentration drops to 0.18 mM Ti(IV) abruptly, and then increases gradually until it reaches a maximum supersaturation at 168 min (5.6τ) (Figure 3.1) after which it suddenly drops to 0.7 mM at 184 min (Figure 3.1), representing 99.7% precipitation w.r.t to 0.2M Ti(IV) feed concentration. After this point, Ti(IV) and Na⁺ concentrations do not deviate significantly and the process is deemed to have reached steady state. The shape of the curve can be partly explained by LaMer's theory of nucleation: the increase in Ti(IV) concentration after the continuous pumping of the feed solution started indicates the rate of addition of Ti(IV) to the solution is greater than the rate of precipitation. The slow rate of precipitation may indicate that heterogeneous nucleation leading to modest growth of the pre-continuous operation formed precipitate – as it can be deduced from the TEM image of Figure 3.2(b) – is most likely the prevailing mechanism. The Ti(IV) concentration keeps on increasing until it reaches a critical supersaturation level triggering the onset of homogeneous nucleation and then drops down until the solution reaches a steady state Ti(IV) concentration [36]. The nanocrystallites at this point, as it can be observed from the TEM image in Figure 3.2(c) have clearly developed their crystal planes and assumed their final size of 5-6 nm or so. The steady-state product is characterized in detail in Section 3.4.2.

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Figure 3.1: Ti(IV) and Na⁺ concentration in the outlet stream. Test conditions: T = 80 °C, $[\text{TiCl}_4]_{feed} = 0.2 \text{ M}, \text{pH}_{steady-state} = 3, \tau$: 30 min.

3.4.2 Steady-state nanoanatase product characterization

A summary of tests carried out to investigate the effects of steady-state pH, temperature, and $TiCl_4$ feed concentration on the characteristics of the nano-anatase products is provided in Table 3.1. The products were characterized and the obtained results are discussed in the following sections.

X-ray diffraction analysis: Effects of temperature, pH, and concentration

Temperature effect

Figure 3.3 shows the XRD patterns of steady-state TiO₂ products obtained at 70 °C, 80 °C, and 90 °C. Samples taken at a) 80 °C and b) 90 °C show peaks at $2\theta = 25.3^{\circ}$ (101), 37.0° (004), 48.0° (200), 53.9° (105), and 62.1° (213), all characteristic of body-centered tetragonal anatase phase according to JCPDS # 00-021-1272. The absence of diffraction peaks at $2\theta = 27.5^{\circ}$ and 30.8° signify the absence of rutile and brookite, according to JCPDS # 00-001-1292 and JCPDS # 00-029-1360 respectively [37], and hence the as-synthesized product is pure anatase. Moreover, the peaks are broad and low intensity, indicative of nanosized crystals [29]. For 70 °C, the peaks are very low intensity and around $2\theta = 53.9^{\circ}$, 62.1° and 62.7° the peaks can barely be distinguished from the



Figure 3.2: Evolution of nano-TiO₂ precipitate during start-up operation: (a) time 0 min; left shows low magnification image, and right shows high magnification image (receiving solution), (b) 168 min (concentration build up period), and (c) 184 min (beginning of steady-state); refer to concentration profile in Figure 3.1

Table 3.1	: Characteristics of anatase TiO_2 nanomaterial produced under various synthesis
	conditions. (Default conditions: T=80 °C, $[TiCl_4]_{feed} = 0.2$ M, $pH_{steady-state}$
	$= 3, \tau = 30 \text{ min}, \text{ agitation } 800 \text{ rpm})$

Temp-	Feed	рН	XRD	BET Sur-	BET	BJH pore	$\operatorname{Bandgap}^{b}$
erature	Concen-		Equivalent	face Area	Equivalent	width	(eV)
$(^{\circ}C)$	tration		$\operatorname{Diameter}^1$	(m^2/g)	Diameter	(Å)	
	(M)		(nm)		(nm)		
80	0.1	3	4.92	248.06	6.21	77.54	3.16
80	0.2	3	4.34	232.56	6.62	83.09	3.19
80	0.3	3	4.61	221.43	6.96	86.63	3.14
80	0.4	3	4.05	216.47	7.12	52.43	3.15
80	0.5	3	3.96	216.17	7.13	90.32	3.21
70	0.1	3	4.01	283.51	5.43	75.32	3.26
90	0.1	3	5.5	199.96	7.70	154.05	3.12
80	0.2	2	4.67	160.98	9.57	84.3	3.17
80	0.2	4	4.39	220.35	6.99	107.69	3.15
80	0.2	5	4.39	264.16	5.83	113.02	3.14
80*	0.2	3	4.92	185.02	8.33	82.23	3.16
80#	0.1	3	4.34	147.95	10.41	79.59	-
90	0.2	3	5.2	191.60	7.33	103.27	3.09
90	0.5	3	4.66	190.54	7.37	128.31	3.17
90	0.2	2	5.20	161.3	8.70	92.37	3.16
90	0.2	1	4.92	170.7	8.22	95.37	3.07

* Mean retention time: 60 min

 $^{\#}$ Agitation speed: 1200 rpm

 1 Scherrer method

 2 UV-vis tauc plot method; refer to Figure A.10 $\,$

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Figure 3.3: XRD patterns of TiO₂ products synthesized at: (a) 70 °C, (b) 80 °C, and (c) 90 °C compared to anatase reference pattern. Constant conditions: $[TiCl_4]_{feed}$ = 0.1 M, pH_{steady-state} = 3, τ : 30 min.

background disturbance, showing the poor crystalline nature of the nano-TiO₂ powder [37]. Therefore, no more tests were conducted at 70 °C. As the temperature increases, the peak intensity increases, and peak width decreases, indicative of higher crystallinity, and larger average crystallite size respectively [37]. Applying Scherrer's equation on the $2\theta = 25.3^{\circ}$ peak, average diameters of the anatase crystallites have been calculated to be 4.01 nm, 4.92 nm and 5.5 nm for 70 °C, 80 °C, and 90 °C, respectively, that nicely agree with the TEM crystallite size data (Figure 3.2(c)). Comparing the results with the equivalent batch process [29], the present continuous process produces pure anatase (as opposed to majority anatase phase), and the yield is >99% instead of 90%. This is attributed to both the steady-state supersaturation environment as well as the favorable pH (=3) as opposed to the batch reaction that had progressively decreasing supersaturation and pH triggering the transformation of anatase to brookite/rutile.

pH and concentration effect

Figure 3.4 shows XRD patterns of TiO₂ product obtained at steady state operation for various TiCl₄ feed concentrations and changing steady state pH. For this series of tests 80 °C was selected. In Figure 3.4 (e)-(i), all XRD patterns corresponding to various $TiCl_4$ feed concentrations exhibit peaks characteristic of phase-pure anatase similar to Figure 3.3. For the higher concentrations, 0.4M and 0.5M TiCl₄, however the peaks at $2\theta = 62.1^{\circ}$, 62.7° show very low intensity. The peaks overall get shorter and broader as the $TiCl_4$ feed concentration increases, revealing a decrease in crystallinity [37]. The observed deterioration of crystallinity with increasing concentration is most likely linked to polymerization of Ti(IV)-Cl-H₂O precursor complexes [38, 39] that were shown to interfere with the nucleation process in previous work [22]. No higher concentrations were investigated since it gets difficult to maintain steady-state solution pH as the feed concentration increases but also because generally, increasing precursor concentration leads to rutile formation [22]. For changing solution pH, characteristic peaks of phase-pure anatase are evident up to pH 4. At pH 5 a slight rutile peak at 27.5° is evident. At pH 6 the product became amorphous (refer to Figure A.3). Tests were conducted at 90 °C at pH 1 and pH 2 (see Figure A.4) and no particular trend in change of crystal size/degree of crystallinity could be observed. According to previous work by Li and Demopoulos [40] the production of pure rutile was observed in 0.5-2M TiCl₄ aqueous solutions, under forced hydrolysis at 95 °C; there was a gradual increase in anatase content as pH was increased from 1.3 to 6 by addition of MgO. Pottier et al. [24] reported the formation of nanoanatase by batch aging an aqueous TiCl₄ solution at 60 °C for 24 hours over the pH range 1-6; however their anatase contained small amounts (5-20%) of rutile and brookite for pH 1-2 and pH 2-6 respectively as opposed to the present CSTR process that yielded phase-pure anatase. As in the present work, Pottier et al. [24] also observed crystallinity to drop significantly at pH 6.



Figure 3.4: XRD patterns of steady state products compared to anatase reference pattern: The effect of pH: (a) pH 2, (b) pH 3, (c) pH 4, (d) pH 5; constant conditions: T = 80 °C, $[TiCl_4]_{feed} = 0.1 \text{ M}$, $\tau = 30 \text{ min}$. The effect of $[TiCl_4]_{feed}$: (e) 0.1 M, (f) 0.2 M, (g) 0.3 M, (h) 0.4 M, (i) 0.5 M; constant conditions: T = 80°C, $pH_{steady-state} = 3$, $\tau = 30 \text{ min}$.

Mechanism of anatase formation

Role of pH

To explain the importance of maintaining the pH in the range 2 < pH < 6 to promote the formation of anatase crystallites the following mechanism is proposed: In an aqueous solution TiCl₄ undergoes partial hydrolysis giving rise to $[Ti(OH)_x Cl_z \cdot (OH_2)_{6-x-z}]^{4-(x+z)}$ complexes, where the exact form is pH and Cl^{-} ion activity dependent [21, 41]. Since in the present study the maximum Ti(IV) concentration was 0.5 M (or 2 M Cl⁻) the precursor complexes can be taken to be free of chloride anions, as according to Ciavatta et al. [41] there is <7% chlorocomplexes of Ti(IV) in 3 M Cl⁻ solution. Hence the mechanism of anatase formation can be discussed on the basis of the Cl-free six-fold coordinated monomers $[Ti(OH)_x(OH_2)_{6-x}]^{4-x}$ [21, 42]. As a result of this partial hydrolysis the prepared solutions are acidic; for example in the case of 0.1 M Ti(IV) feed solution the natural pH as determined by titration at room temperature was ≈ 0.42 . As a reminder the feed solution was kept in an ice-bath to prevent premature/uncontrolled precipitation of TiO_2 . In this acidic and cold solution the probable form of the Ti(IV)complex is $[Ti(OH)(OH_2)_5]^{3+}$, which due to the large positive charge [42] and low activity arising from the low temperature does not render itself to any condensation reactions. The Ti(IV) feed is continuously pumped into the steady-state reactor solution where the pH is maintained typically at 3 and temperature at 80 °C. Thanks to CSTR's inherent functionality the feed solution spontaneously reaches the steady-state Ti(IV) concentration that is more than two orders lower than the inlet value ($\approx 0.7 \text{ mM}$ -refer to Figure 3.1). As such the governing high $[H_2O]/[Ti(IV)]$ ratio in concert with the elevated pH (>1; lower H⁺ activity) and temperature (> 70 $^{\circ}$ C) increase the hydrolytic driving force leading via deprotonation to low charge octahedral $[Ti(OH)_3(OH_2)_3]^+$ monomers that are edge-bonded in pairs by oxolation creating the characteristic anatase prototypical structural feature [42]. By contrast at low pH corner-shared bonds dominate in complex association favoring linear chains as precursor to rutile crystal formation [21].

Role of CSTR

Furthermore, the combination of employing a CSTR and elevated pH in the range 1 < pH < 6, in the present work has led to phase-pure anatase, while in previous studies employing batch reactors but otherwise operating at the same pH range the anatase nanoparticle product was contaminated with small amounts of rutile and/or brookite [24]. The critical role of CSTR in obtaining phase-pure anatase is attributed to its well-mixed and low (but constant) supersaturation regime. In batch reactors the supersaturation tends to change with the progress of precipitation triggering transformation of the initially nucleated anatase phase to the intermediate stability brookite phase or to the rutile phase that is the most stable one [1]. In the present study, solution pH is maintained at 3 and agitation of solution ensures there are no local variations in pH throughout the operation, thus proton-catalyzed dissolution of anatase nanoparticles is inhibited and pure anatase phase is formed, which is collected and quenched in a relatively short period of time, i.e. 30 minutes. Moreover, the steady-state, low supersaturation regime ensures only one nucleation path, that of anatase in the selected pH range as just discussed. Therefore, the elevated pH and steady-state low supersaturation kinetically stabilize the metastable anatase phase nanoparticles. Additionally through aggregation as discussed later, the surface energy of the nanocrystallites is reduced contributing further to stabilization of the anatase phase.

Particle and composition analysis

BET surface area

BET surface area of all TiO₂ products was determined as listed in Table 3.1 along with the equivalent non-porous particle size. All powders possess exceptionally high surface area with equivalent particle size ranging from 6 - 10 nm depending on the experimental conditions. Some interesting trends can be identified by examining all data as shown in Figure A.5. By far the strongest influence on surface area is exerted by pH, followed by temperature, and TiCl₄ feed concentration. When process pH is increased,

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Figure 3.5: Adsorption–desorption isotherm of TiO₂. Test conditions: T = 80 °C, $[\text{TiCl}_4]_{feed} = 0.1 \text{ M}, \text{ pH}_{steady-state} = 3, \tau : 30 \text{ min.}$

the surface area of the resulting anatase product was observed to increase, or equivalently the crystallite size decreased. At the lower pH range, the anatase product undergoes dissolution-recrystallization mechanism involving Ostwald ripening [39, 43] hence the observed reduction in surface area. On the other hand at the high pH end (5-6) the product had somewhat lower degree of crystallinity as evident by the XRD that can also explain the higher surface area. The effect of temperature and concentration on surface area can also be linked to the product crystallinity. A typical adsorption-desorption isotherm is given in Figure 3.5, the BJH desorption pore width of the particular TiO₂ product being 77.54 Å (Table 3.1). The isotherm belongs to type IV category according to BDDT Brunauer–Deming–Deming–Teller classification, characteristic of a mesoporous solid [44]. The hysteresis loop belongs to H3 IUPAC type, indicative of slit-shaped pores [45]. The high surface area and mesoporous nature of the anatase product is of prime importance in applications such as photovoltaics, catalysis, or lithium-ion batteries [5, 34, 46].

Aggregate morphology

Figure 3.6 shows the TEM images of nano-anatase products. Figure 3.6 (a) and (b) show TiO_2 anatase particles exist in forms of nanocrystallite aggregates measuring up

to $\approx 1 \ \mu$ m. Figure 3.6 (c) shows a higher magnification of the aggregates, in which the primary anatase nanocrystallites are distinguishable. As reported, the surface area of these secondary particles is 200-250 m²/g, corresponding to an equivalent BET diameter of 6-8 nm. The TEM images therefore are consistent with the high surface area and mesoporous adsorption isotherm results. Further the primary nanoparticles of 5-6 nm in diameter show a very narrow size distribution as shown in Figure A.6 in addition to Figure 3.6. The d-spacing of the nanoparticles from the TEM images is determined to be 0.36 nm (Figure 3.6 (c)), very close to the 0.352 nm d-spacing of anatase (101) plane according to JCPDS # 00-021-1272 hence confirming the XRD phase identification results. The SAED pattern (Figure 3.6 (d)) shows a continuous ring pattern, indicating the anatase product is polycrystalline [47].

Mechanism of aggregation

The formation of the mesoporous aggregates is attributed first to the operating pH range $(1 \le pH \le 6)$ that is away from the high acidic $(pH \le 1)$ or high alkaline $(pH \ge 12)$ environment that favors nanoparticle peptization [48]. But in addition to pH, the prevailing ionic strength further promotes nanoparticle aggregation [49]. French et al. [49] reported that the aggregate size of 4-5 nm titanium dioxide nanoparticles increased from an average diameter of 50-60 nm at pH 4.5 in a NaCl suspension adjusted to an ionic strength of 0.0045 M, to micron-sized stable aggregates at the same pH when the ionic strength increased to 0.0165 M. At higher pH approaching the point-of-zero-charge $(PZC) \approx 6.8$ [48, 49] even lower ionic strength was required for aggregate formation. The formation of micron-sized aggregates was spontaneous within 15 minutes or less. In the present work the preferred operating pH was 3 for which a higher ionic strength is available ensuring effective aggregation. Ionic strength is essentially controlled by the generated NaCl, which for a 0.2 M Ti(IV) feed will be theoretically 0.8 M (or in practical terms ≈ 0.7 M as it can be verified by the Na⁺ concentration data of Figure 3.1). Hence the prevailing pH and ionic strength are conducive to the formation of the 500 - 1,500 nm aggregates, an advantageous product property both from the point of nanomaterial



Figure 3.6: TEM images of anatase nanocrystalline aggregates acquired at T = 90 °C, $[TiCl_4]_{feed} = 0.2$ M, $pH_{steady-state} = 3$, τ : 30 min. (a) and (b) low magnification images of aggregates, (c) high magnification images showing nanoparticle morphology, (d) SAED pattern. handling and applications.

Composition

A typical FTIR spectrum of TiO₂ product is shown in Figure A.7. The band at 1650 cm⁻¹ is assigned to H-O-H bending of molecularly adsorbed H₂O while the broad band centered at 3200 $\rm cm^{-1}$ indicates presence of surface or structurally incorporated –OH groups [22, 40, 50, 51]. In order to quantify the molecularly adsorbed H_2O and surface/structural -OH groups [51] TGA was conducted. The TGA curve in Figure 3.7 yields 10.79% total weight-loss. There are three noticeable endothermic peaks and corresponding weight loss stages at 120 °C, 223 °C and 400 °C. The first weight loss (3.21%) is from physically adsorbed molecular H₂O, the combined second and third weight loss ($\approx 6.17\%$) can be attributed to chemically bound water and chemisorbed surface OH groups [51, 52] while the last loss (1.445%) may be attributed to structurally incorporated -OHgroups (via incomplete ligand exchange during hydrolysis as discussed in connection to the nucleation mechanism of anatase) [29]. In dye sensitized solar cells, the surface -OH groups assist in stabilizing dye molecules on TiO₂ surface via H-bond bridges [53], whereas in photocatalysis, the reaction between surface -OH groups and holes generates hydroxyl radicals (OH), the active species in degradation of organic molecules [54]. XPS analysis (Figure 3.8) of anatase sample gave the characteristic TiO_2 peaks with respective binding energies, Ti $2p_{3/2}$ at 465.78 eV, Ti $2p_{1/2}$ at 459.68 eV, and O 1s at 531 eV [8, 37]. The Ti:O:Na atomic ratios were determined by Avantage software to be 1:2.22:0.15 (refer to Figure A.8 and Table A.1), i.e. 31.05%, and O: 68.95%, (the $\approx 1.445\%$ structural OH could not be distinguished) Finally it is noted that the anatase synthesized in the present CSTR system contains only half of the OH/OH_2 that is contained in the anatase product obtained in a batch reactor [29]. This difference is attributed to the controlled supersaturation regime of the CSTR that enables fuller crystallization of phase-pure anatase, i.e. fewer uncoordinated surface sites. Since crystal phase and surface reactivity can influence the semiconductor and photocatalytic or other properties of the material [5, 21] the present results manifest the importance of studies involving CSTR-based



Figure 3.7: TGA curve of anatase-TiO₂ nanocrystalline product. T = 80 °C, $[\text{TiCl}_4]_{feed}$ = 0.2 M, pH_{steady-state} = 3, τ : 30 min.

synthesis of nanomaterials.

Bandgap characterization

The bandgap of the CSTR-synthesized anatase semiconductor product was determined from absorption spectra using the following relation:

$$\alpha h\nu = A(h\nu - E_q)^n \tag{3.4}$$

Where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the bandgap energy, A is the band tailing parameter, and the value of n depends on the type of allowed interband electronic transitions [55, 56]. The value of absorption coefficient, α is determined from diffuse reflectance measurements (R_{∞} via the Kubelka-Munk function, $F(R_{\infty})$ [57],

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$
 (3.5)

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Figure 3.8: Nanoanatase XPS spectra of Ti 2p and O 1s peaks.

Anatase is an indirect semiconductor with n=2 [58]. The relation of equation 3.4 in the form of a Tauc plot, whereby $(\alpha h \nu)^{1/n}$ is plotted against the photon energy $(h\nu)$, and the extrapolation of linear section of the curve to $\alpha=0$ gives the band-gap energy [55, 56]. A typical absorption spectrum and Tauc plot of the synthesized TiO₂ is given in Figure A.10.

The determined band-gap energies of the various synthesized anatase crops are given in Table 3.1. The bandgap energies vary between 3.07 - 3.26 eV. If we focus on the 80 °C/pH 3 nanoanatase product the mean bandgap is 3.168 ± 0.026 eV. Comparable values have been reported in literature [37, 39, 59] whereby the observed variability in measured bandgap reflects its dependence on the size of the nanoparticles [60].

3.4.3 Applications

Photocatalysis

Figure 3.9 shows the percent degradation of methyl orange by the as-synthesized anatase aggregates in an aqueous suspension. When the suspension is irradiated with UV radiation electrons in the valence band of TiO_2 are excited and transfer to the conduction band forming electron-hole pairs. Research suggests that the holes migrate to the TiO_2 surface and react with adsorbed OH^- or H_2O molecules to form the OH radical and the electrons from the conduction band react with the molecular oxygen forming the

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Figure 3.9: Photocatalytic activity of CSTR-synthesized anatase aggregates expressed as percent degradation of methyl orange under UV-light irradiation (nano-TiO₂ bandgap = 3.16 eV) (anatase produced at T = 80 °C, $[TiCl_4]_{feed} = 0.1$ M, $pH_{steady-state} = 3, \tau$: 30 min).

superoxide radical - these two radicals then cause the decomposition of methyl orange, while some evidence also points towards direct hole oxidation being responsible for dye degradation [32, 54, 61]. These preliminary results show that the synthesized anatase can be potentially used for degradation of organic pollutants and other photocatalyst-based environmental applications.

Dye-sensitized solar cells

In this application the nanoanatase aggregates were used to fabricate mesoporous dyesensitized solar cell photoanodes via paste screen printing and sintering. Based on previous research [53] the CSTR-synthesized anatase aggregates were blended with rutile sub-micron sized particles also synthesized in a CSTR (Chapter 4), plus P25 in 40/40/20anatase/rutile/P25 ratio to fabricate dye-sensitized photoanodes. TiO₂ photoanodes with variable film thicknesses were prepared by multiple screen-printing cycles. Top-view and cross-section images of the sintered film are given in Figure 3.10 (a) and (b) respectively. Both images show uniform films devoid of cracks. Table 3.2 compares the photovoltaic performance of photoanodes fabricated with aqueous-synthesized anatase obtained by



Figure 3.10: (a) Top-view of sintered TiO_2 (40A/40R/20P25) film (C3), (b) cross-section of film.

both batch and continuous stirred-tank reactor processes for comparative evaluation (J-V curves given in Figure A.9). For each set of similar photoanode film thickness the cells assembled with CSTR powders show better efficiency, owing to higher short circuit current density (J_{sc}). Highest efficiency, 4.72% is reported for $\approx 13 \ \mu m$ thick photoanodes produced with CSTR powders compared to 3.88% efficiency for the batch reactor powders. While the open-circuit voltage (V_{oc}) does not show any specific trends, the fill factor (FF) is also higher for CSTR powders. The enhanced performance of the CSTR anatase-made photoanodes is attributed to the higher anatase phase purity and in particular its mesoporous aggregate structure that facilitates electrolyte infiltration and redox species diffusion [51].

Li-ion batteries

The CSTR-synthesized anatase aggregates were employed as an active material in fabricating Li-ion intercalation electrodes. Electrodes were built via the standard binderbased method [34]. The as-prepared CSTR anatase material exhibited high rate capability, namely 115 mAh g⁻¹ at 10 C rate (1 C=168 mA g⁻¹) due to its large surface area and mesoporous nature allowing for fast Li-ion diffusion rates. Annealing of the anatase material resulted in higher Li-ion storage capacity, 150 mAh g⁻¹ after 100 cycles at 1C rate proving that the CSTR-synthesized anatase can have its properties fine tuned for
Table 3.2: Photovoltaic performance parameters of dye-sensitized photoanodes made with aqueous-synthesized anatase products. (B indicates anatase produced through batch process, C indicates anatase produced through continuous process.) (J-V curves are given in Figure A.9)

Type	Film Thick-	Layers	Efficiency	V_{oc} (V)	J_{sc}	FF (%)
	ness (μm)		(%)		(mA/cm^2)	
B1	3.71	1	3.51	0.75	6.69	69.65
B2	8.06	2	3.69	0.68	7.76	70.41
B3	12.47	3	3.88	0.70	7.93	69.61
C1	3.77	1	3.87	0.77	6.82	74.0
C2	9.28	2	4.43	0.70	8.54	73.82
C3	13.97	3	4.72	0.70	9.16	73.29

different Li-ion battery applications (power vs. energy density) [34]. This was further exemplified with the construction of 3-D Li-ion battery electrodes with the CSTR anatase product that gave very stable and highly reversible intercalation capacity, namely 185 mAh g⁻¹ after 100 cycles at 1C rate [35].

3.4.4 Assessment of CSTR-based aqueous synthesis process

Currently a combination of sol-gel synthesis and hydrothermal processing is the preferred route for producing TiO₂ nanoparticles as it provides excellent particle size and phase control. However, the requirement of prolonged autoclaving, and use of expensive organic precursors leaves much margin for improvement. Compared with chemicals used in sol-gel synthesis, i.e. titanium isopropoxide, ethanol, surfactants and water, our process requires inexpensive precursors – titanium tetrachloride ($\approx 20\%$ of the price of titanium isopropoxide), water, and NaOH. While sol-gel synthesis is conducted at room temperature, it is followed typically by autoclaving at 250 °C for > 6 hours. On the other hand, the new process described in this work is conducted at 80 °C with

only 1 hour residence time and does not require any thermal post-treatment – thus it offers an advantage over sol-gel process on reagent, energy and equipment cost. The prominent distinguishing feature of CSTR-based aqueous process is its ability to produce large quantities of phase-pure anatase with reproducible properties thanks to its steadystate regime, as opposed to sol-gel synthesis that can variability from batch to batch. Combining the cost and scalability advantages with its 100% organic-free operation it makes the present processing option highly attractive as demand for wider and sustainable use of functional nanomaterials constantly increases.

3.5 Conclusion

The proposed CSTR-based process yields nanocrystalline anatase primary particles (5-10 nm) assembled into high-surface area, micron-sized, mesoporous aggregates. pH control between 1 - 6, combined with the low supersaturation environment maintained by the use of CSTR at 80 - 90 °C promote anatase nucleation pathways, while simultaneously discouraging transformation to subsequent phases. Higher pH increases rate of hydrolysis thus increases the surface area, at the cost of crystallinity, whereas change in temperature has the opposite effect. The intermediate pH range and steady ionic strength maintained in the CSTR are conducive to the formation of mesoporous aggregates, an advantageous product property both from the point of nanomaterial handling and application. The as-synthesized anatase possesses excellent functionality as demonstrated in various photocatalytic, photovoltaic and lithium ion storage tests. Due to its reduced environmental impact, and scalability, this process offers a low-cost alternative in producing phase-pure nanoanatase.

3.6 References

- H. Zhang and J. F. Banfield. "Understanding polymorphic phase transformation behavior during growth of nanocrystalline aggregates: insights from TiO₂". In: *The Journal of Physical Chemistry B* 104.15 (2000), pp. 3481–3487.
- M. Ranade, A. Navrotsky, H. Zhang, J. Banfield, S. Elder, A. Zaban, P. Borse,
 S. Kulkarni, G. Doran, and H. Whitfield. "Energetics of nanocrystalline TiO₂". In: Proceedings of the National Academy of Sciences 99.suppl 2 (2002), pp. 6476–6481.
- [3] Y. Bai, I. Mora-Seró, F. De Angelis, J. Bisquert, and P. Wang. "Titanium dioxide nanomaterials for photovoltaic applications". In: *Chemical Reviews* 114.19 (2014), pp. 10095–10130.
- [4] H. A. Foster, I. B. Ditta, S. Varghese, and A. Steele. "Photocatalytic disinfection using titanium dioxide: spectrum and mechanism of antimicrobial activity". In: *Applied Microbiology and Biotechnology* 90.6 (2011), pp. 1847–1868.
- [5] Z. Weng, H. Guo, X. Liu, S. Wu, K. Yeung, and P. K. Chu. "Nanostructured TiO₂ for energy conversion and storage". In: *RSC Advances* 3.47 (2013), pp. 24758– 24775.
- [6] Z. M. Seeley, A. Bandyopadhyay, and S. Bose. "Titanium dioxide thin films for high temperature gas sensors". In: *Thin Solid Films* 519.1 (2010), pp. 434–438.
- [7] R. Vijayalakshmi and V. Rajendran. "Synthesis and characterization of nano-TiO₂ via different methods". In: Archives of Applied Science Research 4.2 (2012), pp. 1183–1190.
- [8] K. Parmar, E. Ramasamy, J. W. Lee, and J. S. Lee. "A simple method for producing mesoporous anatase TiO₂ nanocrystals with elevated photovoltaic performance". In: *Scripta Materialia* 62.5 (2010), pp. 223–226.
- [9] N. K. Memon, D. H. Anjum, and S. H. Chung. "Multiple-diffusion flame synthesis of pure anatase and carbon-coated titanium dioxide nanoparticles". In: *Combustion* and Flame 160.9 (2013), pp. 1848–1856.

- [10] M. Malekshahi Byranvand, A. Nemati Kharat, L. Fatholahi, and Z. Malekshahi Beiranvand. "A Review on Synthesis of Nano-TiO₂ via Different Methods". In: *Journal of NanoStructures* 3.1 (2013), pp. 1–9.
- [11] M. Fernandez-Garcia, C. Belver, J. C. Hanson, X. Wang, and J. A. Rodriguez. "Anatase-TiO₂ nanomaterials: analysis of key parameters controlling crystallization". In: *Journal of the American Chemical Society* 129.44 (2007), pp. 13604– 13612.
- [12] Nanostructured Titanium Dioxide Materials: Properties, Preparation and Applications. World Scientific Publishing Co. Pte. Ltd, 2012.
- [13] B. L. Bischoff and M. A. Anderson. "Peptization process in the sol-gel preparation of porous anatase (TiO₂)". In: *Chemistry of Materials* 7.10 (1995), pp. 1772–1778.
- [14] R. R. Bacsa and M. Grätzel. "Rutile formation in hydrothermally crystallized nanosized titania". In: *Journal of the American Ceramic Society* 79.8 (1996), pp. 2185–2188.
- [15] K. Sabyrov, V. Adamson, and R. L. Penn. "Two-step phase transformation of anatase to rutile in aqueous suspension". In: *CrystEngComm* 16.8 (2014), pp. 1488– 1495.
- [16] G. Oskam, A. Nellore, R. L. Penn, and P. C. Searson. "The growth kinetics of TiO₂ nanoparticles from titanium (IV) alkoxide at high water/titanium ratio". In: *The Journal of Physical Chemistry B* 107.8 (2003), pp. 1734–1738.
- [17] C. Pighini, D. Aymes, N. Millot, and L. Saviot. "Low-frequency Raman characterization of size-controlled anatase TiO₂ nanopowders prepared by continuous hydrothermal syntheses". In: *Journal of Nanoparticle Research* 9.2 (2007), pp. 309– 315.
- [18] Y. Jiao, B. Zhao, F. Chen, and J. Zhang. "Insight into the crystal lattice formation of brookite in aqueous ammonia media: the electrolyte effect". In: *CrystEngComm* 13.12 (2011), pp. 4167–4173.

- [19] H. Cheng, J. Ma, Z. Zhao, and L. Qi. "Hydrothermal preparation of uniform nanosize rutile and anatase particles". In: *Chemistry of Materials* 7.4 (1995), pp. 663–671.
- [20] F. Dufour, S. Cassaignon, O. Durupthy, C. Colbeau-Justin, and C. Chanéac. "Do TiO₂ nanoparticles really taste better when cooked in a microwave oven?" In: *European Journal of Inorganic Chemistry* 2012.16 (2012), pp. 2707–2715.
- [21] J.-G. Li, T. Ishigaki, and X. Sun. "Anatase, brookite, and rutile nanocrystals via redox reactions under mild hydrothermal conditions: phase-selective synthesis and physicochemical properties". In: *The Journal of Physical Chemistry C* 111.13 (2007), pp. 4969–4976.
- [22] C. Charbonneau, R. Gauvin, and G. Demopoulos. "Nucleation and growth of self-assembled nanofibre-structured rutile (TiO₂) particles via controlled forced hydrolysis of titanium tetrachloride solution". In: *Journal of Crystal Growth* 312.1 (2009), pp. 86–94.
- [23] S. Ngamta, N. Boonprakob, N. Wetchakun, K. Ounnunkad, S. Phanichphant, and B. Inceesungvorn. "A facile synthesis of nanocrystalline anatase TiO₂ from TiOSO₄ aqueous solution". In: *Materials Letters* 105 (2013), pp. 76–79.
- [24] A. Pottier, S. Cassaignon, C. Chanéac, F. Villain, E. Tronc, and J.-P. Jolivet.
 "Size tailoring of TiO₂ anatase nanoparticles in aqueous medium and synthesis of nanocomposites. Characterization by Raman spectroscopy". In: *Journal of Materials Chemistry* 13.4 (2003), pp. 877–882.
- [25] H. Yin, Y. Wada, T. Kitamura, T. Sumida, Y. Hasegawa, and S. Yanagida. "Novel synthesis of phase-pure nano-particulate anatase and rutile TiO₂ using TiCl₄ aqueous solutions". In: *Journal of Materials Chemistry* 12.2 (2002), pp. 378–383.
- [26] S.-i. Kawasaki, Y. Xiuyi, K. Sue, Y. Hakuta, A. Suzuki, and K. Arai. "Continuous supercritical hydrothermal synthesis of controlled size and highly crystalline anatase TiO₂ nanoparticles". In: *The Journal of Supercritical Fluids* 50.3 (2009), pp. 276–282.

- [27] K. A. Malinger, A. Maguer, A. Thorel, A. Gaunand, and J.-F. Hochepied. "Crystallization of anatase nanoparticles from amorphous precipitate by a continuous hydrothermal process". In: *Chemical Engineering Journal* 174.1 (2011), pp. 445– 451.
- [28] S. Mohammadi, A. Harvey, and K. V. Boodhoo. "Synthesis of TiO₂ nanoparticles in a spinning disc reactor". In: *Chemical Engineering Journal* 258 (2014), pp. 171– 184.
- [29] C. Charbonneau, R. Gauvin, and G. Demopoulos. "Aqueous solution synthesis of crystalline anatase nanocolloids for the fabrication of DSC photoanodes". In: *Journal of The Electrochemical Society* 158.3 (2011), H224–H231.
- [30] N. P. Benehkohal and G. P. Demopoulos. "Green-Engineered All-Substrate Mesoporous TiO₂ Photoanodes with Superior Light-Harvesting Structure and Performance". In: *ChemSusChem* 7.3 (2014), pp. 813–821.
- [31] K. E. Lee, C. Charbonneau, and G. P. Demopoulos. "Thin single screen-printed bifunctional titania layer photoanodes for high performing DSSCs via a novel hybrid paste formulation and process". In: *Journal of Materials Research* 28.03 (2013), pp. 480–487.
- [32] B. Choudhury, B. Borah, and A. Choudhury. "Extending photocatalytic activity of TiO₂ nanoparticles to visible region of illumination by doping of cerium". In: *Photochemistry and Photobiology* 88.2 (2012), pp. 257–264.
- [33] S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Pechy, and M. Grätzel.
 "Fabrication of screen-printing pastes from TiO₂ powders for dye-sensitised solar cells". In: *Progress in Photovoltaics: Research and Applications* 15.7 (2007), pp. 603–612.
- [34] M. J. Sussman, A. Yasin, and G. P. Demopoulos. "On the complex interplay of crystallinity and surface area effects on Li-ion intercalation and pseudocapacitive storage properties of nanocrystalline anatase". In: *Journal of Power Sources* 272 (2014), pp. 58–67.

- [35] M. J. Sussman, N. Brodusch, R. Gauvin, and G. P. Demopoulos. "Engineering 3-D Li-Ion Electrodes with Enhanced Charge Storage Properties Based on Solution-Processed and Sintered Anatase Nanocrystal-Carbon Mesoporous Structures". In: ACS Sustainable Chemistry & Engineering 3.2 (2015), pp. 334–339.
- [36] G. Demopoulos. "Aqueous precipitation and crystallization for the production of particulate solids with desired properties". In: *Hydrometallurgy* 96.3 (2009), pp. 199–214.
- [37] K. H. Leong, P. Monash, S. Ibrahim, and P. Saravanan. "Solar photocatalytic activity of anatase TiO₂ nanocrystals synthesized by non-hydrolitic sol-gel method". In: Solar Energy 101 (2014), pp. 321–332.
- [38] Z. Yanqing, S. Erwei, C. Zhizhan, L. Wenjun, and H. Xingfang. "Influence of solution concentration on the hydrothermal preparation of titania crystallites". In: Journal of Materials Chemistry 11.5 (2001), pp. 1547–1551.
- [39] D. Reyes-Coronado, G. Rodriguez-Gattorno, M. Espinosa-Pesqueira, C. Cab, R. De Coss, and G. Oskam. "Phase-pure TiO₂ nanoparticles: anatase, brookite and rutile". In: *Nanotechnology* 19.14 (2008), p. 145605.
- [40] Y. Li and G. P. Demopoulos. "Precipitation of nanosized titanium dioxide from aqueous titanium (IV) chloride solutions by neutralization with MgO". In: *Hydrometallurgy* 90.1 (2008), pp. 26–33.
- [41] D. Ferri, G. Riccio, et al. "On the hydrolysis of the titanium (IV) ion in chloride media". In: *Polyhedron* 4.1 (1985), pp. 15–22.
- [42] S. Aruna, S. Tirosh, and A. Zaban. "Nanosize rutile titania particle synthesis via hydrothermal method without mineralizers". In: *Journal of Material Chemistry* 10.10 (2000), pp. 2388–2391.
- [43] S. Cassaignon, M. Koelsch, and J.-P. Jolivet. "Selective synthesis of brookite, anatase and rutile nanoparticles: thermolysis of TiCl₄ in aqueous nitric acid". In: *Journal of Materials Science* 42.16 (2007), pp. 6689–6695.

- [44] J. Yu, Q. Li, and Z. Shu. "Dye-sensitized solar cells based on double-layered TiO₂ composite films and enhanced photovoltaic performance". In: *Electrochimica Acta* 56.18 (2011), pp. 6293–6298.
- [45] F. Rojas, I. Kornhauser, C. Felipe, J. Esparza, S. Cordero, A. Dominguez, and J. Riccardo. "Capillary condensation in heterogeneous mesoporous networks consisting of variable connectivity and pore-size correlation". In: *Physical Chemistry Chemical Physics* 4.11 (2002), pp. 2346–2355.
- [46] A. Burri, N. Jiang, and S.-E. Park. "High surface area TiO₂-ZrO₂ prepared by caustic solution treatment, and its catalytic efficiency in the oxidehydrogenation of para-ethyltoluene by CO₂". In: *Catalysis Science & Technology* 2.3 (2012), pp. 514–520.
- [47] S. Dai, Y. Wu, T. Sakai, Z. Du, H. Sakai, and M. Abe. "Preparation of highly crystalline TiO₂ nanostructures by acid-assisted hydrothermal treatment of hexagonalstructured nanocrystalline titania/cetyltrimethyammonium bromide nanoskeleton". In: Nanoscale Research Letters 5.11 (2010), pp. 1829–1835.
- [48] S. Hore, P. Nitz, C. Vetter, C. Prahl, M. Niggemann, and R. Kern. "Scattering spherical voids in nanocrystalline TiO₂-enhancement of efficiency in dye-sensitized solar cells". In: *Chemical Communications* 15 (2005), pp. 2011–2013.
- [49] R. A. French, A. R. Jacobson, B. Kim, S. L. Isley, R. L. Penn, and P. C. Baveye. "Influence of ionic strength, pH, and cation valence on aggregation kinetics of titanium dioxide nanoparticles". In: *Environmental Science & Technology* 43.5 (2009), pp. 1354–1359.
- [50] K. Parida and N. Sahu. "Visible light induced photocatalytic activity of rare earth titania nanocomposites". In: *Journal of Molecular Catalysis A: Chemical* 287.1 (2008), pp. 151–158.
- [51] K. Lee, M. Gomez, S. Elouatik, G. Shan, and G. Demopoulos. "Vibrational Spectroscopic Imaging of N719-TiO₂ Films in the High Wavenumber Region

Coupled to EIS Analysis". In: *Journal of The Electrochemical Society* 158.7 (2011), H708–H714.

- [52] K. E. Lee, M. A. Gomez, S. Elouatik, and G. P. Demopoulos. "Further understanding of the adsorption mechanism of N719 sensitizer on anatase TiO₂ films for DSSC applications using vibrational spectroscopy and confocal Raman imaging". In: Langmuir 26.12 (2010), pp. 9575–9583.
- [53] K. E. Lee, M. A. Gomez, C. Charbonneau, and G. P. Demopoulos. "Enhanced surface hydroxylation of nanocrystalline anatase films improves photocurrent output and electron lifetime in dye sensitized solar cell photoanodes". In: *Electrochimica Acta* 67 (2012), pp. 208–215.
- [54] Y. Su, Y. Yang, H. Zhang, Y. Xie, Z. Wu, Y. Jiang, N. Fukata, Y. Bando, and Z. L. Wang. "Enhanced photodegradation of methyl orange with TiO₂ nanoparticles using a triboelectric nanogenerator". In: *Nanotechnology* 24.29 (2013), p. 295401.
- [55] F. C. Jentoft. "Electronic Spectroscopy: Ultra Violet-Visible and Near IR Spectroscopies". In: Characterization of Solid Materials and Heterogeneous Catalysts: From Structure to Surface Reactivity, Volume 1&2 (2012), pp. 89–147.
- [56] S. Sathiyamoorthy, B. E. Caroline, and J. G. Jayanthi. "Emerging trends in science, engineering and technology". In: International Conference on Emerging Trends in Science, Engineering and Technology INCOSET-2012, India, Springer. Springer. 2012, pp. 599–600.
- [57] A. E. Morales, E. S. Mora, and U. Pal. "Use of diffuse reflectance spectroscopy for optical characterization of un-supported nanostructures". In: *Revista Mexicana de Fisica S* 53.5 (2007), p. 18.
- [58] C. Magne, F. Dufour, F. Labat, G. Lancel, O. Durupthy, S. Cassaignon, and T. Pauporté. "Effects of TiO₂ nanoparticle polymorphism on dye-sensitized solar cell photovoltaic properties". In: *Journal of Photochemistry and Photobiology A: Chemistry* 232 (2012), pp. 22–31.

- [59] R. Thapa, S. Maiti, T. Rana, U. Maiti, and K. Chattopadhyay. "Anatase TiO₂ nanoparticles synthesis via simple hydrothermal route: Degradation of Orange II, Methyl Orange and Rhodamine B". In: *Journal of Molecular Catalysis A: Chemical* 363 (2012), pp. 223–229.
- [60] K. M. Reddy, S. V. Manorama, and A. R. Reddy. "Bandgap studies on anatase titanium dioxide nanoparticles". In: *Materials Chemistry and Physics* 78.1 (2003), pp. 239–245.
- [61] L. Yu, J. Xi, H. T. Chan, T. Su, D. L. Phillips, W. K. Chan, et al. "The degradation mechanism of methyl orange under photo-catalysis of TiO₂". In: *Physical Chemistry Chemical Physics* 14.10 (2012), pp. 3589–3595.

Chapter 4

Steady-state, scalable production of mesoporous rutile and brookite particles and their use as light scattering layer in solar cells

In continuation of the research presented in Chapter 3, this chapter documents synthesis of the other two common TiO_2 polymorphs - rutile and brookite. The critical role of Ti(IV) concentration in affecting the formation of the two phases, along with particle sizes, phase transformation, and reaction kinetics is discussed. In the end, efficacy of brookite and rutile as scattering particles (as opposed to anatase as transparent particles) in DSSC photoanodes is investigated. This research has been accepted for publication in: Yasin, A., Guo, F., Sussman, M.J., Gauvin, R. & Demopoulos, G.P., *Steady-state, scalable production of mesoporous rutile and brookite particles and their use as light scattering layer in solar cells,* ChemNanoMat, 2016, 2(10), pp.980-988. Supporting Information is given in Appendix B.

4.1 Abstract

Mesoporous TiO₂ rutile crystals possessing cauliflower-like morphology and an internal structure of self-assembled nano-needles were synthesized in a novel Ti(IV) chloride aqueous-solution hydrolysis process. In a unique effort to make nanostructured rutile synthesis cost-effective and green, the process was conducted at steady-state in a continuous-stirred tank reactor (CSTR) below 100 °C. High TiCl₄ concentration 0.5-1 M yielded rutile, while lowering the concentration to 0.1 M led to the crystallization of brookite nano-platelets. Apart from phase control, specific surface area and particle size of rutile may be tuned via TiCl₄ concentration regulation from 85 to 500 m²/g. Investigation into phase evolution during the transient process revealed that low pH/high Ti(IV) concentration conditions yielded only rutile-type nuclei during steady state that grow radially outward into nano-needle structured cauliflower particles with nanoscale edgy surface. The unique steady-state produced micron-sized mesoporous rutile particles were shown to have excellent light scattering properties in a bi-layer photoanode structure resulting in 42.5% increase in photovoltaic efficiency.

4.2 Introduction

Research on synthesis and applications of nano-TiO₂ has seen enormous growth due to its long-term stability, non-toxicity, and variable functionality [1–3]. Rutile, the most stable and abundant polymorph of TiO₂, is used in light scattering applications [4, 5], gas sensors [6], capacitors, and high k-gate insulators for its semiconducting, and dielectric behavior [7]. In addition to rutile, nanocrystalline TiO₂ has two metastable polymorphs – anatase and brookite. Anatase finds applications in photovoltaics [8], photocatalysis [9], and Li-ion batteries [3] owing to its high surface area, favorable band-gap, and intercalation properties. Brookite in the meantime, partly because of difficulties with its synthesis [5, 6] has been less explored in terms of light harvesting [6, 9] or energy storage applications [8].

Low-temperature chemical processes, for example, solvothermal, sol-gel, hydrothermal,

and aqueous solution are widely used in nano- TiO_2 powder preparation as these tend to enable fine control over particle characteristics [10]. However, their cost of production can vary greatly depending on the type of precursor chemicals and solvent used as well as processing conditions. Typically, these processes use Ti(IV) salts dissolved in aqueous, organic, or mixed solvents, often accompanied with additives. Process parameters such as temperature, concentration, pH and aging time are tuned to achieve selective phase synthesis among anatase, brookite, and rutile, and hydrothermal treatment at elevated temperatures (250 - 400 °C) to induce crystallization. For example, Lee et al. [11, 12] synthesized pure brookite, or a mixture of anatase/rutile/brookite by refluxing a sol of $TiCl_4$ made in isopropyl alcohol and water with HCl as a catalyst. Dambournet et al. [13] conducted thermolysis of titanium oxysulfate-sulfuric acid complex hydrate $TiOSO_4 \cdot H_2O/H_2SO_4$ using $Li_2C_2O_4$ in different ratios to either act as a chelating agent to stabilize rutile, or as a ligand to produce $Ti_2O_3(H_2O)_2(C_2O_4) \cdot H_2O$, which upon annealing at 300 °C, produced brookite. Karim et al. [10] synthesized microporous rutile particles with high surface area $\approx 132 \text{ m}^2/\text{g}$ through HCl-assisted hydrolysis of titanium isopropoxide in water. Wang et al. [14] conducted hydrothermal synthesis of amorphous titania gel in presence of different acids and observed that Cl⁻ and NO_3^- catalyzed rutile synthesis. Mamakhel *et al.* [15] achieved direct synthesis of rutile nanorod without any intermediate phases by hydrothermal treatment of titanium isopropoxide and glycolic acid mixture at 200 °C. Bakardjieva et al. [16] studied phase transformation of aqueous synthesized pure phase brookite to rutile by heating the brookite precipitate and determined that brookite transforms to rutile via anatase and achieves complete transformation at 800 °C whereas Zhang and Banfield [17] suggest the phase transformation sequence to be anatase, brookite, and rutile. An extensive review of the different nano- TiO_2 synthesis studies reveals that most of these processes are not scalable for cost-effective, high volume production. Scale-up is not straightforward owing to their multi-step approach and multi-organic chemical use in addition to the often-adopted hydrothermal treatment in autoclaves, which renders the processes capital and operating cost intensive. Considering that product properties and hence their final performance heavily depends on the mode of crystallization reactor operation, it becomes critical that scalable chemical processes are adopted early in nanomaterial synthesis research. This is exemplified with the present work that investigates the production of different nano- TiO_2 phases (rutile and brookite) for energy conversion and storage applications. According to earlier studies in our laboratory involving forced hydrolysis of $TiCl_4$ aqueous solution in a 0.2 L batch stirred reactor at 80 °C, nanostructured rutile particles were produced from 0.5-0.8 M [18] solution and anatase nanocrystallites from 0.1-0.2 M solution [8]. The 'one pot', direct procedure and the absence of organic chemicals made this hydrolysis process ideal to be scaled up for high volume and green synthesis of nano-TiO₂. However, merely increasing the solution volume would not be effective since instantaneous heating of the pre-diluted $TiCl_4$ solution to 80 °C is imperative for nanocrystal formation as opposed to amorphous particle formation [8]. For this purpose a continuous stirred-tank reactor (CSTR) was used for conducting forced hydrolysis of TiCl₄ aqueous solution. As a result of changing the type of reactor the supersaturation regime changed [18] altering the crystallization path. Thus brookite instead of anatase was produced this time from dilute TiCl₄ solution and rutile from concentrated solution. As reported elsewhere, by controlling the pH > 1 the synthesis of metastable anatase nanoparticles became possible in a CSTR [19]. In this paper the employment of aqueous synthesis in a CSTR is shown to allow for nano- TiO_2 phase, crystal shape, and size/surface area control via concentration regulation. As a result the synthesis of rutile micron-sized mesoporous particles with preferentially oriented internal nano-needle structure is accomplished, the surface area of which can be tuned from 80 to $500 \text{ m}^2/\text{g}$ over the concentration range 0.5-1.0 M. At the same time the facile synthesis of brookite nanoplatelets is favoured at 0.1 M concentration. The paper further elucidates the unsteady state mechanism leading up to rutile or brookite crystallization, and finally demonstrates the rutile particles to exhibit excellent scattering properties, leading to 42.5% efficiency increase in a dye-sensitized bi-layer photoanode cell (DSSC) structure.

4.3 Experimental

4.3.1 Synthesis

For a detailed description of the CSTR apparatus and operational procedure refer to reference [19]. For preparation of nano-TiO₂ (brookite, rutile or mixed phase), 1 L of 0.05 M TiCl₄ (ReagentPlus[®], 99.9% trace metals basis, Sigma-Aldrich) aqueous solution was initially charged (to serve as receiving solution) and agitated at 800 rpm in the 2 L capacity CSTR and heated until it reached 80 °C. The continuous operation was started by feeding a continuous inlet stream of 0.1-1.0 M TiCl₄ (maintained at 0 °C) to the receiving solution in the reactor, while simultaneously pumping solution out of the reactor. The inlet and outlet streams were pumped at 16.67 mL/min to maintain a residence time (τ) of 1 hour. Once the process reached steady state, the outlet colloidal suspension was washed with deionized water and centrifuged alternatively twice followed by a third wash with anhydrous ethanol. The obtained nanocrystalline material was dried at 80 °C and ground in a mortar and pestle to obtain white TiO₂ powder.

4.3.2 Paste preparation & DSSC assembly

Screen-printable paste of the synthesized rutile was prepared following Ito *et al.*'s protocol [20]. 6 g dry rutile powder was mixed with 1 mL acetic acid, 5 mL water, and 30 mL ethanol in mortar and pestle with intermittent grinding. The mixture was transferred to a beaker and 20 mL terpineol and 30 g solution of 10 wt.% ethyl cellulose in ethanol were added, alternated with ultrasonic horn and magnetic stirring for robust dispersion. Excess ethanol was evaporated in a rotary evaporator at 45 °C under vacuum.

Fluorine-doped tin oxide (FTO) glass was cleaned in an ultrasonic bath, followed by UV-ozone treatment. For photoanode preparation, FTO glass was immersed in 50 mM TiCl₄ at 80 °C and sintered at 400 °C for 30 minutes. Dyesol 18NRT paste (anatase, \approx 20nm) was deposited on the glass with a screen-printer (Atma Champ Ent. Corp., Taiwan; 45T mesh) in 2 printing cycles followed by one printing cycle of the synthesized rutile paste. The films were sintered at 450 °C for 30 minutes followed by TiCl₄ post-treatment and sintered again at 450 °C for 30 minutes. They were then kept in 52 mM N719 dye solution for 24 hours, and washed with ethanol to remove the excess dye. For counter-electrode preparation, $2x3 \text{ cm}^2$ FTO glass pieces were pierced with holes and platinized with 5 mM H₂PtCl₆-propanol solution and sintered at 400 °C for 30 minutes. The photo- and counter-electrodes were sandwiched with thermoplastic sealant (Surlyn[®]-30, Dyesol) and hot pressed. Commercial iodide based electrolyte (EL-HPE, Dyesol) was injected through the holes in the counter electrode; the holes were covered with the sealant followed by amorphous glass and hot pressed to complete the assembly. The assembled cell was coated with indium metal at the terminals.

4.3.3 Characterization

The nano-TiO₂ product was characterized with X-ray diffraction (XRD) on a Bruker D8 Diffractometer equipped with a Cu K α 1 source ($\lambda = 1.5406$ Å), operated at 40 kV and 40 A. Scans were taken between 20° and 70° with a step size of 0.005° . EVA software was used to conduct background subtraction and smoothening; and phase analysis and % crystallinity were determined by conducting Rietveld refinement on X'pert HighScore. The obtained patterns were compared against JCPDS #01-071-1166, #00-016-0617, and #01-079-5858 for anatase, brookite, and rutile respectively [21]. Surface area was determined through multipoint BET (Brunauer-Emmett-Teller) analysis conducted on Micromeritics TriStar 3000 using nitrogen. The powder was degassed with nitrogen gas at 70 °C for 10 hours beforehand. Ti(IV) concentration of supernatant of samples regularly taken from the reactor was measured through ICP-AES (inductive coupled plasma-atomic emission spectroscopy). TEM (transmission electron microscope) images were taken on a Philips CM-200 at 200 kV. SEM (scanning electron microscope) images were taken on a Hitachi SU-8230. Solar cells were tested for photovoltaic performance under simulated AM 1.5 conditions using a solar cell I-V curve testing system (PV Measurements, Inc., Colorado). Electrochemical impedance spectroscopy (EIS) was conducted with a 10 mV

AC perturbation in 50 mHz-100 kHz range using a VSP instrument (BioLogic, Claix, France) and analysed with Z-view software. Film transmission and quantum efficiency measurements were taken on a Quantum Efficiency measurement system, Model QEX10 (PV Measurements, Inc., Colorado).

4.4 Results & Discussion

Figure 4.1 presents the X-ray diffraction patterns of TiO₂ nanocrystalline products obtained at different inlet $TiCl_4$ concentrations. Pattern (a) corresponds to $TiCl_4$ inlet concentration of 1 M; extremely broad rutile peaks in the XRD pattern indicate existence of small nanoparticles. In patterns (b) and (c), ([TiCl₄]=0.8 M and 0.5 M respectively), sharper peaks at 27.2° (110), 36.1° (101), 41.1° (111) clearly indicate the presence of rutile phase, according to JCPDS #01-079-5858. Upon lowering the TiCl₄ concentration further to 0.2 M and 0.1 M (patterns (d)-(e)) brookite phase was detected in addition to rutile, evident by emergence of peaks at 25.5° (120), and 30.5° (121), according to JCPDS #00-016-0617. Since the primary peak of TiO₂ anatase phase appears at 25.3° (JCPDS #01-071-1166) an anatase peak at 75.05° was identified as the sole peak that does not overlap with brookite or rutile, and its absence in Figure 4.1 is taken as confirmation of absence of anatase. Phase ratios were determined using X'Pert HighScore and are given in Table 4.1. Hence, lowering the $TiCl_4$ concentration to 0.2 M and further to 0.1 M brookite synthesis was favoured, with residual amount of rutile (<10%) present in the 0.1 M product. At 0.2 M a mixed phase product is obtained. In diluted TiCl₄ solution (high water activity prevailing) hydrolysis leads to formation of $[Ti(OH)_a Cl_b (OH_2)_{(6-a-b)}]^{(4-a-b)+}$ complexes with simultaneous release of Cl⁻ and H^+ ions. Therefore, in our process, the concentration of H^+ ions and thus the acidity of the reactor solution is determined by the inlet $TiCl_4$ concentration – higher $TiCl_4$ concentration leads to higher proton concentration and thus lower pH and vice versa. The results agree with previous findings in published literature insofar they show rutile was observed under high Ti(IV) concentration and consequently high acidity conditions, and brookite was produced under low Ti(IV) concentration, high acidity solution [21–23]. It is interesting to note here that based on our previous study, anatase synthesis could only be achieved by maintaining solution pH between 2-5 by continuous addition of sodium hydroxide. Moreover at pH 2-5 conditions, there was no rutile or brookite formed [19]. Hence, the combined effect of solution pH and Ti(IV) concentration is the driving force for the different TiO₂ phase(s) formed upon hydrolysis of TiCl₄ in a CSTR. From Table 4.1 the crystallinity of rutile decreased by 9% with an increase in concentration from 0.5 M to 0.8 M. This observation concurs with Charbonneau *et al.*'s work [21] which attributes higher crystallinity to faster kinetics due to higher water activity for low concentration solution [10, 21]. (The lower TiCl₄ concentration solutions yielded mixed phase titania and since each phase follows different crystallization mechanism [22], the respective product crystallinity were not considered for this analysis.)

Experiments were also conducted to observe the effect of temperature, agitation, and residence time on the ratio of brookite/rutile phases and results are given in Figure B.1. Change of any of these parameters for 0.1 M Ti(IV) solution produced brookite-rich TiO₂ nanoparticles. Higher temperature and longer residence time led to growth of brookite crystals possessing lower surface area.

4.4.1 Transient state analysis: nucleation and phase transformation

Figure 4.2 shows the outlet concentration of unreacted Ti(IV), and percentage precipitation relative to the TiCl₄ inlet concentration with time for two different inlet TiCl₄ concentrations, (a) 0.1 M, and (b) 0.5 M. In both scenarios, the initial Ti(IV) concentration was non-zero owing to the hydrolysis of the 0.05 M receiving solution. Figure 4.2(a) shows 88% conversion and an unsteady-state period of \approx 8 hours, and Figure 4.2(b) shows 76% conversion and an unsteady-state period of \approx 6 hours. Percent precipitation decreased with increasing Ti(IV) concentration in the inlet stream (Figure 4.2).

This can be explained considering that water is essentially a reactant in the hydrolysis of $TiCl_4$ – in high Ti(IV) concentration, or low water activity solution, less number of hydrated Ti octahedra condense to form nuclei. At time 0, the receiving solution



Figure 4.1: XRD patterns of TiO₂ produced at T=80 °C, τ =1 hour, 800 rpm, [TiCl₄]_{feed} = a) 0.1M b) 0.2M c) 0.5M d) 0.8M e) 1M

TiCl4	Rutile (%)	Brookite (%)	Crystallinity	$7 BET sur-face area(m^2/g)$	Equivalent diameter (nm)	Size (nm)
1 M	100	0	-	495.6	2.9	3-5
0.8 M	100	0	82	84.4	16.9	500-
						800
$0.5 \ \mathrm{M}$	100	0	91	102	14.0	200-
						300
$0.2 \ \mathrm{M}$	60	40	-	122.4	11.7	-
$0.1 \ \mathrm{M}$	8	92	-	123.9	11.5	25-
						105

Table 4.1: Phase composition and crystal properties of TiO₂ produced at steady-state $(T=80 \ ^{\circ}C, \tau=1 \text{ hour, } 800 \text{ rpm})$

Ti(IV) concentration is very low, $\approx 10^{-3}$ order of magnitude, and as a consequence it undergoes rapid hydrolytic precipitation; as more TiCl₄ is flown into the reactor during the start up period the concentration of unreacted Ti(IV) increases due to increasing competition for solvation with water molecules. Another observation entails that high TiCl₄ concentration also leads to high Cl⁻ concentration in the solution; these ions occupy the first coordination shell of Ti(IV) hindering their hydrolysis [21], and thus a higher proportion of unreacted Ti(IV) reports in the outlet stream.

Figure 4.3 shows XRD patterns of TiO₂ phase nucleation and evolution during the unsteady-state operation of CSTR yielding as final product either a) rutile (0.5 M) or b) brookite (0.1 M). Focusing on Figure 4.3 (a), at time 0 the only phase appearing is anatase. This phase represents the initially nucleated product of the receiving solution (0.05 M TiCl₄) as it was heated up from 0 °C to 80 °C. XRD taken at 30 minutes shows appearance of rutile at 27.2°; thereafter an increase in intensity of rutile (110) peak at 27.2°, and simultaneous decrease in anatase (101) peak intensity at 25.5°, indicate

increasing rutile proportion and less anatase with time, and after 5.5 hours only rutile was produced. It is to be noted that brookite did not appear in the high concentration (0.5-1.0 M) rutile crystallization pathway. The solution pH at time 0 was 0.93 (generated from the hydrolysis of the 0.05 M receiving solution) at which the homogeneously nucleated titania according to the XRD pattern shows very low crystallinity. Homogeneous nucleation of anatase occurs in aqueous solution due to favourable surface energy changes since anatase nanoparticles have smallest surface energy for particle size less than 14 nm [17, 24]. Moreover, under the given Cl^- concentration (<0.2 M) [25] and pH (0.93), Ti(IV) octahedra of the form $[Ti(OH)_3(OH_2)_3]^+$ are expected, which undergo condensation along apical direction to yield anatase [25].

The 0.5 M TiCl₄ solution entering into the reactor had two effects: firstly, increase in Ti(IV) ion concentration in the solution and subsequent increase in free proton (H^+) concentration as a result of its hydrolysis causing the pH in the reactor to drop down to pH 0.14. The increase in acid concentration promotes anatase crystallite growth via ripening involving acid dissolution of the finest of homogeneously formed nuclei followed by heterogeneous growth due to the availability of more Ti(IV) ions; as anatase crystallites keep growing they become unstable and undergo in-situ lattice rearrangement to form the stable rutile phase [22]. Secondly, there was a continuous flow of inlet and outlet streams in the CSTR. If it is argued that the precipitated anatase did not undergo transformation, the continuous flow would force anatase to be purged out of the reactor gradually. Moreover, increase in acid concentration promotes the protonated form of Ti(IV), which serves as monomer for rutile synthesis [25]. At steady state conditions, the solution Ti(IV) concentration was 0.12 M (Figure 4.2 (a)) and pH was 0.06; in such an environment only rutile type monomers can form [22] and hence no anatase/brookite was observed. The observed transient state formation of rutile via transformation of initially nucleated metastable anatase is consistent with previous studies carried out in hydrothermal batch reactors at temperatures much higher than the present study, namely at 200 °C [24] and 300 °C [26]. In contrast Mamakhel et al. [15] reported the direct hydrothermal formation of rutile without any intermediate phases. This was demonstrated with in-situ experiments at 300 °C and 400 °C but could not be demonstrated at 200 °C because the weak Bragg peaks were obscured by strong scattering signal. It is possible that at such high temperature (>300 °C) phase transformation kinetics are too fast (< 1 min), making difficult the detection of any intermediate phase(s).

Figure 4.3(b) presents phase evolution for 0.1 M TiCl₄ solution. Similar to the case for 0.5 M discussed in the earlier paragraph, at time 0 anatase phase is observed. At 30 minutes a brookite peak appears at 30.8° and at 1 hour, a rutile peak appears. After 1 hour, the peaks just keep increasing in intensity, indicative of growing crystallinity until they reach steady-state intensities at 5 hours. Reves-Coronado et al. [24] propose that while both rutile and brookite are synthesized under similar conditions of high acid concentration, the reaction pathways are highly sensitive to HCl concentration. In high acidic concentration and presence of Cl⁻ ions, Ti(IV) exists as an octahedral complex with Cl^- , OH^- and OH_2 ligands. As HCl concentration increases the number of coordinated chloride ions increases in the titania chloro-complex making it more symmetric. Since symmetry of titania octahedra is higher in rutile than in brookite, Reves-Coronado et al. [24] suggest that $[Ti(OH)_2Cl(OH_2)_3]^+$ is the monomer for brookite while the more symmetric $[Ti(OH)_2Cl_4]^{2-}$ monomer leads to formation of rutile through hydrolysis-oxolation. As a consequence, the synthesis of brookite-rich TiO₂ was facilitated at 0.1 M TiCl₄ concentration while higher concentrations favour rutile crystallization. This is clearly evident with the results presented in Table 4.1 according to which 8%, 60%, and then 100% rutile is obtained with 0.1 M, 0.2 M, and 0.5 M TiCl₄ respectively.

We have further determined that as in the case of rutile, brookite forms during the transient stage via the transformation of initially nucleated anatase. For example for 30-minute residence time (Figure B.1 (a) and Table B.1) a mixture of anatase and brookite was obtained (with 0.1 M Ti(IV) solution) but for 4-hours residence time the product is a mixture of brookite and rutile (Figure B.1 (c)), i.e. brookite starts transforming to rutile at longer residence times. Therefore, the synthesis of brookite is kinetically-controlled in the dilute concentration regime.

In the parallel study that we conducted on anatase synthesis in a CSTR, anatase

was produced at 0.5 M by maintaining the solution pH at 3 via continuous addition of NaOH [19]. At pH 3 the Ti octahedra are in deprotonated form, undergoing rapid condensation into anatase nuclei that resist dissolution-recrystallization because of the absence of protons that drive the dissolution part of the transformation process. Figure B.4 presents a graphical summary of the operating parameters under which the three polymorphs are obtained by hydrolysis in the CSTR at 80-90 °C.

4.4.2 Properties of steady-state rutile & brookite crystals

Table 4.1 lists the BET surface area for rutile and brookite crystals produced at steadystate. Rutile surface area decreased from $102 \text{ m}^2/\text{g}$ to $84.4 \text{ m}^2/\text{g}$, or equivalently, the crystallite size increased when the TiCl₄ concentration increased from 0.5 M to 0.8 M. The higher water activity for lower concentration solution accelerates hydrolysis having as a result formation of large number of nuclei that undergo limited growth [5]. The surface area is extremely high for 1 M TiCl₄, which agrees with the broad peaks in the respective XRD pattern (Figure 4.1(a)), indicative of poorly crystalline particles. We have been unable to locate rutile particles with comparable surface area in literature. However, studies have used copolymer templates or surfactants to facilitate synthesis of high surface area rutile [27–29]. By tuning the surface area and nanoparticle size via direct control of the experimental conditions without any special treatment or additives makes the novel CSTR-based aqueous solution process highly attractive.

Figure 4.4 (a) shows image of an isolated nano-fibre structured rutile crystal with elongated morphology produced with 0.2 M TiCl₄ inlet concentration. Figure 4.4 (b) shows rutile primary crystals produced with 0.5 M TiCl₄; the crystals of approximate dimensions of 200-500 nm appear to have grown into semi-spheroidal shape from individual crystallites (see Figure 4.4 (a)) that serve as the building blocks [10]. Figure 4.4 (c) shows a high magnification cross-section image of Figure 4.4 (b) emphasizing the fibrous (needle-like) structure of the crystal. In Figure 4.4 (d) the d-spacing of the crystal planes is measured to be 3.2 Å corresponding to (110) rutile plane d-spacing of 3.24 Å (JCPDS #01-079-5858); as it can be deduced from these images crystal growth occurred along



Figure 4.2: Variation of outlet concentration of unreacted Ti(IV) and % precipitation during start-up/transient operation with (a) 0.1 M and (b) 0.5 M inlet Ti(IV) concentration. ($\tau = 1$ hour, T = 80 °C)



Figure 4.3: TiO₂ phase evolution during the transient/start-up period: (a) rutile production (T=80 °C, τ =1 hour, 800 rpm, [TiCl₄]_{feed}=0.5 M) and (b) brookite production (T=80 °C, τ =1 hour, 800 rpm, [TiCl₄]_{feed}=0.1 M).

the (110) plane, and the crystal morphology is dominated by (110) planes. This type of preferential orientation is also revealed by the broad arcs in the SAED pattern (Figure 4.4 (d) inset) [21]. Figure 4.4 (e), (f) show SEM images of cauliflower-shaped secondary rutile particles around 2 μ m in size; a close-up image reveals the fringes seen in Figure 4.4 (d). The images in Figure 4.4 suggest the rutile cauliflower-shaped particles with preferentially-oriented nano-needle interior structure to be porous. This was confirmed by BET analysis-the results are given in Appendix B. For powders obtained at steadystate at 0.1 M and 0.5 M TiCl₄ solutions (Figure B.5) the BET adsorption/desorption isotherms show hysteresis loops and thus are classified as IUPAC Type IV, typical of mesoporous adsorbents [30]. Figure B.5 (b) possesses type H2 hysteresis loop indicating presence of small spherical particles and bottleneck pores [31].

Before we discuss the brookite crystallization results it is noteworthy to comment on the observed direct formation of rutile in the continuous-stirred tank reactor (steady-state product) as opposed to its formation via transformation of anatase and brookite during the transient (non steady-state) operation despite using the same inlet/starting solution. We attribute the direct formation of rutile to the unique steady-state supersaturation and seeded environment of the CSTR that differs from that of batch reactors that dominate laboratory research studies [18]. In a batch reactor nucleation occurs spontaneously while acid concentration is low; however, in a CSTR the acid concentration is high, ≈ 4 times the concentration of Ti(IV). In such an environment rutile precursor $[Ti(OH)_2Cl_4]^{2-}$ monomers dominate [22, 24] hence by-passing altogether the formation of intermediate phases like anatase and brookite. Moreover, the rutile product crystals in the CSTR act effectively as seed and as consequence lower the activation energy of rutile's nucleationgrowth kinetics. Thus fully grown cauliflower-shaped nanostructured rutile crystals were produced in the CSTR with only 1 hr residence time at steady-state, while equivalent crystals were obtained via the phase transformation path in the transient reactor after >5 hrs operation (Figure 4.3 (a)). The CSTR-based direct formation of rutile in this work is even more remarkable if we contrast it with the recent study by Mamakhel et al. [15] who also reported direct formation of rutile nanoparticles but at 300 °C and 400

°C rather than below 100 °C. Hence crystal nucleation and growth in the steady-state regime of CSTR provides a mostly unexplored avenue in nanomaterial synthesis with great potential in altering crystal properties while achieving high production yield.

In contrast to rutile's 3D cauliflower crystal morphology, the brookite crystals were in the form of planar nanoplatelets (Figure 4.5). Figure 4.5 (a) shows the brookite particles to have a wide size distribution, 27-105 nm. The BET surface area (Table 4.1) is 123 m^2/g with an equivalent diameter of 11 nm; thus the individual crystals are porous with high surface area. Figure 4.5 (b) shows a higher magnification image revealing more clearly the porosity within the individual crystals. Figure B.5 (a) shows the BET adsorption/desorption isotherms of the respective powder to follow the IUPAC Type IV isotherm that is characteristic of mesoporous materials [30]. Figure 4.5 (c) shows an SEM image of the particles in which they appear to be quite planar. In Figure 4.5 (d) inter-planar distance is measured to be 3.5Å, which concurs with the d-spacing of brookite (120) plane.

4.5 Energy conversion and storage applications

Dye-sensitized solar cells were constructed with two configurations of photoanodes to evaluate the applicability of new mesoporous rutile crystals as scattering particles. In the first type, two screen printed layers of Dyesol 18NRT paste constituted the semiconductor film, and in the second type, two 18NRT layers were overlaid with a layer of a paste carrying the synthesized rutile particles (TiCl₄ concentration: 0.5 M) to act as the scattering layer.

Figure 4.6(a) shows the J-V curves corresponding to the photovoltaic performance of dye-sensitized cells made with photoanodes with and without rutile scattering layer, and Table 4.2 lists the values of open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and photoconversion efficiency (η). V_{oc} reflects the difference in Fermi level of the TiO₂ semiconductor and redox potential of the I_3^-/I^- electrolyte [32]. The bandgap of rutile was found to be 3.0 (see Figure B.3) which is lower than the



Figure 4.4: Steady-state rutile crystals: (a) TEM image of rutile (mixed with brookite) produced with 0.2 M TiCl₄ inlet concentration; (b) TEM image of rutile produced with 0.5 M [TiCl₄]_{feed} inlet concentration; (c,d) high magnification images of TEM image in b), inset shows SAED pattern; (e,f) SEM images of rutile cauliflower particles produced with 0.5 M [TiCl₄]_{feed}.



Figure 4.5: (a) TEM image of brookite nanoplatelets; (b) higher magnification image in which the porosity of the nanoplatelets is evident; (e) SEM image of brookite product; and (d) higher magnification TEM image of brookite nanoplatelets (Inlet concentration: 0.1 M [TiCl₄]_{feed})

bandgap of anatase particles, hence the presence of rutile is not expected to contribute towards cell voltage, reflected in similar V_{oc} values for both cell types. The short circuit current increases from 8.54 mA/cm² to 12.03 mA/cm² with the addition of the scattering layer. Therefore, the increase in efficiency from 4.02% to 5.71% is solely attributed to the increase in current generation. This statement is supported by Figure 4.6(b) which shows incident light transmission decreased to 30% from 70% due to the addition of scattering layer; in other words the transmitted part of incident light was reflected back into the anatase film hence increasing the light harvesting capability of the solar cell [33]. (Also see Figure B.7). IPCE (incident photon to electron conversion efficiency) curves for 18NRT cell and 18NRT+scattering layer cell given in Figure 4.6(c) show a nominal increase in IPCE. Peaks at \approx 340 nm and \approx 530 nm correspond to intrinsic light absorption of TiO₂ and N719 respectively [33].

Electrochemical impedance spectroscopy (EIS) was conducted to understand the kinetics of interfacial charge transfer processes impacted by the incorporation of the rutile scattering layer. Three distinct semicircles characteristic of DSSCs appear on Nyquist plot as shown in Figure 4.6(d). The left semicircle corresponding to high frequencies represents the charge transfer processes at FTO/TiO₂ interface, and Pt counter electrode/electrolyte, (R_{CE}) . The middle semicircle at intermediate frequencies represents charge transport resistance in TiO_2 film (R_t), and recombination resistance at the $TiO_2/dye/electrolyte$ interface (R_{rec}), and the third semi-circle at low frequencies represents the Nernst diffusion resistance within the electrolyte [33, 34]. In the two EIS spectra in Figure 4.6(d) the third semicircle only appears for the cell with the scattering layer, and can be attributed to the presence of two layers of drastically different size particles, which affects electrolyte diffusion in the film [35]. Electrochemical parameters based on equivalent circuit model were fitted with Z-view[®] and their values are given in Table 4.2. The data show the cell with scattering layer to have higher transport resistance within the TiO₂ film (R_t) which can be easily attributed to the higher thickness of the film. In addition, the film with scattering layer also has a higher recombination resistance (R_{rec}) – one possible explanation could be that the larger rutile particles block the flow of electrons to the electrolyte hence decreasing the unfavourable electron recombination at the TiO_2 /electrolyte interface [33]. Thus, the addition of scattering layer improves the DSSC efficiency by increasing absorption of incident light via reflectance, and by decreasing electron recombination.

The cells were also investigated using the OCVD (open circuit voltage decay) technique that measures the electron lifetime in DSSCs to further probe the interfacial recombination processes [36]. The cell is allowed to reach steady state under simulated illumination signifying equilibrium between electron injection and electron recombination at the TiO_2/FTO interface. Then the illumination is turned off and the decay in photoinduced voltage is monitored (see Figure 4.6(f)). The decay reflects the decrease of electron concentration at the FTO surface due to recombination with the electrolyte.

Figure 4.6(d) shows a very steep decrease in V_{oc} (< 20 seconds) for only transparent film based cell, while in the cell with scattering layer the decrease takes around 100 seconds; this been attributed to the increased optical path length of the incident light due to the presence of the scattering layer [37]. From the OCVD measurements, electron lifetime is calculated according to Equation 4.1

$$\tau = -\frac{k_B T}{e} \left(\frac{dVoc}{dt}\right)^{-1} \tag{4.1}$$

Where k_B is Boltzmann constant, T is temperature, e is electron charge and (dV_{OC}/dt) is the time derivative of open-circuit voltage [33]. Figure 4.6(e) shows the electron lifetime is longer for the cell with scattering layer [38]. The anatase particles, being smaller in size have grain boundaries that act as surface traps and reduce the electron lifetime [33]. When a scattering layer is applied the anatase particles are 'capped' by the bigger rutile particles that block the electrons from entering the electrolyte resulting in longer electron lifetimes [33].

The 42.5% increase in solar cell efficiency from 4.02% to 5.71% imparted by the incorporation of our mesoporous cauliflower-shaped rutile crystals as scattering layer is comparable or better than that imparted by other forms of rutile particles produced via exotic and costly synthesis routes. Thus Lv *et al.* [39], among the different rutile

particle architectures they synthesized, found hollow TiO₂ microspheres to impart the highest increase in efficiency, namely 30%. Their hollow spheres were prepared though via low yield solvothermal alcoholysis involving thermal treatment at 110 °C for 2 weeks. On the other hand sub-micrometer sized rutile TiO₂ nanorod microspheres having some resemblance to our mesoporous rutile crystals also resulted in a 40% increase in efficiency when used as scattering layer [4]. In the latter study the rutile microspheres had been synthesized via hydrothermal treatment of a 0.3 M TiCl₄/3 M NaCl solution at 120 °C for 12 hours. On the other hand, our mesoporous rutile particles are prepared via a high throughput, ambient pressure, continuous process with apparent economic and environmental advantages. It is clear that the mesoporous rutile particles with their internal structure of self-assembled fibrous planes provide an ideal scattering medium for enhanced light harvesting as exhibited by the increased photocurrent generation while their size and porosity allows for optimum packing and intra-film electrolyte diffusion.

Table B.2 presents the photovoltaic performance of cells with brookite as the light scattering layer. The V_{oc} remains the same as is the case for rutile scattering layer; however cells with rutile show slightly better improvement in J_{sc} than brookite, probably due to the larger crystal sizes and 3D vs. 2D morphology multiplying light scattering. The overall change in efficiency otherwise is similar for both titania varieties. In addition, the brookite nanoplatelets synthesized in this study demonstrated extremely stable cycling performance (see Figure B.7) as Li-ion intercalation electrode in Li-ion batteries as described elsewhere [40]. The mesoporous 2-D crystal morphology provides both favorable large electrolyte/material interface and short Li-ion diffusion length resulting in good Li-ion intercalation performance. What is very interesting is that the CSTR synthesized brookite nanoplatelets were found to progressively undergo crystal structure enhancement upon cycling despite certain lattice distortion occurring during lithiation that allows them to quickly relax upon delithiation in an extremely efficient (> 99.7% coulombic efficiency) reversible manner translating to excellent Li-ion intercalation stability.

Chapter 4. Steady-state, scalable production of mesoporous rutile and brookite particles and their use as light scattering layer in solar cells



Figure 4.6: (a) J-V curves of DSSCs with and without rutile scattering layer; (b) film transmittance; (c) external quantum efficiency; (d) Nyquist plot; (e) electron lifetime; (f) open circuit voltage decay.

4.6 Conclusion

In a departure from the bulk of laboratory studies that focus on synthesis of nanostructured particles in batch reactors, here it is shown that synthesis in a continuous-stirred tank reactor is a promising and mostly unexplored avenue in altering nanocrystal properties while achieving high production yield with obvious material and application advantages. In particular, micron-sized nanostructured rutile particles are synthesized via hydrolysis of 0.5-0.8M TiCl₄ aqueous solution at 80 °C, in a CSTR. At steady-state the CSTR solution has constant supersaturation and seeded regime with high acidity

	PV performance				EIS performance				
	Thickness	$\mathrm{S} \mathrm{V}_{oc} \mathrm{(V)}$	\mathbf{J}_{sc}	$\eta~(\%)$	\mathbf{FF}	\mathbf{R}_{ce}	\mathbf{R}_t	\mathbf{R}_{rec}	au'
	(μm)		(mA/cm^2)		(ω)	(ω)	(ω)	(ns)	
Dyesol	10.32	0.69	8.54	4.02	68.20	5.48	0.87	14.65	98.49
Anatase	± 0.15	± 0.007	± 0.55	± 0.36	± 3.11	± 2.4	± 0.93	± 0.76	
Dyesol	15.64	0.68	12.03	5.71	69.45	4.12	1.1	16.45	119.7
Anatase	± 0.30	± 0.003	± 0.42	± 0.31	± 0.90	± 0.18	± 0.41	± 0.21	
+ Rutile									
Scat-									
tering									
Layer									

Table 4.2: Photovoltaic and impedance spectroscopy parameters of DSSCs

such that the incoming TiCl₄ gets hydrolysed to only yield monomers conducive to direct formation of rutile as opposed to previous studies in hydrothermal batch reactors where rutile is obtained via phase transformation of anatase or brookite precursor crystallites. The latter crystallization path was also observed to occur in the present work during transient state operation of the CSTR. At lower inlet TiCl₄ concentrations (0.1-0.2 M), mixed phase titania – brookite and rutile – is produced at steady-state, with brookite as the majority phase (90-94%) at 80-90 °C and 0.1 M TiCl₄. The rutile crystals are mesoporous according to BET measurements possessing a cauliflower morphology measuring \approx 300 nm and an interior characterized by preferentially-oriented fibres growing in the (110) plane. These crystals are aggregated into micron-sized particles that were shown to act as effective light scattering layer when overlaid on transparent TiO₂-anatase film resulting in increased short circuit current, and 42% increase in the efficiency of assembled solar cells from 4.02% to 5.71%. Such performance was shown to match or exceed that of rutile microspheres or hollow tube particles, which are produced by low yield, complex and prohibitively expensive crystallization methods. In the meantime the present work offers a new scalable process for 2-D brookite crystals (mesoporous nanoplatelets) that have interesting Li-ion intercalation properties for energy storage applications.

4.7 References

- M. Landmann, E. Rauls, and W. Schmidt. "The electronic structure and optical response of rutile, anatase and brookite TiO₂". In: *Journal of Physics: Condensed Matter* 24.19 (2012), p. 195503.
- H. He, C. Liu, K. D. Dubois, T. Jin, M. E. Louis, and G. Li. "Enhanced charge separation in nanostructured TiO₂ materials for photocatalytic and photovoltaic applications". In: *Industrial & Engineering Chemistry Research* 51.37 (2012), pp. 11841–11849.
- [3] V. Aravindan, Y.-S. Lee, R. Yazami, and S. Madhavi. "TiO₂ polymorphs in 'rocking-chair' Li-ion batteries". In: *Materials Today* 18.6 (2015), pp. 345–351.
- [4] Y. Rui, Y. Li, Q. Zhang, and H. Wang. "Facile synthesis of rutile TiO₂ nanorod microspheres for enhancing light-harvesting of dye-sensitized solar cells". In: *CrystEngComm* 15.8 (2013), pp. 1651–1656.
- [5] Y. Rui, Y. Li, Q. Zhang, and H. Wang. "Size-tunable TiO₂ nanorod microspheres synthesised via a one-pot solvothermal method and used as the scattering layer for dye-sensitized solar cells". In: *Nanoscale* 5.24 (2013), pp. 12574–12581.
- [6] H.-y. Yang, X.-L. Cheng, X.-F. Zhang, Z.-k. Zheng, X.-f. Tang, Y.-M. Xu, S. Gao, H. Zhao, and L.-H. Huo. "A novel sensor for fast detection of triethylamine based on rutile TiO₂ nanorod arrays". In: Sensors and Actuators B: Chemical 205 (), pp. 322–328.
- M. Kadoshima, M. Hiratani, Y. Shimamoto, K. Torii, H. Miki, S. Kimura, and T. Nabatame. "Rutile-type TiO₂ thin film for high-k gate insulator". In: *Thin Solid Films* 424.2 (2003), pp. 224–228.

- [8] C. Charbonneau, R. Gauvin, and G. Demopoulos. "Aqueous solution synthesis of crystalline anatase nanocolloids for the fabrication of DSC photoanodes". In: *Journal of The Electrochemical Society* 158.3 (2011), H224–H231.
- [9] X. Lü, D. Mao, X. Wei, H. Zhang, J. Xie, and W. Wei. "Tunable synthesis of enhanced photodegradation activity of brookite/anatase mixed-phase titanium dioxide". In: *Journal of Materials Research* 28.03 (2013), pp. 400–404.
- [10] M. R. Karim, M. T. I. Bhuiyan, M. A. Dar, A. H. Seikh, M. Ali Shar, M. B. Zaman, C. J. Lee, H. J. Kim, and M. S. Lee. "Synthesis and characterization of highly organized crystalline rutile nanoparticles by low-temperature dissolution-reprecipitation process". In: *Journal of Materials Research* 30.12 (2015), pp. 1887–1893.
- B. I. Lee, X. Wang, R. Bhave, and M. Hu. "Synthesis of brookite TiO₂ nanoparticles by ambient condition sol process". In: *Materials Letters* 60.9–10 (2006), pp. 1179– 1183.
- [12] R. C. Bhave and B. I. Lee. "Experimental variables in the synthesis of brookite phase TiO₂ nanoparticles". In: *Materials Science and Engineering: A* 467.1–2 (2007), pp. 146–149.
- [13] D. Dambournet, I. Belharouak, and K. Amine. "Tailored preparation methods of TiO₂ anatase, rutile, brookite: mechanism of formation and electrochemical properties". In: *Chemistry of Materials* 22.3 (2010), pp. 1173–1179.
- [14] Z. Wang, D. Xia, G. Chen, T. Yang, and Y. Chen. "The effects of different acids on the preparation of TiO₂ nanostructure in liquid media at low temperature". In: *Materials Chemistry and Physics* 111.2–3 (2008), pp. 313–316.
- [15] A. Mamakhel, C. Tyrsted, E. D. Bøjesen, P. Hald, and B. B. Iversen. "Direct Formation of Crystalline Phase Pure Rutile TiO₂ Nanostructures by a Facile Hydrothermal Method". In: *Crystal Growth & Design* 13.11 (2013), pp. 4730– 4734.
- [16] S. Bakardjieva, V. Stengl, L. Szatmary, J. Subrt, J. Lukac, N. Murafa, D. Niznansky, K. Cizek, J. Jirkovsky, and N. Petrova. "Transformation of brookite-type TiO₂ nanocrystals to rutile: correlation between microstructure and photoactivity". In: *Journal of Materials Chemistry* 16.18 (2006), pp. 1709–1716.
- [17] H. Zhang and J. F. Banfield. "Understanding polymorphic phase transformation behavior during growth of nanocrystalline aggregates: insights from TiO₂". In: *The Journal of Physical Chemistry B* 104.15 (2000), pp. 3481–3487.
- [18] G. Demopoulos. "Aqueous precipitation and crystallization for the production of particulate solids with desired properties". In: *Hydrometallurgy* 96.3 (2009), pp. 199–214.
- [19] A. Yasin, F. Guo, and G. P. Demopoulos. "Continuous-reactor, pH-controlled synthesis of multifunctional mesoporous nanocrystalline anatase aggregates". In: *Chemical Engineering Journal* 287 (2016), pp. 398–409.
- [20] S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Pechy, and M. Grätzel.
 "Fabrication of screen-printing pastes from TiO₂ powders for dye-sensitised solar cells". In: *Progress in Photovoltaics: Research and Applications* 15.7 (2007), pp. 603–612.
- [21] C. Charbonneau, R. Gauvin, and G. Demopoulos. "Nucleation and growth of self-assembled nanofibre-structured rutile (TiO₂) particles via controlled forced hydrolysis of titanium tetrachloride solution". In: Journal of Crystal Growth 312.1 (2009), pp. 86–94.
- [22] Z. Yanqing, S. Erwei, C. Zhizhan, L. Wenjun, and H. Xingfang. "Influence of solution concentration on the hydrothermal preparation of titania crystallites". In: Journal of Materials Chemistry 11.5 (2001), pp. 1547–1551.
- [23] A. Pottier, C. Chanéac, E. Tronc, L. Mazerolles, and J.-P. Jolivet. "Synthesis of brookite TiO₂ nanoparticles by thermolysis of TiCl₄ in strongly acidic aqueous media". In: *Journal of Materials Chemistry* 11.4 (2001), pp. 1116–1121.

- [24] D. Reyes-Coronado, G. Rodriguez-Gattorno, M. Espinosa-Pesqueira, C. Cab, R. De Coss, and G. Oskam. "Phase-pure TiO₂ nanoparticles: anatase, brookite and rutile". In: *Nanotechnology* 19.14 (2008), p. 145605.
- [25] S. Aruna, S. Tirosh, and A. Zaban. "Nanosize rutile titania particle synthesis via hydrothermal method without mineralizers". In: *Journal of Material Chemistry* 10.10 (2000), pp. 2388–2391.
- [26] J.-L. Mi, C. Clausen, M. Bremholm, N. Lock, K. M. Ø. Jensen, M. Christensen, and B. B. Iversen. "Rapid Hydrothermal Preparation of Rutile TiO₂ Nanoparticles by Simultaneous Transformation of Primary Brookite and Anatase: An in Situ Synchrotron PXRD Study". In: Crystal Growth & Design 12.12 (2012), pp. 6092– 6097.
- [27] X. Jiang and C. J. Brinker. "Rigid templating of high surface-area, mesoporous, nanocrystalline rutile using a polyether block amide copolymer template". In: *Chemical Communications* 46.33 (2010), pp. 6123–6125.
- [28] M. Inada, K. Mizue, N. Enomoto, and J. Hojo. "Synthesis of rutile TiO₂ with high specific surface area by self-hydrolysis of TiOCl₂ in the presence of SDS". In: *Journal of the Ceramic Society of Japan* 117.1367 (2009), pp. 819–822.
- [29] S. Yamabi and H. Imai. "Synthesis of rutile and anatase films with high surface areas in aqueous solutions containing urea". In: *Thin Solid Films* 434.1–2 (2003), pp. 86–93.
- [30] C. Weidenthaler. "Pitfalls in the characterization of nanoporous and nanosized materials". In: *Nanoscale* 3.3 (2011), pp. 792–810.
- [31] F. Rojas, I. Kornhauser, C. Felipe, J. Esparza, S. Cordero, A. Dominguez, and J. Riccardo. "Capillary condensation in heterogeneous mesoporous networks consisting of variable connectivity and pore-size correlation". In: *Physical Chemistry Chemical Physics* 4.11 (2002), pp. 2346–2355.

- [32] A. E. Shalan, M. M. Rashad, Y. Yu, M. Lira-Cantú, and M. S. A. Abdel-Mottaleb. "Controlling the microstructure and properties of titania nanopowders for high efficiency dye sensitized solar cells". In: *Electrochimica Acta* 89 (2013), pp. 469– 478.
- [33] J. Xu, K. Li, W. Shi, R. Li, and T. Peng. "Rice-like brookite titania as an efficient scattering layer for nanosized anatase titania film-based dye-sensitized solar cells". In: Journal of Power Sources 260 (2014), pp. 233–242.
- [34] N. P. Benehkohal and G. P. Demopoulos. "Green-Engineered All-Substrate Mesoporous TiO₂ Photoanodes with Superior Light-Harvesting Structure and Performance". In: *ChemSusChem* 7.3 (2014), pp. 813–821.
- [35] K. E. Lee, C. Charbonneau, and G. P. Demopoulos. "Thin single screen-printed bifunctional titania layer photoanodes for high performing DSSCs via a novel hybrid paste formulation and process". In: *Journal of Materials Research* 28.03 (2013), pp. 480–487.
- [36] K. E. Lee, M. A. Gomez, C. Charbonneau, and G. P. Demopoulos. "Enhanced surface hydroxylation of nanocrystalline anatase films improves photocurrent output and electron lifetime in dye sensitized solar cell photoanodes". In: *Electrochimica Acta* 67 (2012), pp. 208–215.
- [37] T. Deepak, G. Anjusree, S. Thomas, T. Arun, S. V. Nair, and A. S. Nair. "A review on materials for light scattering in dye-sensitized solar cells". In: *RSC Advances* 4.34 (2014), pp. 17615–17638.
- [38] H. Yu, S. Zhang, H. Zhao, G. Will, and P. Liu. "An efficient and low-cost TiO₂ compact layer for performance improvement of dye-sensitized solar cells". In: *Electrochimica Acta* 54.4 (2009), pp. 1319–1324.
- [39] F. Lv, S. Xiao, J. Zhu, and H. Li. "Dye-sensitized solar cells with enhanced efficiency using hierarchical TiO₂ spheres as a scattering layer". In: *RSC Advances* 4.68 (2014), pp. 36206–36211.

[40] M. J. Sussman, A. Yasin, and G. P. Demopoulos. "On the complex interplay of crystallinity and surface area effects on Li-ion intercalation and pseudocapacitive storage properties of nanocrystalline anatase". In: *Journal of Power Sources* 272 (2014), pp. 58–67.

Chapter 5

Aqueous, screen-printable paste for fabrication of mesoporous composite anatase-rutile TiO₂ nanoparticle thin films for (photo)electrochemical devices

In Chapter 3 the anatase particles synthesized with continuous-stirred tank reactor (CSTR) were mixed with rutile particles (Chapter 4) and P25 titania in a paste formulation adopted from literature [1], and assembled into dye-sensitized solar cells (DSSCs). The respective organic paste formulation contains the toxic α -terpineol and the water-insoluble ethyl cellulose. These factors leave much margin for improvement in the paste formulation to make the process of DSSC fabrication environmentally benign. This chapter documents a systematic investigation undertaken for a novel aqueous paste formulation that replaces the α -terpineol with propylene glycol, and ethyl-cellulose with polyethylene glycol, molecular weight: 20,000 (PEG MW: 20,000). The paste is printed to yield TiO₂ thin films and assembled into DSSCs - the crux of this chapter discusses the correlation between paste properties, sintered TiO₂ films, and DSSC photovoltaic performance. The results of

this investigation have been published in: Yasin, A., Guo, F. & Demopoulos, G.P., Aqueous ¹, screen-printable paste for fabrication of mesoporous composite anatase-rutile TiO_2 nanoparticle thin films for (photo)electrochemical devices, ACS Sustainable Chemistry & Engineering, 2016, 4 (4), pp. 2173-2181. Supporting Information is presented in Appendix C.

5.1 Abstract

Mesoporous TiO₂ films are employed in solar cells, lithium ion batteries, air and water purification systems, to name a few applications. Film fabrication via coating the substrate with an organic suspension or paste carrying TiO₂ nanoparticles is a common method. To lessen the adverse environmental impact, use of water as solvent and non-toxic chemicals is being preferred over commonly used organic components. In this research, a water-based, nano-TiO₂ printable paste formulation with polyethylene glycol (MW 20,000) and propylene glycol was developed and seamlessly interfaced with TiO₂ aqueous synthesis for sustainable manufacturing. The innovative combination of propylene glycol and polyethylene glycol is demonstrated to lead to improved paste rheology and sintered film properties. Dye-sensitized solar cells were assembled from the screen-printed films and the effect of film surface area and porosity on photovoltaic performance was studied. The new aqueous-based paste yielded comparable power conversion efficiency to benchmark organic-based paste made of α -terpineol, ethyl cellulose and ethanol, opening the avenue for lower cost, green fabrication of mesoporous thin film electrodes.

5.2 Introduction

Mesoporous (pore size 2-50 nm) films of nanocrystalline TiO_2 are widely used in applications ranging from air and water purification to solar fuels or solar energy-conversion cells and lithium ion batteries [2–6]. Nanoscale TiO_2 in its different polymorphs is used

¹This paste is called aqueous due to the use of water compatible chemicals

as photocatalyst or energy conversion and storage material due to its strong oxidation ability, and semiconducting and intercalation properties, not to mention its high stability, non-toxicity, abundance and ease of synthesis [7–9]. However, it is not practical to use free flowing TiO₂ nanopowders. In photocatalysis use of fine powders poses the problem of separation of the powders from the medium post-treatment, therefore, TiO₂ particles are fixed on immovable substrate as films [7]. In solar cells and lithium ion batteries, TiO₂ thin films offer favorable interfaces as part of the light capturing and electron conducting network structure or as one of the Li-ion intercalation electrodes. Flat TiO₂ films yield poor efficiency systems due to low surface area; this problem is addressed by use of crack-free mesoporous films of nanoparticles, having a high surface area, and effective pore size distribution to allow infiltration of the surrounding medium in the TiO₂ network [10–13].

One application in which the architecture of TiO_2 thin films is critical are dye-sensitized solar cells (DSSCs) [14]. In a DSSC, nanocrystalline TiO_2 is deposited on glass coated with conductive oxide. Organic dye molecules are adsorbed on the TiO_2 forming the photoanode of the cell. Platinized conductive glass serves as the counter electrode (cathode) and an iodide/triiodide redox electrolyte completes the circuit. Photon absorption and electron excitation take place in the dye molecules while charge transport from the anode to glass substrate and to the external load occurs through the TiO_2 semiconductor network; hence it is termed as a photoelectrochemical cell [15].

The architecture of the porous semiconductor layer characterized in terms of interparticle necking, surface area, porosity, electrode thickness, roughness, and adhesion is very critical for good DSSC performance [1, 16–18] and is determined and controlled by the TiO₂ deposition process. Mesoporous films are successfully fabricated by a number of methods, such as, electrophoretic deposition [19], dip or spin coating of TiO₂ particles synthesized through sol-gel synthesis [20, 21]. The most common – benchmark – method entails dispersing TiO₂ nanoparticles in an organic-medium paste, and coating it on conductive glass via doctor blading [22] or screen-printing [16], followed by decomposition of organic chemicals and sintering of nanoparticles to yield a porous network. The paste formulation commonly consists of α -terpineol, ethyl cellulose, and acetic acid dissolved in ethanol [1, 16]. The rheological properties of the paste influence the electrode structure and consequently DSSC performance. For paste deposition, screen-printing is common due to rapidity of the process, easy control of photoanode thickness, low cost and the possibility for large-scale production [16, 18, 23].

The current TiO_2 film technology that relies on a combined sol-gel/hydrothermal process for the synthesis of the nanoparticles [24], paste making and screen-printing [1] makes heavy use of organic chemicals in an expensive multi-step manufacturing route. Thus, significant research has been pursued to replace among the chemicals used the toxic terpineol, and water-insoluble ethyl cellulose with environmentally friendly, and water-soluble analogues. To this end a common approach has been the replacement of ethyl cellulose with the water-soluble polyethylene glycol (PEG) as the binder [25]. Tasic et al. [26] investigated various high molecular weight (MW) PEGs (MW: 1000-20000) as binders, in combination with stearic acid (anti-flocculant), α -terpineol, and low molecular weight PEG (MW: 200) as plasticizer, dissolved in isopropanol and found the paste with PEG with MW: 8000 to yield the highest DSSC efficiency. Ma et al. [23] used PEG 600 as the only organic chemical (dissolved in ethanol) and were able to print crack-free films. Krasovec et al. [27] used the Pechini sol-gel method to form a sol of titanium isopropoxide, citric acid, and ethylene glycol, and mixed it with commercial TiO_2 , nanopowder to obtain a printable paste. Finally Tsai et al. [28] used both Triton-X and PEG 20000 to act as binder and plasticizer respectively. However, these processes resort to using expensive organic Ti alkoxide precursors or organic solvents (ethanol or isopropanol). In the research presented herein, we propose a water-based paste formulation integrated with our continuous aqueous TiO_2 synthesis process [28], paving the way for an integrated green TiO_2 thin-film fabrication process.

In a departure from previous studies, propylene glycol (PG) is used here for the first time as the plasticizer/rheological agent, while polyethylene glycol (PEG), MW: 20000 is used as binder in formulating the paste. By changing the proportion of PEG and PG the paste viscosity and pore-forming properties were extensively characterized and optimized, resulting in sintered thin film photoanodes with comparable DSSC performance to organicbased benchmark paste. Further the paste features two types of TiO_2 nanoparticles, anatase and rutile, for maximizing photoenergy conversion via a combination of light absorption and scattering effects [29]. The integration of the novel aqueous paste with scalable continuous-stirred tank reactor synthesis described elsewhere [29] provides a cost-effective and all-aqueous process for fabrication of TiO_2 thin films in full sync with the sustainable renewable energy and environmental technologies in which they find applications.

5.3 Experimental

5.3.1 Paste preparation & analysis

The anatase (surface area: $220 \text{ m}^2/\text{g}$) and rutile (surface area: $80 \text{ m}^2/\text{g}$) nanostructured powders were synthesized in our lab in a CSTR (continued stirred tank reactor) [29]. The two TiO_2 varieties either in powder or colloid form (as elaborated later in Section 5.4) were typically combined in mass ratio 80%Anatase/20%Rutile [30] for a total of 3 g TiO₂ in a glass mortar. 0.5 mL of 17 M acetic acid (Fisher Scientific; Acetic acid, Glacial), and 50 mL of ethanol/water (1:1 volumetric ratio) solution were added and the mixture was ground for 20 minutes. The mixture was transferred to a beaker with another 50 mL of water/ethanol solution. The suspension was stirred and sonicated with an ultrasound horn (40% powder, 2 sec on, 2 sec off, for 2 minutes) alternatively 3 times. Propulene glycol (Fisher Scientific) and polyethylene glycol MW: 20,000 (Avocado) (as a 10 wt.% aqueous solution) were added followed by the same stirring and sonication routine. The mixture was transferred to a rotary evaporator and the solvent was evaporated at 60 $^{\circ}\mathrm{C}$ (atmospheric pressure). Viscosity of the resulting paste was measured with Brookfield viscometer (Model LVDV-E). Thermogravimetric Analysis (TGA) was performed on TA Instruments Q500 TGA to determine the TiO₂ loading. TGA analysis of the pastes involved heating up to 600 °C at 10 °C/minute in a N_2 atmosphere.

5.3.2 Photoanode fabrication

For photoanode preparation, fluoride doped tin oxide glass (Sigma-Aldrich[®], $\approx 7 \omega/sq.$) was used as the glass substrate. It was submerged in a 50 mM $TiCl_4$ aqueous solution at 80 °C for 30 minutes, and then calcined at 400 °C for 30 minutes. Photoanode films measuring $0.25 \text{ cm} \ge 0.25 \text{ cm}$ were deposited by printing the paste on the pre-treated glass using a screen-printer (Atma Champ Ent. Corp., Taiwan) with 45T mesh. After each printing cycle, the paste was allowed to settle down at room temperature for 20 minutes, dried at 80 °C for 15 minutes, and allowed to cool down to room temperature before printing the second layer. The films were sintered at 450 °C for 30 minutes, post-treated with 50 mM TiCl₄ and sintered again at 450 °C for 30 minutes as per previously reported protocols [5, 22]. Thickness of photoanode films was measured on Dektak surface profiler. BET (Brunauer-Emmett-Teller) surface area and BJH (Barrett-Joyner-Halenda) pore size analyses were conducted on Micromeritics TriStar 3000. For sample preparation, the paste was doctor-bladed on 5 microscopic slides and sintered at 450 °C for 30 minutes. The powder was scraped off the film and degassed at 150 °C for 1 hour prior to analysis. For determination of dye loading, the films printed on the FTO glass were immersed in the dye for 24 hours at room temperature, then taken out and immersed in 0.1 M NaOH solution in water for 1 minute to extract the dye. Absorption spectra of the solutions were obtained on Evolution300 UV-visible spectrometer; intensity of the absorption peak at 500 nm was used to quantify amount of dye adsorbed. Scanning Electron Microscope images of TiO_2 films were taken on a Hitachi SU8230.

5.3.3 DSSC assembly

The sintered photoanodes were immersed in N719 dye for 24 hours at room temperature in the dark, and washed with ethanol just before being assembled into solar cells. Counter electrodes were prepared by platinizing FTO glass with H_2PtCl_6 (in isopropanol) and sintered at 400 °C for 30 minutes. The photoanode and counter-electrode were sealed with thermoplastic sealant (Surlyn[®]-30, Dyesol) at 110 °C. An I⁻/I₃⁻ based electrolyte (EL-HPE, Dyesol) was injected into the sandwich through holes already pierced in the counter electrode. The holes were then sealed using the sealant and microscopic slide and pressed at 110 °C. Terminals of the electrodes were soldered with molten indium. Solar cells were tested under AM 1.5 conditions using an ABA grade solar simulator/J-V curve testing system (PV Measurements Inc., model IV5).

5.4 Results & Discussion

The anatase nanocolloids and rutile scattering particles used in this research were synthesized in an aqueous solution via controlled forced hydrolysis of TiCl₄ carried out in a continuous stirred-tank reactor that constitutes a green and easily scalable process [29]. (For characterization details of anatase and rutile particles refer to Figure C.1-C.2, Table C.1). Description of the synthesis process is subject of another investigation; however it is critical to highlight that the paste-formulation presented herein is seamlessly integrated with the synthesis process as the TiO₂ powders are used wet following centrifugation and washing thus avoiding the energy cost associated with drying; as a whole the process emphasizes shift away from using water-insoluble, hazardous chemicals, towards eco-friendly, inexpensive chemicals.

The anatase nanocrystallites serve to form the photoanode scaffold that collects and transports the electrons generated by the photoactive molecular dye adsorbed on TiO₂ surface. The incorporation of the rutile sub-micron size particles serves to increase light trapping via scattering. This type of bifunctional anatase-rutile composite photoanode with mass ratio 80%Anatase/20%Rutile has been found to be equally effective as photoanodes made with separate layers of anatase and rutile components [30]. Previously, anatase and rutile particle suspensions, produced separately via adjustment of TiCl₄ forced hydrolysis conditions [5, 31] were concentrated as wet colloid and dried to obtain the respective powders. The dried powders were then milled to break the agglomerates formed during drying, and mixed to prepare an organic-based paste comprising acetic acid, ethyl cellulose, α -terpineol and ethanol [1]. The paste was screen-printed and

Table 5.1: Comparing DSSC performance of photoanodes made with dry TiO₂ powders vs. wet TiO₂ colloid following organic-based protocol (TiO₂ phase mixture: 40%Anatase/40%Rutile/20%P25)

	Film Thickness (μm)	$\eta~(\%)$	V_{oc} (V)	$J_{sc} (mA/cm^2)$	FF (%)
I2-powder	13.10	4.42	0.72	8.38	73.5
K2-gel	10.02	4.85	0.74	8.48	76.92

subsequently subjected to controlled sintering [29]. With the view of simplifying the interfacing of the paste preparation stage with the aqueous synthesis stage, as first step of the present work the organic paste formulation was tested with dry TiO₂ powders (as commonly practiced) and as wet colloids following their washing. The TiO₂ blend used consisted of aqueous-synthesized anatase (A) and rutile (R) plus mixed phase P25 at a ratio 40%A/40%R/20% P25 [29]. The organic paste made either with dry or wet TiO₂ particles was built into sintered photoanodes and their DSSC performance was evaluated (Table 5.1, Figure C.3). The cells built with the paste made directly with wet TiO₂ colloid (Paste K) showed marginally better performance than those built with the paste made from the dry powder based cells (Paste I).

Once it was determined that the TiO_2 colloid can be substituted directly for the dry powders, the next step was to replace the water-insoluble chemicals from the organic-medium paste, with less toxic, water soluble, chemicals thus enabling the green integration (water based) of paste making with aqueous synthesis of anatase and rutile. The preparation flowchart of the new aqueous paste is significantly simpler than the corresponding one for the commercial organic paste as they can be compared in Figure 5.1.

5.4.1 Paste rheology analysis – effect of PG and PEG on viscosity

In the formulation proposed, TiO_2 , acetic acid, polyethylene glycol (PEG), MW: 20000, and propylene glycol (PG) were added to mixed ethanol/water (1:1 volumetric ratio)

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Figure 5.1: Comparison of flowcharts for the commonly used organic-based vs. the all-aqueous paste formulation options

solvent. Pastes were prepared with variable amounts of PEG and PG, as listed in Table 5.2 (quantity of ethanol and water given is prior to rotary evaporation).

First, pastes with water as the only solvent were fabricated. These pastes were highly unstable and as soon as the paste was taken off the rotary evaporator and allowed to cool down from 60 °C to room temperature the particles aggregated. This was attributed to the high surface tension of water (72.88 mN/m [32]) that is known to induce cracking during the thermal processing/annealing of the films [16]. The particle aggregation and film cracking problem was solved by using a mixed 1:1 (v/v) water/ethanol (surface tension 31.36 mN/m [32]) and this was used for all investigations to follow.

Effect of propylene glycol (PG)

The use and amount of propylene glycol was critical in obtaining pastes with suitable viscosity, and appropriate drying and adhesion characteristics. A standard amount of 10g or 3.3 g-PG/g-TiO_2 was selected. In the case of excess PG amount as indicated by the U6 paste that contained 15 g, the paste had a very low viscosity to be used. When the paste made with 15 g PG was screen-printed it showed poor wettability in contact with the glass substrate forming a highly non-uniform film. On the other hand, exclusion of PG (as is the case of Paste X1 that was prepared with 0 g PG; Table 5.2) yielded

Paste ID	Binder	ler Quantity (g)		Quantity (g)
T1	PEG [#]	1.5	PG^*	10
U2	PEG	1	\mathbf{PG}	10
U3	PEG	3	PG	10
U4	PEG	0	PG	10
U5	PEG	2.5	PG	10
U6	PEG	2	PG	15
U7	PEG	2	PG	10
X1	PEG	2	\mathbf{PG}	0

Table 5.2: Paste formulations investigated (Remaining paste components: $3g \text{ TiO}_2-$ 80%Anatase/20% Rutile, 50 mL water, 50mL ethanol)

PEG: Polyethylene glycol *PG: Propylene glycol

easily cracking and flaking films as soon as they were printed and dried in air even before sintering. These tests proved that propylene glycol is an essential component in making aqueous-based paste with relatively good adhesion and adequate mechanical stability but the paste needed further optimization to improve film uniformity; this was achieved with the co-addition of polyethylene glycol as described next.

The use of propylene glycol as paste plasticizer in this work aims at the replacement of α -terpineol in the standard organic-based paste formulation. Propylene glycol is more eco-friendly and less toxic alternative. While α -terpineol calls for stringent disposal protocols as it cannot be released to the environment, propylene glycol is known to undergo biodegradation in soil, water, and air hence it offers a clear sustainability advantage [33].

Effect of polyethylene glycol (PEG)

Polyethylene glycol (PEG), MW: 20,000 is used as the binder, replacing ethyl cellulose from the organic-based protocol. Ethyl cellulose is immiscible with water, and only soluble

in organic solvents. Thus, beyond the use of organic chemicals in the paste formulation, handling and clean-up of ethyl-cellulose becomes more expensive and hazardous. Figure 5.2(a) shows the viscosity as a function of shear rate for a subset of pastes presented in Table 5.1 (pastes with different PEG content that were able to yield uniform films are included). Note that the viscosity reported is that of final paste obtained after evaporation of the solvent. Paste U7 exhibited the behavior of non-Newtonian, pseudoplastic fluid whereby the viscosity decreased as shear rate increased – paste behavior that is desirable for screen-printing [34]. The rest of the fluids showed no significant change in viscosity with application of high stress, which is indicative of quasi-Newtonian fluids, and such pastes are not deemed suitable for screen-printing [16]. Figure 5.2 (b) presents the effect of PEG amount (0 g - 2.5 g) on paste viscosity and film thickness. Paste U4 with 0 g PEG content possessed very low viscosity (94 cP at 60 rpm) proving that PEG because of its high molecular weight contributed significantly to the paste viscosity. The paste viscosity had the highest value at 2 g (480 cP) decreasing for higher and lower values. Similar trend had been observed in benchmark organic-based pastes, which incorporate ethyl-cellulose as the binder [16]. In this respect, by using PEG along PG it is possible to produce a paste similar to the organic-based formulation without the need of using the toxic α -terpineol chemical. Moreover, when 3 g PEG was added, transparent globules were seen in the paste after solvent evaporation, (this paste was not further used). It is hypothesized that as the PEG amount increased, its miscibility in the suspension decreased, and eventually, for 3 g PEG it was clearly visible in the suspension. Similarly, it can be argued that at 2.5 g PEG addition, its dispersion in the paste had decreased, leading to more TiO_2 nanoparticle aggregation, which in turn caused viscosity to decrease [35].

The thickness of sintered films followed the opposite trend to that of viscosity. Increasing the PEG amount increased the fluid viscosity, increasing the resistance to flow and therefore decreasing the amount of deposition. TGA analysis revealed the solid TiO_2 content to be in the range 15-20% Figure C.4.

	Standard organic p	aste	Novel aqueous paste			
Solvent	43.3 L Ethanol 8.9 $\rm USD/m^3$		16.67 L Water 16.67 L Ethanol	$\begin{array}{c} 0.66 \ \mathrm{USD/m^3} \\ 8.9 \ \mathrm{USD/m^3} \end{array}$		
Binder	0.5 kg Ethyl cellu- 4.3 USD/kglose		0.67 kg Polyethylene glycol	$3.33~\mathrm{USD/kg}$		
Plasticizer	3.33 kg terpineol	$9.5~\mathrm{USD/kg}$	3.33 kg Propylene glycol	$1.5~\mathrm{USD/kg}$		
Total cost		34.17 USD		7.36 USD		

Table 5.3: Cost comparison of paste components (1 kg TiO_2 basis) [36]

Cost comparison

In addition to environmental benefits, the new aqueous paste formulation offers substantial potential for cost reduction as it can be deduced from the indicative data presented in Table 5.3. Both the binder and plasticizer in the proposed aqueous protocol are significantly less costly than their respective counterparts in the organic paste (>5 fold reduction). And this represents only the paste-making step. Given the integration of paste making with aqueous synthesis as described in Figure 5.1, it can be appreciated that the economic benefits from the integrated green fabrication method are even higher. Therefore, use of water and aqueous-compatible chemicals confers significant cost advantage, in addition to being environmentally benign.

5.4.2 Mesoporous film structure analysis

Figure 5.3(a) shows the film morphology of sintered film U7 that exhibited the best performance (2 g PEG, 10 g PG). The film was seen to be continuous, uniform and devoid of cracks. This was further confirmed with the cross section view presented in Figure 5.3(b). The thickness of the film was in the order of 14 μ m that is considered



Figure 5.2: (a) Viscosity flow curve of pastes with variable PEG content and (b) Paste viscosity (at 60 rpm) and film thickness (2 screen-printed layers) as a function of PEG quantity (Remaining paste components: 3 g TiO₂ (80%Anatase/20%Rutile), 0.5 mL Acetic acid, 10 g PG, 50 mL Water, 50 mL Ethanol).

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Figure 5.3: (a) Top-view of film fabricated with paste U7 and (b) Cross section of film fabricated with paste U7. (Remaining paste components: 3 g TiO₂ (80%Anatase/20%Rutile), 0.5 mL Acetic acid, 2 g PEG, 10 g PG, 50 mL Water, 50 mL Ethanol).

appropriate in dye-sensitized solar cells. This film was obtained with deposition of two layers by screen-printing (mesh size 45T). The new paste can be easily deposited in 3 layers for thicker films if desired.

Figure 5.4 presents film surface area and pore width determined through BET (Brunauer-Emmett-Teller) surface area and BJH (Barrett-Joyner-Halenda) pore size analyses as function of added PEG mass (For cumulative pore volume see Figure C.5). The surface area and pore width were in the range $\approx 80\text{-}107 \text{ m}^2/\text{g}$ and 99-156 Å, respectively confirming the mesoporous nature of the film (mesoporous: 2 nm< pore width
<50 nm). The highest surface area was observed for T1 (1.5 g PEG) and the highest pore width was observed for U7 (2 g PEG). First, the pastes with PEG $\neq 0$ are considered. PEG is believed to coat the TiO₂ nanoparticles via hydrogen bonding between the ether oxygen of PEG and surface hydroxyl groups on TiO₂ and prevent aggregation [37]. We propose that with increasing PEG quantity from 1 g to 1.5 g the greater mass of PEG dispersed in the paste resulting in increased surface area following sintering. However, when the amount of PEG increased further to 2 g (U7) its miscibility with the

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Figure 5.4: BET surface area and BJH average pore width as a function of PEG quantity. (Remaining paste components: 3 g TiO₂ (80%Anatase/20%Rutile), 0.5 mL Acetic acid, 10 g PG, 50 mL Water, 50 mL Ethanol).

water/ethanol based suspension decreased (as has been discussed earlier) resulting in PEG clusters that occupy more volume, hence increasing the pore width and decreasing the surface area relative to T1 (1.5 g). Upon further increasing the PEG quantity to 2.5 g the pore width decreased; we believe that as PEG occupied more volume in the paste the TiO₂ particle network collapsed upon PEG burnout during sintering, consequently decreasing the surface area and pore width of the film [34, 38] Paste U4 with 0 g PEG exhibited the least pore size underlining the critical role of PEG as pore-forming agent.

Figure 5.5 shows the N_2 adsorption/desorption isotherms for the sintered films and the respective BJH desorption pore size distribution curves as insets. The shape of the isotherms of all the films is classified as type IV of Brunauer-Deming-Deming-Teller (DMMG) classification which is characterized by the presence of mesopores [39]. The hysteresis loops for all the films classify as H3 IUPAC type [40]. The BJH curves show the majority of data points in 2-30 nm, with a few outliers; hence the films are characterized as mesoporous.





Figure 5.5: N₂ adsorption/desorption isotherms of the sintered films with BJH desorption pore size distribution curves as insets, (a) Paste U4, 0 g PEG; (b) Paste U2, 1 g PEG; (c) Paste T1, 1.5 g PEG; (d) Paste U7, 2 g PEG; (e) Paste U5, 2.5 g PEG. (Remaining paste components: 3 g TiO₂ (80%Anatase/20%Rutile), 0.5 mL Acetic acid, 10 g PG, 50 mL Water, 50 mL Ethanol). 140

Film	PEG	Viscosity	$\eta_{average}$	V_{oc} (V)	J_{sc}	\mathbf{FF}
ID	(g)	(cP)	(%)		$(\mathrm{mA/cm^2})$	
T1	1.5	431	4.15 ± 1.10	0.71 ± 0.03	6.41 ± 0.22	69.5 ± 9.4
U2	1	304	3.54 ± 0.17	0.74 ± 0.02	6.47 ± 0.15	73.8 ± 0.3
U4	0	94	2.81 ± 0.43	0.68 ± 0.03	6.44 ± 0.02	63.9 ± 7.3
U5	2.5	355	3.86 ± 0.08	0.69 ± 0.0	7.69 ± 0.20	72.8 ± 1.0
U7	2	480	4.43 ± 0.20	0.72 ± 0.0	8.52 ± 0.37	72.6 ± 0.8

Table 5.4: Paste characterization and DSSC performance parameters (film thickness was kept at $\approx 15 \mu m$)

5.4.3 Effect of film microstructure on photovoltaic performance

Having successfully printed films using the new green paste formulation, the sintered anatase-rutile composite films were sensitized with N719 dye and then assembled into dye-sensitized solar cells (DSSCs). Table 5.4 summarizes the photovoltaic parameters of the assembled DSSCs (J-V curves are given in Figure C.6).

In Figure 5.6 the DSSC efficiency for cells superimposed with corresponding film pore size and paste viscosity shows direct dependence on paste viscosity and film pore size. The highest efficiency 4.43% was observed for 2 g PEG (U7 film), followed by 4.15% for 1.5 g PEG (T1 film). Determination of the dye loading as function of pore width (Figure C.7) however did not reveal any particular dependency. This apparently implies that in addition to dye sensitization the shuttling of the I^-/I_3^- redox couple inside and out of the mesoporous electrode was also dependent on pore width [41]. Since for higher conversion efficiency, faster regeneration of the dye by the redox couple is required [41] we surmise that the faster diffusion of the latter through the larger porous network greatly improved cell performance. Similar to dye loading, the BET surface area of the film (Figure C.8) did not have a direct impact on efficiency. U7 film owing to its well-developed mesoporous structure as described earlier also had the highest short circuit current (J_{sc}) at 8.52 mA/cm². Interestingly, highest open circuit voltage (V_{oc}) is exhibited by U2 film Chapter 5. Aqueous, screen-printable paste for fabrication of mesoporous composite anatase-rutile TiO_2 nanoparticle thin films for (photo)electrochemical devices



Figure 5.6: Paste viscosity, BJH pore width, and DSSC efficiency as a function of PEG quantity. (Remaining paste components: 3 g TiO₂ (80%Anatase/20%Rutile), 0.5 mL Acetic acid, 10 g PG, 50 mL Water, 50 mL Ethanol).

(1g PEG paste). The open-circuit voltage depends on the interconnectivity of particles [16]. Since U2 film has lower pore width (refer to Figure 5.4), charge recombination is discouraged resulting in high V_{oc} . It is exactly these opposite dependencies of J_{sc} and V_{oc} on film structure that demand its optimization as demonstrated in the present work that focuses on paste properties and their effects.

5.4.4 DSSC performance: comparison of pastes

Up to this point the development of the aqueous-based paste was done using 80%Anatase/20%Rutile nanoparticles. As explained earlier, the incorporation of rutile opaque particles (size \approx 200-500 nm) helps increase light scattering inside the photoanode hence eliminating the need for a separate scattering layer [30]. However the large size difference between the transparent anatase nanoparticles (\approx 10 nm) and the opaque rutile particles may not allow for optimum particle packing and connectivity. For that reason intermediate size (\approx 21 nm) mixed phase (anatase/rutile) TiO₂ particles available as the commercial product P25 (Evonik) were also introduced and a second TiO₂ composition, 40%Anatase/40%Rutile/20%P25 was tried. Both composite-TiO₂ compositions were used to make photoanodes with either the benchmark organic paste protocol or the new aqueous-based protocol. The DSSC performance data of the various photoanode sis presented in Table 5.5. For 80%Anatase/20%Rutile, U7 (aqueous) photoanode shows 4.43% conversion efficiency, while N5 (organic) photoanode shows 4.95%. For 40%Anatase/40%Rutile/20%P25, V4 (aqueous) shows 4.17%, while K2 (organic) shows 4.85%. It appears that the benchmark organic paste yielded slightly higher overall power conversion efficiency vis-a-vis the newly formulated aqueous paste. However from a sustainability (less toxic organic chemical use) and cost point of view, the new aqueous paste formulation fares better, especially when it is integrated with the all-aqueous synthesis process (see Figure 5.1) that is described elsewhere [29].

Finally, DSSCs were also assembled with commercially available Dyesol 18NR-AO paste - this organic paste is a mixture of anatase particles measuring ≈ 20 nm and ≈ 450 nm to serve as the active and scattering particles respectively. The photoanodes were fabricated with two screen-printed layers of 18NRT-AO yielding sintered films measuring 15 μ m. Comparing the results with the best cell from our proposed protocol, it is apparent that the difference in efficiency, 6.02% vs. 4.43% is attributed towards increase in ${\rm J}_{sc}$ (12.75 vs. 8.52 mA/cm^2). The active anatase particles used in our protocol were 6-7 nm in size, whereas anatase in Dyesol 18NR-AO is $\approx 20 \text{ nm}$ [22]. The difference in TiO₂ particle sizes can lead to varying pore size distribution allowing better infiltration of dye and electrolyte in the films prepared with commercial paste. Moreover, the ratio of active to scattering particles in 18NR-AO is unknown and any difference in the respective ratios between the commercial and our proposed paste can affect the photovoltaic performance. However, it is to be noted that the V_{oc} and FF of the DSSCs assembled from the proposed protocol in this work are higher than the commercial benchmark. In conclusion the higher efficiency obtained with the commercial pastes is attributed to differences in the type and blend of anatase particles (transparent vs. scattering) used than the paste formulation (aqueous vs. organic) itself-the focus of the present work.

composition, using the benchmark organic and new proposed aqueous protocol as well as commercial pastes. Film ID n (%) V_{ec} (V) J_{ec} FF (%) Paste TiO₂-

Table 5.5: Photovoltaic performance of DSSCs built with variable anatase/rutile/P25

Film ID	$\eta~(\%)$	V_{oc} (V)	\mathbf{J}_{sc}	FF (%)	Paste	TiO_{2} -	
			$(\mathrm{mA/cm^2})$			mixture*	
U7	4.43	0.72	8.52	72.6	Aqueous	80A/20R	
N5	4.95	0.70	9.65	73.2	Organic	80A/20R	
V4	4.17	0.74	7.81	72.4	Aqueous	40A/40R/20P25	
K2	4.85	0.74	8.48	76.9	Organic	40A/40R/20P25	
18NR-AO	6.02	0.71	12.75	66.5	Commercial	Proprietary	
					Organic	anatase	
						(20 nm/450 nm)	
						mixture	
¥ A	.1 .	1 /		.1 .			

*Aqueous synthesized anatase. R: Aqueous synthesized rutile. P: Evonik P25.

5.5 Conclusion

In conclusion, a water-based screen-printable TiO₂ paste was developed using aceticacid/propylene glycol/high MW polyethylene glycol (MW: 20,000). Propylene glycol, which was used in DSSC application for the first time, proved to be essential for endowing the film with mechanical stability and good adhesion to the substrate. Meanwhile, polyethylene glycol added in the right amount helps regulate paste viscosity while also allowing for increased porosity to be created in the sintered film. By far pore width (99-156 Å) was determined to be the most critical film property. A direct correlation among paste viscosity, pore size in films, and DSSC efficiency was established. Photoanodes built with the aqueous paste yielded almost the same photovoltaic performance (4.43% vs. 4.95%) with the photoanodes built with the benchmark organic paste. The aqueous paste can be conveniently interfaced with aqueous synthesis [29] of TiO₂ without necessitating prior drying of the TiO₂ colloid for apparent environmental and economic benefits.

5.6 References

- S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Pechy, and M. Grätzel. "Fabrication of screen-printing pastes from TiO₂ powders for dye-sensitised solar cells". In: *Progress in Photovoltaics: Research and Applications* 15.7 (2007), pp. 603–612.
- [2] H. Choi, E. Stathatos, and D. D. Dionysiou. "Photocatalytic TiO₂ films and membranes for the development of efficient wastewater treatment and reuse systems". In: *Desalination* 202.1 (2007), pp. 199–206.
- [3] L. Zhang, Y. Zhu, Y. He, W. Li, and H. Sun. "Preparation and performances of mesoporous TiO₂ film photocatalyst supported on stainless steel". In: *Applied Catalysis B: Environmental* 40.4 (2003), pp. 287–292.
- [4] M. J. Sussman, N. Brodusch, R. Gauvin, and G. P. Demopoulos. "Engineering 3-D Li-Ion Electrodes with Enhanced Charge Storage Properties Based on Solution-

Processed and Sintered Anatase Nanocrystal-Carbon Mesoporous Structures". In: ACS Sustainable Chemistry & Engineering 3.2 (2015), pp. 334–339.

- [5] C. Charbonneau, R. Gauvin, and G. Demopoulos. "Aqueous solution synthesis of crystalline anatase nanocolloids for the fabrication of DSC photoanodes". In: *Journal of The Electrochemical Society* 158.3 (2011), H224–H231.
- [6] K. Yan and G. Wu. "Titanium dioxide microsphere-derived materials for solar fuel hydrogen generation". In: ACS Sustainable Chemistry & Engineering 3.5 (2015), pp. 779–791.
- J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, and
 D. W. Bahnemann. "Understanding TiO₂ photocatalysis: mechanisms and materials". In: *Chemical Reviews* 114.19 (2014), pp. 9919–9986.
- [8] Z. Weng, H. Guo, X. Liu, S. Wu, K. Yeung, and P. K. Chu. "Nanostructured TiO₂ for energy conversion and storage". In: *RSC Advances* 3.47 (2013), pp. 24758– 24775.
- [9] Y. Bai, I. Mora-Seró, F. De Angelis, J. Bisquert, and P. Wang. "Titanium dioxide nanomaterials for photovoltaic applications". In: *Chemical Reviews* 114.19 (2014), pp. 10095–10130.
- S. Xu, C.-h. Zhou, Y. Yang, H. Hu, B. Sebo, B.-l. Chen, Q.-d. Tai, and X. Zhao.
 "Effects of ethanol on optimizing porous films of dye-sensitized solar cells". In: *Energy & Fuels* 25.3 (2011), pp. 1168–1172.
- C.-Y. Huang, Y.-C. Hsu, J.-G. Chen, V. Suryanarayanan, K.-M. Lee, and K.-C. Ho. "The effects of hydrothermal temperature and thickness of TiO₂ film on the performance of a dye-sensitized solar cell". In: *Solar Energy Materials and Solar Cells* 90.15 (2006), pp. 2391–2397.
- [12] N. Li, G. Liu, C. Zhen, F. Li, L. Zhang, and H.-M. Cheng. "Battery performance and photocatalytic activity of mesoporous anatase TiO₂ nanospheres/graphene composites by template-free self-assembly". In: Advanced Functional Materials 21.9 (2011), pp. 1717–1722.

- [13] A. A. Ramirez-Santos, P. Acevedo-Pena, and E. M. Cordoba. "Enhanced photocatalytic activity of TiO₂ films by modification with polyethylene glycol". In: *Quimica Nova* 35.10 (2012), pp. 1931–1935.
- [14] B. Zhao, J. Wang, H. Li, Y. Xu, H. Yu, X. Jia, X. Zhang, and Y. Hao. "Solar-toelectric performance enhancement by titanium oxide nanoparticles coated with porous yttrium oxide for dye-sensitized solar cells". In: ACS Sustainable Chemistry & Engineering 3.7 (2015), pp. 1518–1525.
- [15] B. O'Regan and M. Grätzel. "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films". In: *Nature* 353.6346 (1991), pp. 737–740.
- [16] P. Gemeiner and M. Mikula. "The relation between TiO₂ nano-pastes rheology and dye sensitized solar cell photoanode efficiency". In: *Materials Science in Semiconductor Processing* 30 (2015), pp. 605–611.
- [17] A. S. Nair, R. Jose, Y. Shengyuan, and S. Ramakrishna. "A simple recipe for an efficient TiO₂ nanofiber-based dye-sensitized solar cell". In: *Journal of Colloid* and Interface Science 353.1 (2011), pp. 39–45.
- [18] D. Zhang, S. Ito, Y. Wada, T. Kitamura, and S. Yanagida. "Nanocrystalline TiO₂ electrodes prepared by water-medium screen printing technique." In: *Chemistry Letters* 10 (2001), pp. 1042–1043.
- [19] N. P. Benehkohal and G. P. Demopoulos. "Electrophoretically self-assembled mixed metal oxide-TiO₂ nano-composite film structures for photoelectrochemical energy conversion: probing of charge recombination and electron transport resistances".
 In: Journal of Power Sources 240 (2013), pp. 667–675.
- [20] R. Dong, F. Wang, Z. Li, Z. Chen, H. Zhang, and C. Jin. "Honeycombed TiO₂ films prepared by combining breath figure and sol gel methods". In: Surface and Coatings Technology 276 (2015), pp. 391–398.
- [21] Y.-C. Liu, Y.-F. Lu, Y.-Z. Zeng, C.-H. Liao, J.-C. Chung, and T.-Y. Wei. "Nanostructured mesoporous titanium dioxide thin film prepared by sol-gel method for dye-sensitized solar cell". In: *International Journal of Photoenergy* 2011 (2011).

- [22] C. Charbonneau, K. Lee, G. Shan, M. Gomez, R. Gauvin, and G. Demopoulos. "Preparation and DSSC performance of mesoporous film photoanodes based on aqueous-synthesized anatase nanocrystallites". In: *Electrochemical and Solid-State Letters* 13.8 (2010), H257–H260.
- [23] T. Ma, T. Kida, M. Akiyama, K. Inoue, S. Tsunematsu, K. Yao, H. Noma, and E. Abe. "Preparation and properties of nanostructured TiO₂ electrode by a polymer organic-medium screen-printing technique". In: *Electrochemistry Communications* 5.4 (2003), pp. 369–372.
- [24] Nanostructured Titanium Dioxide Materials: Properties, Preparation and Applications. World Scientific Publishing Co. Pte. Ltd, 2012.
- [25] J. Calderon-Moreno, S. Preda, L. Predoana, M. Zaharescu, M. Anastasescu, M. Nicolescu, M. Stoica, H. Stroescu, M. Gartner, O. Buiu, et al. "Effect of polyethylene glycol on porous transparent TiO₂ films prepared by sol-gel method". In: *Ceramics International* 40.1 (2014), pp. 2209–2220.
- [26] N. Tasić, Z. Branković, Z. Marinković-Stanojević, and G. Branković. "Effect of binder molecular weight on morphology of TiO₂ films prepared by tape casting and their photovoltaic performance". In: Science of Sintering 44.3 (2012), pp. 365–372.
- [27] U. O. Krašovec, M. Berginc, M. Hočevar, and M. Topič. "Unique TiO₂ paste for high efficiency dye-sensitized solar cells". In: *Solar Energy Materials and Solar Cells* 93.3 (2009), pp. 379–381.
- [28] T.-H. Tsai, S.-C. Chiou, S.-M. Chen, and K.-C. Lin. "Enhanced photoelectrochemical performance of dye-sensitized solar cells base on iodine-PEDOT composited film". In: *International Journal of Electrochemical Science* 6 (2011), pp. 3938–3950.
- [29] A. Yasin, F. Guo, and G. P. Demopoulos. "Continuous-reactor, pH-controlled synthesis of multifunctional mesoporous nanocrystalline anatase aggregates". In: *Chemical Engineering Journal* 287 (2016), pp. 398–409.

- [30] K. E. Lee, C. Charbonneau, and G. P. Demopoulos. "Thin single screen-printed bifunctional titania layer photoanodes for high performing DSSCs via a novel hybrid paste formulation and process". In: *Journal of Materials Research* 28.03 (2013), pp. 480–487.
- [31] C. Charbonneau, R. Gauvin, and G. Demopoulos. "Nucleation and growth of self-assembled nanofibre-structured rutile (TiO₂) particles via controlled forced hydrolysis of titanium tetrachloride solution". In: Journal of Crystal Growth 312.1 (2009), pp. 86–94.
- [32] I. S. Khattab, F. Bandarkar, M. A. A. Fakhree, and A. Jouyban. "Density, viscosity, and surface tension of water+ethanol mixtures from 293 to 323K". In: *Korean Journal of Chemical Engineering* 29.6 (2012), pp. 812–817.
- [33] C. A. Staples and J. W. Davis. "An examination of the physical properties, fate, ecotoxicity and potential environmental risks for a series of propylene glycol ethers". In: *Chemosphere* 49.1 (2002), pp. 61–73.
- [34] K. Fan, M. Liu, T. Peng, L. Ma, and K. Dai. "Effects of paste components on the properties of screen-printed porous TiO₂ film for dye-sensitized solar cells". In: *Renewable Energy* 35.2 (2010), pp. 555–561.
- [35] P. Gemeiner and M. Mikula. "Effi ciency of dye sensitized solar cells with various compositions of TiO₂ based screen printed photoactive electrodes". In: Acta Chimica Slovaca 6.1 (2013), pp. 29–34.
- [36]

.

- [37] C.-H. Zhou, X.-Z. Zhao, B.-C. Yang, D. Zhang, Z.-Y. Li, and K.-C. Zhou. "Effect of poly(ethylene glycol) on coarsening dynamics of titanium dioxide nanocrystallites in hydrothermal reaction and the application in dye sensitized solar cells". In: *Journal of Colloid and Interface Science* 374.1 (2012), pp. 9–17.
- [38] H.-L. Hsu, C.-F. Tien, and J. Leu. "Effect of pore size/distribution in TiO₂ films on agarose gel electrolyte-based dye-sensitized solar cells". In: *Journal of Solid State Electrochemistry* 18.6 (2014), pp. 1665–1671.

- [39] J. Yu, Q. Li, and Z. Shu. "Dye-sensitized solar cells based on double-layered TiO₂ composite films and enhanced photovoltaic performance". In: *Electrochimica Acta* 56.18 (2011), pp. 6293–6298.
- [40] F. Rojas, I. Kornhauser, C. Felipe, J. Esparza, S. Cordero, A. Dominguez, and J. Riccardo. "Capillary condensation in heterogeneous mesoporous networks consisting of variable connectivity and pore-size correlation". In: *Physical Chemistry Chemical Physics* 4.11 (2002), pp. 2346–2355.
- [41] C. J. Barbé, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, and M. Grätzel. "Nanocrystalline titanium oxide electrodes for photovoltaic applications". In: Journal of the American Ceramic Society 80.12 (1997), pp. 3157–3171.

Chapter 6

SnS₂ as the Sn source and ligand for all-aqueous deposition of light-absorbing CZTS (Cu₂ZnSnS₄) thin films

In the last part of this research, principles of colloidal aqueous solution synthesis are applied towards synthesis of CuS/ZnS powders with the ultimate objective of fabrication of CZTS (Cu₂ZnSnS₄) thin films. Keeping with the objective of this research of avoiding the use of toxic organic chemicals Sn was added to CuS/ZnS powders in the form of an aqueous solution of SnS₂. The effects of varying annealing conditions (atmosphere, time, temperature) on the elemental composition of CZTS films were probed. Stoichiometry of the CZTS films was tuned to be optimum as is considered best for application in thin-film solar cells. Photoluminescence measurements were taken to prove the optical functionality of the resulting films. The results of this investigation are to be submitted to *Materials Letters*. Supporting Information is provided in Appendix D.

6.1 Abstract

CZTS (Cu₂ZnSnS₄) thin films were prepared following a hydrothermal/spin-coating/annealing route. A mixture of nanocrystalline CuS and ZnS powders was prepared via hydrothermal treatment. SnS₂ dissolved in aqueous (NH₄)₂S was the key in producing high quality CZTS. The CuS/ZnS nanocrystals were added to the aqueous SnS₂-containing solution to form a suspension which was spin-coated on Mo-sputtered glass. The effects of varying annealing atmosphere (inert, tin, tin and sulfur), time (1-2 hours) and temperature (500-600 °C) were investigated. In-situ Raman spectra were collected during film annealing to probe the formation of CZTS kesterite phase. Annealing at 600 °C yielded by far the best crystallinity phase-pure kesterite associated with high photoluminescence without the need for sulfur addition.

6.2 Introduction

CZTS (Cu₂ZnSnS₄) with kesterite crystal structure has emerged as a promising light absorbing material for thin-film solar cells due to its non-toxic and abundant elemental composition and its electronic and optical properties. It is a p-type semiconductor with a direct band-gap around 1.4-1.6 eV, and high absorption coefficients of 10^{4} - 10^{5} cm⁻¹ [1–3]. Having similar electronic and optical properties to material CIGS (Cu(In,Ga)Se₂), which has already been employed commercially in thin-film solar cells, CZTS can benefit from R&D and device architecture already optimized for CIGS based cells [4].

The champion method in deposition of high quality CZTS films is the hydrazine solution based approach involving dissolution of the starting precursors; it has the dual advantage of suppressing formation of secondary phases as well as preventing sulfur from evaporating. However, hydrazine is a highly toxic and explosive/flammable solvent requiring extreme caution for handling [5]. Other solution synthesis methods often require the use of organic surfactants and solvents [6–8]. In this respect Camara *et al.* [9] demonstrated a simple water-based method to form CZTS nanocrystals via hydrothermal treatment of a solution of $CuCl_2 \cdot 2 H_2O$, ZnCl, $SnCl_2 \cdot 2 H_2O$ and $Na_2S \cdot 9 H_2O$ in 16 mL

DI water. However, the scale of the process renders it challenging for commercialization. In a similar approach it was demonstrated that use of $\text{SnCl}_4 \cdot \text{H}_2\text{O}$ and 34 mL of water required the use of thioglycolic acid to prevent formation of SnO_2 [10]. Hence, the need remains to be fulfilled for a non-organic, scalable solution synthesis process for CZTS thin films.

This paper documents a simple approach entailing synthesis of CuS/ZnS nanocrystals with $CuCl_2 \cdot 2 H_2O$, ZnCl, and $Na_2S \cdot 9 H_2O$ dissolved in water, followed by inclusion of Sn as SnS₂ in $(NH_4)_2S$ which also serves as a ligand to stabilize the nanoparticle suspension for spin-coating.

6.3 Experimental

6.3.1 Aqueous precursor synthesis

The chemicals used for aqueous synthesis of precursors are $\text{CuCl}_2 \cdot 2 \text{ H}_2\text{O}$, ZnCl_2 , and $\text{Na}_2\text{S} \cdot 9 \text{ H}_2\text{O}$ (all purchased from Sigma-Aldrich[®]). The anionic solution¹ comprises 48.0 g of $\text{Na}_2\text{S} \cdot 9 \text{ H}_2\text{O}$ dissolved in 250 mL DI water. To prepare the cationic solution², 17.2 g $\text{CuCl}_2 \cdot 2 \text{ H}_2\text{O}$ and 6.8 g ZnCl₂ were dissolved in 250 mL DI water. The cationic solutions were pumped into the anionic solution at 2 mL/min. The anionic solution was subjected to mechanical agitation at 800 rpm, while the cationic solution was magnetically stirred. Once the pumping finished, the receiving (anionic) solution was agitated for another 30 minutes, before being transferred to non-agitated autoclaves. Hydrothermal treatment was carried out at 180 °C for 8 hours. After the autoclaves cooled down to room temperature the black colloidal suspension was centrifuged and washed alternatively with DI water three times followed by a last wash with anhydrous ethanol, and dried in an oven at 70 °C. The dried solid was ground for further use and characterization.

 $^{^1\}mathrm{The}$ anionic solution contains the desired anion for CZTS, i.e. sulfide

 $^{^2\}mathrm{The}$ cationic solution contains the desired cations for CZTS, i.e. copper, tin, and zinc

6.3.2 Ink preparation & film deposition

SnS₂ compound was prepared following a published procedure [11]. 0.304 g of prepared (dried) SnS₂ was dissolved in 0.5 mL (NH₄)₂S solution (48% in H₂O; Sigma-Aldrich[®]), and 4.5 mL DI water under magnetic stirring. 0.5 g dried hydrothermal formed precursor powder was added to the SnS₂ solution and mixed under magnetic stirring overnight. The ink was deposited on $2x2 \text{ cm}^2$ Mo sputtered glass substrates via 5 spin coating cycles. For each cycle, the substrate was loaded with 200 μ L ink and rotated at 2500 rpm for 20 seconds, followed by drying at 200 °C for two minutes on a hot plate. The films were annealed in an Argon atmosphere – the effect of addition of excess tin and/or sulfur powder was investigated. Annealing temperature and time were varied between 500 °C and 600 °C, and 1 and 2 hours.

6.3.3 Characterization

X-ray diffraction (XRD) was performed on a Bruker D8 Discovery X-Ray Diffractometer equipped with a copper target λ (CuK α 1) = 1.5406 Å and operated at 40 kV and 40 mA. Scanning took place between 20° and 70° (2 θ) with 0.005° step/second. Raman spectroscopy was performed on Bruker Senterra confocal Raman microscope at 532 nm, 10 mW. Photoluminescence spectra and in-situ Raman spectra were measured on Renishaw inVia Raman microscope. SEM images were taken on Hitachi SU-8230. XPS (X-ray photoelectron spectroscopy) was conducted on Thermo Scientific K-Alpha XPS System. The films were etched with Ar⁺ ion bombardment with energy of 3 keV for 60s to remove any carbon-based contaminants. For depth profile each etching was conducted at 3 keV for 100 seconds.

6.4 Results & Discussion

XRD of CuS and ZnS precursors are given in Figure D.1. The precursor nanopowders were added to an aqueous solution of SnS_2 in $(NH_4)_2S$; SnS_2 serves as the tin source as well acts as a ligand to stabilize the CuS/ZnS nanoparticles in a suspension to allow

for spin-coating [11]. The spin-coated films were annealed at 500 °C for 1 hour under three different annealing atmospheres: excess tin powder (0.1 g), excess tin and sulphur powders (0.1 g each) and no added S or Sn powders. In the XRD patterns, (Figure 6.1(a)) the peaks at $2\theta = 28.5^{\circ}$, 33.1° , 47.3° , 56.1° , correspond to the (112), (200), (220), and (312) planes for CZTS kesterite phase (JCPDS #26-0575). However, the XRD peaks of CZTS kesterite overlap with those of ZnS (JCPDS #65-1691) and Cu₂SnS₃ (JCPDS #27-0198) [12]. Hence Raman spectra for all samples were taken ((Figure 6.1(b))) and show peaks at 280 cm⁻¹ and 335 cm⁻¹ [13] that are particular only to CZTS kesterite; the absence of any other peaks means no other phases present in the films.

Table 6.1 shows the compositions of the films determined via XPS. As expected, presence of excess tin powder decreases the elemental ratios relative to Sn. The intended application for these films is for thin-film solar cells and following literature on the preference for Cu-poor/Zn-rich with ideal ratio Zn/Sn \approx 1.1-13, and Cu/(Zn+Sn) \approx 0.8-0.9 [14], the annealing with no excess powder was deemed appropriate. While Larramona *et al.* [15] controlled the Sn content of the film by varying the composition of the ink, they still employed tin sulphide dissolved in a water/ethanol solution as the primary Sn source. As reported earlier, use of SnCl₂ · xH₂O in water as the Sn source, without use of organic solvents leads to oxidation of Sn²⁺ to SnO₂ [10]. In contrast, by using SnS₂ dissolved in (NH₄)₂S as the only Sn source we bypass the use of ethanol and make the process free of organic chemicals.

Another investigation was conducted to observe the effect of annealing temperature and time. Figure 6.1(a and b) shows the films to still be formed of only CZTS kesterite phase free of any secondary phases. No particular trend could be established and the elemental ratios seem to occur within statistical error. Similarly, Maeda *et al.* also found no particular difference in elemental composition between 500 and 600 °C [16].

Figure 6.1 (c) presents in-situ Raman spectra of a film subjected to heating from 25 °C to 360 °C. At room temperature, there is a sharp peak at 471 cm⁻¹ representing Cu_{2-x}S [17]; and smaller peaks occur at 276 and 325 cm⁻¹ (ZnS) and 301 cm⁻¹ (Cu₂SnS₃) [12]. At 120 °C, 301 cm⁻¹ peak disappears. At 240 °C a peak centered at 335 cm⁻¹ starts

	500 °C 1h				no powder			
	Before an-	Inert atmo-	Sn powder	Sn & S	$500~^{\rm o}{\rm C}$ 1 h	$500~^{\rm o}{\rm C}$ 2h	$600~^{\circ}\mathrm{C}$ 1 h	$600~^{\circ}\mathrm{C}$ 2h
	nealing	sphere		powder				
%Cu	16.5 ± 9.36	$17.18 {\pm} 0.4$	$12.6 {\pm} 0.54$	16.49 ± 1	$17.18 {\pm} 0.4$	33.7 ± 0	$18.54 {\pm} 0.74$	$16.87 {\pm} 0$
%Sn	$12.8 {\pm} 7.68$	$8.22{\pm}0.19$	$9.63{\pm}0.37$	$7.12 {\pm} 0.19$	$8.22{\pm}0.19$	31.36 ± 0	$9.57{\pm}0.38$	$8.03{\pm}022$
%Zn	12.03 ± 5.52	$9.53 {\pm} 0.16$	$12.54{\pm}0.03$	$9.51{\pm}0.06$	$9.53{\pm}0.16$	15.21 ± 0	$11.32{\pm}0.45$	$10.22{\pm}0.28$
%S	58.68 ± 22.56	$65.08 {\pm} 0.75$	$65.24{\pm}0.2$	$66.88{\pm}1.26$	$65.08{\pm}0.75$	19.74 ± 0	$60.57 {\pm} 1.57$	$64.89{\pm}0$
$\mathrm{Cu/Sn}$	1.29	2.09	1.31	2.32	2.09	1.94	1.71	2.10
Cu/Zn	1.37	1.80	1.00	1.73	1.80	1.64	1.37	1.65
$\rm Zn/Sn$	0.94	1.16	1.30	1.34	1.16	1.18	1.25	1.27
Cu/(Zn+Sn)	0.66	0.97	0.57	0.99	0.97	0.89	0.76	0.92
S/metal	1.42	1.86	1.88	2.02	1.86	1.54	0.93	1.85

Table 6.1: Elemental compositions of films.

appearing indicating CZTS formation. At 320 °C 276 cm⁻¹ peak completely disappears, showing complete dissolution of ZnS. And finally, at 360 °C peak at 471 cm⁻¹ disappears completely signifying disappearance of copper sulfides.

Figure 6.2 shows the XPS spectra used to determine the oxidation states of the elements. Sn $3d_{5/2}$ and $3d_{3/2}$ peaks are located at 486.3 eV and 494.8 eV with 8.5 eV separation confirming +4 oxidation state for Sn. Cu $2p_{3/2}$ and $2p_{1/2}$ peaks are at 932.7 eV and 952.6 eV respectively with a 19.9 eV separation that suggests +1 oxidation state for Cu. Zn $2p_{3/2}$ and $2p_{1/2}$ peaks are located at 1021.8 eV and 1044.9 eV respectively; peak separation of 23.1 eV corresponds to +2 state. And finally, S $2p_{3/2}$ and $2p_{1/2}$ peaks at 162 eV and 163 eV with 1.2 eV separation lie within the 160-164 eV range expected for sulfide phases [18, 19].

Figure 6.3 shows photoluminescence measurements with the peak for all conditions at $\approx 900 \text{ nm} (1.39 \text{ eV}) [20]$. As the annealing temperature and/or time increase the peak sharpens in correspondence to higher degree of crystallinity obtained with temperature elevation [21].


Figure 6.1: (a) XRD patterns of annealed films (b) Raman spectra of annealed films:
(i) Inert atmosphere, 500 °C, 1hr; (ii) Sn powder, 500 °C, 1hr; (iii) Sn & S powder, 500 °C, 1hr; (iv) Inert atmosphere, 500 °C, 2hr; (v) Inert atmosphere, 600 °C, 1hr; (vi) Inert atmosphere, 600 °C, 2hr; (c) In-situ Raman spectra of a film during annealing.

Chapter 6. SnS_2 as the Sn source and ligand for all-aqueous deposition of light-absorbing $CZTS (Cu_2ZnSnS_4)$ thin films



Figure 6.2: XPS core-level peaks of CZTS film annealed at 500 °C, 1hr.



Figure 6.3: Photoluminescence spectra of CZTS films.

6.4.1 Conclusion

CZTS kesterite phase films were successfully fabricated by spin-coating a suspension of hydrothermally produced CuS and ZnS nanoparticles in a novel aqueous solution of SnS₂ dissolved with $(NH_4)_2S$ followed by annealing at 500-600 °C for 1-2 hours. The use of SnS₂ is critical in controlling CZTS composition and still using an all-aqueous process. Due to the excess of sulfur in the suspension, annealing could be conducted in inert atmosphere without adding extra sulfur. Varying annealing temperature from 500 °C to 600 °C does not appear to significantly vary the elemental composition of the films but the best photoluminescence is obtained at 600 $^{\circ}$ C.

6.5 References

- A. Khalkar, K.-S. Lim, S.-M. Yu, S. P. Patole, and J.-B. Yoo. "Effect of growth parameters and annealing atmosphere on the properties of Cu₂ZnSnS₄ thin films deposited by cosputtering". In: *International Journal of Photoenergy* 2013 (2013).
- [2] J. Henry, K. Mohanraj, and G. Sivakumar. "Electrical and optical properties of CZTS thin films prepared by SILAR method". In: *Journal of Asian Ceramic Societies* 4.1 (2016), pp. 81–84.
- [3] C. Malerba, F. Biccari, C. L. A. Ricardo, M. Valentini, R. Chierchia, M. Müller, A. Santoni, E. Esposito, P. Mangiapane, P. Scardi, et al. "CZTS stoichiometry effects on the band gap energy". In: *Journal of Alloys and Compounds* 582 (2014), pp. 528–534.
- [4] T. J. Huang, X. Yin, G. Qi, and H. Gong. "CZTS-based materials and interfaces and their effects on the performance of thin film solar cells". In: *physica status solidi (RRL)-Rapid Research Letters* 8.09 (2014), pp. 735–762.
- [5] W.-C. Hsu, B. Bob, W. Yang, C.-H. Chung, and Y. Yang. "Reaction pathways for the formation of Cu₂ZnSn(Se,S)₄ absorber materials from liquid-phase hydrazinebased precursor inks". In: *Energy & Environmental Science* 5.9 (2012), pp. 8564– 8571.
- [6] S. Kahraman, S. Çetinkaya, H. Çetinkara, and H. Güder. "A comparative study of Cu₂ZnSnS₄ thin films growth by successive ionic layer adsorption-reaction and sol-gel methods". In: *Thin Solid Films* 550 (2014), pp. 36–39.
- [7] S. K. Saha, A. Guchhait, and A. J. Pal. "Cu₂ZnSnS₄ (CZTS) nanoparticle based nontoxic and earth-abundant hybrid pn-junction solar cells". In: *Physical Chemistry Chemical Physics* 14.22 (2012), pp. 8090–8096.

- [8] Y. Sun, Y. Zhang, H. Wang, M. Xie, K. Zong, H. Zheng, Y. Shu, J. Liu, H. Yan, and M. Zhu. "Novel non-hydrazine solution processing of earth-abundant Cu₂ZnSn(S, Se)₄ absorbers for thin-film solar cells". In: *Journal of Materials Chemistry A* 1.23 (2013), pp. 6880–6887.
- [9] S. M. Camara, L. Wang, and X. Zhang. "Easy hydrothermal preparation of Cu₂ZnSnS₄ (CZTS) nanoparticles for solar cell application". In: *Nanotechnology* 24.49 (2013), p. 495401.
- [10] V. T. Tiong, J. Bell, and H. Wang. "One-step synthesis of high quality kesterite Cu₂ZnSnS₄ nanocrystals-a hydrothermal approach". In: *Beilstein Journal of Nanotechnology* 5.1 (2014), pp. 438–446.
- [11] M. V. Kovalenko, M. I. Bodnarchuk, J. Zaumseil, J.-S. Lee, and D. V. Talapin. "Expanding the chemical versatility of colloidal nanocrystals capped with molecular metal chalcogenide ligands". In: *Journal of the American Chemical Society* 132.29 (2010), pp. 10085–10092.
- [12] M. Karimi, M. Eshraghi, and V. Jahangir. "A facile and green synthetic approach based on deep eutectic solvents toward synthesis of CZTS nanoparticles". In: *Materials Letters* 171 (2016), pp. 100–103.
- [13] J. Zhong, Z. Xia, C. Zhang, B. Li, X. Liu, Y.-B. Cheng, and J. Tang. "One-pot synthesis of self-stabilized aqueous nanoinks for Cu₂ZnSn(S, Se)₄ solar cells". In: *Chemistry of Materials* 26.11 (2014), pp. 3573–3578.
- [14] Y. Feng, B. Yu, G. Cheng, T. Lau, Z. Li, L. Yin, Q. Song, C. Yang, and X. Xiao. "Searching for a fabrication route of efficient Cu₂ZnSnS₄ solar cells by post-sulfuration of co-sputtered Sn-enriched precursors". In: *Journal of Materials Chemistry C* 3.37 (2015), pp. 9650–9656.
- [15] G. Larramona, S. Levcenko, S. Bourdais, A. Jacob, C. Chone, B. Delatouche, C. Moisan, J. Just, T. Unold, and G. Dennler. "Fine-tuning the Sn content in CZTSSe thin films to achieve 10.8% solar cell efficiency from spray-deposited water-ethanol-based colloidal inks". In: Advanced Energy Materials 5.24 (2015).

- [16] K. Maeda, K. Tanaka, Y. Nakano, and H. Uchiki. "Annealing temperature dependence of properties of Cu₂ZnSnS₄ thin films prepared by sol–gel sulfurization method". In: Japanese Journal of Applied Physics 50.5S2 (2011), 05FB08.
- [17] B. Minceva-Sukarova, M. Najdoski, I. Grozdanov, and C. Chunnilall. "Raman spectra of thin solid films of some metal sulfides". In: *Journal of Molecular Structure* 410 (1997), pp. 267–270.
- [18] J. Wang, P. Zhang, X. Song, and L. Gao. "Surfactant-free hydrothermal synthesis of Cu₂ZnSnS₄ (CZTS) nanocrystals with photocatalytic properties". In: *RSC Advances* 4.53 (2014), pp. 27805–27810.
- [19] M. Hurtado, S. Cruz, R. Becerra, C. Calderón, P. Bartolo-Pérez, and G. Gordillo. "XPS analysis and structural characterization of CZTS thin films prepared using solution and vacuum based deposition techniques". In: *Photovoltaic Specialist Conference (PVSC), 2014 IEEE 40th.* IEEE. 2014, pp. 0368–0372.
- [20] J. K. Larsen, S.-Y. Li, J. Scragg, Y. Ren, C. Hagglund, M. Heinemann, S. Kretzschmar, T. Unold, and C. Platzer-Bjorkman. "Interference effects in photoluminescence spectra of Cu₂ZnSnS₄ and Cu (In,Ga)Se₂ thin films". In: *Journal of Applied Physics* 118.3 (2015), p. 035307.
- [21] H. T. Kim, D. Kim, and C. Park. "Temperature Effects on Cu₂ZnSnS₄ (CZTS)
 Films Deposited by Spraying Method". In: *Molecular Crystals and Liquid Crystals* 564.1 (2012), pp. 155–161.

Chapter 7

Synopsis

This chapter brings together the conclusions drawn individually in Chapters 3-6. The conclusions are followed by original contributions to knowledge made during the course of this research. Finally, a few suggestions for future work are presented.

7.1 Global conclusions

• In a departure from the bulk of laboratory studies that focus on synthesis of nanostructured particles in batch reactors, here it is shown that synthesis in a continuous-stirred tank reactor (CSTR) is a promising and mostly unexplored avenue in altering nanocrystal properties while achieving high production yield with obvious material and application advantages.

• TiO₂ nanocrystals were shown to be advantageously synthesized in a CSTR fed with TiCl₄ aqueous solution, opening the way to scalable and green production processing at atmospheric pressure and sub-boiling temperatures (70-90 °C). It was observed that maintaining solution pH at 2-5 via continuous addition of base (NaOH) was vital in producing anatase without co-existence of brookite/rutile in the final TiO₂ product. Anatase was the first polymorph to precipitate out due to favorable surface energy changes; at pH 2-5 its metastability increases as dissolution and subsequent transformation to brookite/rutile

is suppressed.

• The precipitated anatase exists as 1.5 μ m aggregates whereas the primary crystals measure 6-10 nm. However the anatase aggregates also exhibited high surface area ($\approx 250 \text{ m}^2/\text{g}$) proving they are mesoporous. Moreover the aggregates underwent heterogeneous growth, owing to the presence of transient precipitate at the outset of continuous mode of operation.

• When the solution pH was not controlled and was solely determined by the hydrolysis of TiCl₄, brookite and rutile formed depending on the inlet TiCl₄ concentration. It was observed that high TiCl₄ concentration (0.5-1.0 M) and consequently low pH promoted rutile formation; whereas at low TiCl₄ concentration (0.1 M; low pH) brookite polymorph was produced along some rutile (94% B-6%R). The two polymorphs showed considerably different morphologies with rutile appearing as spherical aggregates with a cross section characterized by self-assembled elongated needles; and brookite appearing as 2D nanoplatelets.

• In the crystallization pathway, anatase was the first phase to nucleate, since for both cases the concentration of the receiving solution was 0.05 M TiCl₄. Once the inlet stream was started, for solutions with >0.5 M TiCl₄ rutile started to appear (without any traces of brookite) at the expense of anatase. On the other hand for 0.1 M solutions, brookite started to appear. The inlet stream brings in more TiCl₄ leading to more acid generation due to hydrolysis causing the low pH to catalyze dissolution of the initially nucleated anatase which underwent growth to the more stable polymorphs. Higher TiCl₄ also means higher Ti⁴⁺ and Cl⁻ both of which favor the formation of only rutile type monomers and thus no brookite appeared in the rutile crystallization pathway. It is known that production of brookite as the only phase is difficult; in the current work the employment of CSTR allows for the possibility that some particles spend longer than residence time and hence get transformed to rutile. Thus brookite synthesis is only partially kinetically stabilized in the CSTR. In the meantime, this work showed that use of CSTR is essential in crystallizing rutile directly from aqueous solution without appearance of anatase and/or brookite, owing to its unique ability to maintain steady supersaturation.

• Anatase crystallization which required maintenance of pH within a certain window followed La Mer supersaturation curve. For brookite the outlet concentration of Ti⁴⁺ increased gradually until it reached a steady value. Hence pH not only determined the final phase, but also controlled the extent by controlling precipitation kinetics.

• The anatase particles proved their functionality as photocatalysts in the degradation of methyl orange in water; and also as semiconductor when assembled into DSSCs (dye-sensitized solar cells). The fibrous rutile particles proved their functionality as light scattering layer when overlaid on DSSC in a double layer configuration leading to an efficiency increase from 4.07 % to 5.71%.

• Through a systematic study it was shown that a TiO_2 screen-printable paste can be made comprising of acetic acid, propylene glycol, and polyethylene glycol (molecular weight: 20,000); in such a paste propylene glycol serves as the plasticizer and is essential for mechanical stability and good adhesion between the TiO_2 film and the substrate. Whereas, polyethylene glycol amount has a strong effect on the paste viscosity and also acts as the pore-forming agent upon sintering of the film. This paste has the advantage of having water-soluble and non-toxic components and hence offers an environmentally friendly alternative to the commonly used organic protocol.

• CZTS (Cu_2ZnSnS_4) kesterite phase films were fabricated via spin-coating of hydrothermally prepared ZnS and CuS solid powders dispersed in an aqueous solution of SnS_2 in (NH_4)₂S; thus SnS_2 acts as the tin source as well as a ligand for the dispersion. By dissolving SnS_2 in an aqueous solution of (NH_4)₂S, appearance of SnO_2 which occurs rapidly in water was bypassed, while simultaneously avoiding the use of organic additives and making the process completely water-based. By optimizing the sulfur content in CuS/ZnS and $(NH_4)_2S$, there was no need to provide excess sulfur during annealing. No particular trend in elemental ratios could be observed by varying the annealing conditions at 500-600° for 1-2 hours. However, the highest photoluminescence response was recorded for films annealed at 600° for 2 hours.

7.2 Claims to originality

The most significant contributions to original knowledge made during the course of this study are summarized below:

• It was the first time a continuous stirred-tank reactor (CSTR) was employed for the synthesis of nano-TiO₂ phases, directly from aqueous solution at atmospheric pressure and sub-boiling temperatures.

• It was discovered that use of a CSTR, thanks to steady solution supersaturation, allows for direct nucleation of TiO₂-rutile phase, without the involvement of any metastable phases (i.e. anatase and brookite).

• It was the first time such high surface area rutile particles (495 m^2/g) were synthesized without the use of any templates or copolymers.

• An aqueous screen-printable paste incorporating propylene glycol as the plasticizer was formulated; and a systematic study was conducted to elucidate the individual contributions of propylene glycol and polyethylene glycol to paste rheology.

• Solid CuS and ZnS dispersed in aqueous solution of SnS_2 was used as the precursor for CZTS Cu_2ZnSnS_4 thin-films; it was the first time SnS_2 was used as the sole Sn source as well as a ligand to stabilize the dispersion.

7.3 Suggestions for future work

• For future, it would be interesting to see the photovoltaic performance of the synthesized anatase particles with solid-state sensitizers such as perovskite materials which have gained attention and attained stellar performance in photovoltaics. • Considering the wide variety of applications nano- TiO_2 is employed in, it is recommended that the CSTR-synthesized anatase material is systematically evaluated to be used as photocatalysts.

• The protocol devised in Chapter 5 to construct mesoporous TiO_2 films should be followed to make films for photocatalysis.

• Regarding the CZTS thin films that have been fabricated in this work, the natural next step would be their assembly into solar cells to evaluate their photovoltaic performance.

Appendix A

Additional information to Chapter 3

A.1 Detailed explanation of CSTR operation

A 2L double jacked Applikon[®] bioreactor was customized to be used as a continued stirred tank reactor (CSTR), as shown in Figure A.1. Head plate of the reactor was equipped with two tubes, one for the outlet, one for inlet; three baffles; a shaft with a three-blade marine impeller, and a tube for thermal sensor to monitor the temperature. All the tests used 1L solution volume. For robust mixing of the solution, the reactor was equipped with three baffles and a 45 mm marine impeller whereby the stirring rate was maintained at 800 rpm by the accompanying EZ-controller. To keep the reactor solution at 80 °C, an oil bath circulated silicone oil through the double jacket. A temperature sensor measured the solution temperature and the oil bath temperature was manually changed to maintain a constant solution temperature. The oil bath was kept at 90 °C during start-up and 100 °C during continuous operation since the feed entering the reactor was at 0 °C. Peristaltic pumps external to the reactor were used to deliver the inlet TiCl₄ feed to the reactor and pump the colloidal solution out of the reactor. Flow rate through the two pumps was set equally at 33 ml/min for 30-minute residence time in a 1L solution (16.5 ml/min for 60-minute residence time). Masterflex® norprene tubing (ID: 4.8mm) was used to deliver the inlet and outlet solutions. A pH sensor connected to the EZ-controller measured and controlled the pH at specified value (3-5) through



Figure A.1: Schematic of Applikon[®] reactor used as CSTR

continuous addition of a base using another set of peristaltic pump. NH_4OH (14.5M) was first used following the batch synthesis [1] but was later replaced by NaOH (19M). All the reactor parts were originally stainless steel and were coated with Teflon[®]. The colloidal suspension was cooled in an ice-water bath (≈ 0 °C) and was centrifuged (at 6000 rpm, 30 minutes) and washed alternatively with 50 mL deionized water twice, followed by a third wash with ethanol, to wash away Na⁺ and Cl⁻ ions.

Figure A.2 shows a snapshot of FWHM (full-width at half maximum) determination of XRD peaks using EVA software.

Figure A.3 shows XRD patterns of nanoanatase produced at solution pH 6, 1200 rpm stirrer speed, and residence time of 60 minutes. Steady state TiO_2 product obtained at pH 6 is amorphous, whereas the latter two conditions yield crystalline anatase. Figure A.4 shows XRD patterns for pH 3, pH 2, and pH 1; all patterns show crystalline anatase

peaks that get shorter with decreasing pH, indicative of decreased crystallinity.



Figure A.2: Example of FWHM evaluation of XRD pattern by EVA software



Figure A.3: XRD patterns of steady-state products obtained at

a) T=80 °C, [TiCl₄]_{feed} = 0.1M, pH_{steady-state} = 6, τ = 30 min, 800 rpm; b) T=80 °C, [TiCl₄]_{feed} = 0.1M, pH_{steady-state} = 3, τ = 30 min, 1200 rpm; c) T=80 °C, [TiCl₄]_{feed} = 0.1M, pH_{steady-state} = 3, τ = 60 min, 800 rpm.



Figure A.4: XRD patterns of steady-state products obtained at

- a) T=90 °C, $[\text{TiCl}_4]_{feed} = 0.2\text{M}$, $\text{pH}_{steady-state} = 3$, $\tau = 30 \text{ min}$, 800 rpm;
 - b) T=90 °C, $[\text{TiCl}_4]_{feed} = 0.5\text{M}$, $\text{pH}_{steady-state} = 3$, $\tau = 30 \text{ min}$, 800 rpm;
 - c) T=90 °C, [TiCl₄]_{feed} = 0.2M, pH_{steady-state} = 2, τ = 30 min, 800 rpm;
 - d) T=90 °C, [TiCl₄]_{feed}= 0.2M, pH_{steady-state} = 1, τ = 30 min, 800 rpm;
 - e) T=90 °C, [TiCl₄]_{feed} = 0.1M, pH_{steady-state} = 1, τ = 30 min, 800 rpm.



Figure A.5: BET surface area of TiO₂ anatase nanocrystalline powders; τ : 30 min



Figure A.6: (Left) SEM image of an atase aggregates (Right) TEM image showing primary anatase nanocrystals size and orientation. $[\text{TiCl}_4]_{feed}$ = 0.2M, τ = 30 min, T = 80°C, pH = 3



Figure A.7: FT-IR spectrum of TiO₂ nanocrystalline product. T=80 °C, $[TiCl_4]_{feed} = 0.2M$, $pH_{steady-state} = 3$, τ : 30 min



Figure A.8: XPS spectra of Ti, O, and Na,

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Q
O1s	531.08	1.64	13431.35	62.38	1
Ti2p	459.65	1.58	16123.33	31.56	1
Na1s	1074.03	4.73	2618.39	6.06	1

Table A.1: XPS spectra of Ti, O, and Na, and their atomic%, as determined by Avantage



Figure A.9: J-V curves of DSSCs. B and C distinguish between solar cells employing TiO_2 synthesized from batch and CSTR processes respectively



Figure A.10: UV-vis absorption spectrum and Tauc plot of TiO₂ anatase product. T = 80 °C, $[\text{TiCl}_4]_{feed} = 0.1\text{M}$, $\text{pH}_{steady-state} = 3$, $\tau = 30 \text{ min}$, 800 rpm

A.2 References

 C. Charbonneau, R. Gauvin, and G. Demopoulos. "Aqueous solution synthesis of crystalline anatase nanocolloids for the fabrication of DSC photoanodes". In: *Journal of The Electrochemical Society* 158.3 (2011), H224–H231.

Appendix B

Additional information to Chapter 4

Experiments were conducted to observe the effect of temperature, agitation, and residence time on the ratio of brookite/rutile phases. Figure B.1 presents the X-ray diffraction (XRD) patterns and Table B.1 presents the TiO₂ phase compositions with their respective surface areas. Figure B.1 (a) shows XRD patterns corresponding to 30 minutes of residence time. For longer residence time of 2 and 4 hours (Figure B.1 (b) and (c) respectively) the crystals grew bigger in size, signified by their lower surface areas. Figure B.1 (d) for 400 rpm shows a lesser proportion of brookite. Brookite had the highest purity at 90 °C (Figure B.1 (e),(f)); the high temperature also induced crystal growth indicated by the lower surface area. Finally Figure B.1 (g) shows a mixture of anatase and rutile with no brookite when the TiCl₄ inlet concentration is 0.05 M – the same as the receiving solution.

Figure B.2 presents the reaction profiles of selective experiments. All reaction profiles (also see Figure 4.2) show similar trend of steadily increasing Ti(IV) concentration until the concentration reaches a steady value.

Kubelka-Munc plot was used to determine the bandgap of rutile to be 3.0 eV. (Figure B.3)

Figure B.4 shows a graphical representation of the combination of conditions that favor formation of different TiO_2 phases in the aqueous CSTR process. By maintaining the solution pH 2-5, anatase was formed without the appearance of rutile and brookite (Chapter 3). Without pH control, higher $TiCl_4$ concentration (> 0.5 M) which also leads to higher acidity in the reactor solution, led to rutile formation without the appearance of anatase or brookite, while lower concentrations (0.1-0.2M) resulted in formation of brookite nanoplatelets.

Figure B.5 shows TEM images of product obtained for 0.1-1.0 M inlet $TiCl_4$ concentration.

Figure B.6 shows N_2 adsorption/desorption isotherms for 0.1 M and 0.5 M inlet TiCl₄ concentrations. All isotherms show characteristics of mesoporous solids as is discussed in the main article.

Table B.2 presents the photovoltaic performance of solar cells with 2 printed layers of Dyesol 18NRT as the photoactive part, overlaid with a layer of brookite nanoparticles as the scattering layer. While the photon-to-current conversion efficiency is the same for rutile and brookite scattering layers, the current density (J_{sc}) is higher for rutile scattering layer (Table 2 in the main article) showing that rutile leads to better light scattering performance within the TiO₂ film.

Figure B.7 presents the transmission of Dyesol 18NRT films of two different thickness. This figure is an appendage to Figure 6 in the main article and shows both films, 10 μ m – thickness of Dyesol 18NRT in the photoanode which was assembled into solar cell, and 15 μ m – thickness equivalent to thickness of Dyesol 18NRT+Rutile layer, have similar transmission profile with \approx 70% light transmission, compared with 30% transmission of the 15 μ m thick Dyesol+Rutile layer. Hence it proves that the rutile particles indeed introduce scattering effects in the photoanode.

Figure B.8 presents the cycling performance of brookite nanoplatelets at different rates (1C=168 mA/g). The specific brookite material used in this experimental series had the following mixed phase composition: 72.7% brookite and 27.3% rutile. The capacity data plotted in the graph are for the total mass of TiO₂ (brookite + rutile). Details on the electrochemical investigation are provided in Sussman *et al* [1].



Figure B.1: XRD patterns of TiO_2 produced at different steady-state CSTR operating conditions with 0.1M $TiCl_4$ feed solution

- a) T=80 °C, τ =0.5 hour, 800 rpm, [TiCl₄]_{feed}=0.1M
- b) T=80 °C, τ =2 hour, 800 rpm, [TiCl₄]_{feed}=0.1M
- c) T=80 °C, $\tau{=}4$ hour, 800 rpm, $[\mathrm{TiCl}_4]_{feed}{=}0.1\mathrm{M}$
- d) T=80 °C, τ =1 hour, 400 rpm, [TiCl₄]_{feed}=0.1M
- e) T=80 °C, τ =1 hour, 1600 rpm, [TiCl₄]_{feed}=0.1M
- f) T=80 °C, τ =1 hour, 800 rpm, [TiCl₄]_{feed}=0.1M
- g) T=80 °C, τ =1 hour, 800 rpm, [TiCl₄]_{feed}=0.05M



Figure B.2: Outlet concentration of unreacted $\mathrm{Ti}(\mathrm{IV})$ for variable operating conditions

- a) T=80 °C, $\tau{=}4$ hour, 800 rpm, [TiCl₄]_{feed}=0.1M
- b) T=80 °C, τ =1 hour, 400 rpm, [TiCl₄]_{feed}=0.1M
- d) T=80 °C, $\tau{=}1$ hour, 800 rpm, $[{\rm TiCl_4}]_{feed}{=}0.2{\rm M}$

	Phase compositions (%)			C ($(2/z)$)	
	Anatase	Rutile	Brookite	Surface area (m ⁻ /g)	
(a)	11	39	50	163.3	
(b)	0	18	82	65.4	
(c)	0	18	82	93.2	
(d)	18	9	73	137.5	
(e)	0	11	89	142.7	
(f)	0	6	94	91.1	
(e)	24	76	0	118.0	

Table B.1: Phase composition and particle characteristics of TiO_2 products for parameters corresponding to Figure B.1



Figure B.3: Kubelka-Munc plot to determine band-gap of rutile



Figure B.4: Schematic showing qualitatively the combination of synthesis conditions that

favor the formation of the different ${\rm TiO}_2$ phases

 Table B.2: Photovoltaic parameters of DSSCs employing brookite nanoparticles as the scattering layer

		Thickness	V_{oc} (V)	\mathbf{J}_{sc}	$\eta~(\%)$	FF
		(μm)		$(\mathrm{mA/cm^2})$		
Dyesol A	natase	10.32 ± 0.15	$0.69 {\pm} 0.007$	$8.54 {\pm} 0.55$	4.02 ± 0.36	68.20 ± 3.11
Dyesol	Anatase+	$15.40{\pm}1.42$	$0.66 {\pm} 0.03$	$10.89 {\pm} 0.54$	$5.34 {\pm} 0.62$	74.04 ± 3.6
Brookite Scattering						
Layer						



Figure B.5: Comparison of size and morphology of rutile crystals at steady-state a) 0.1 M b) 0.2 M c) 0.5 M d) 0.8 M e) 1.0 M



Figure B.6: N_2 adsorption/desorption isotherms of TiO₂ steady-state products corresponding to a) 0.1 M (92% brookite, 8% rutile) (b) 0.5 M (rutile)



Figure B.7: Comparison of transmission of Dyesol 18NRT film 10 and 15 μ m in thickness with Dyesol 18NRT+Rutile scattering layer (15 μ m)



Figure B.8: Cycling performance of brookite nanoplatelets at different rates (1C= 168 $$\rm mA/g$)$

B.1 References

 M. J. Sussman, M. Celikin, A. Yasin, and G. P. Demopoulos. "Mesoporous brookite nanoplatelets with superior lithium-ion intercalation stability". In: *Electrochimica Acta* 138 (2014), pp. 215–223.

Appendix C

Additional information to Chapter 5



Figure C.1: (a) XRD pattern of anatase (b) XRD pattern of rutile



Figure C.2: (a) SEM image of dry anatase (b) TEM image of dry anatase (c) SEM image of dry rutile (d) TEM image of dry rutile.

	Anatase	Rutile
Surface area (m^2/g)	232.5	72.7
Equivalent primary particle size (nm)	6.6	19.3

Table C.1: BET surface area and calculated equivalent primary particle diameter



Figure C.3: Comparison of DSSC performance of cells made from TiO_2 powder and TiO_2 colloid following organic protocol



Figure C.4: A representative TGA conducted to determine TiO₂ loading (Paste U7)



Figure C.5: Cumulative pore volume as a function of PEG quantity for the sintered films.



Figure C.6: J-V curves of DSSC assembled from photoanode films prepared from variable PEG amount paste formulation.



Figure C.7: Efficiency and dye loading as a function of pore width; (amount of PEG is given next to each data point): 3g TiO₂ (Anatase 80%, Rutile 20%), 0.5mL Acetic acid, 10g PG, 50 mL Water, 50 mL Ethanol.



Figure C.8: Efficiency and dye loading as a function of surface area; (amount of PEG is given next to each data point): 3g TiO₂ (Anatase 80%, Rutile 20%), 0.5mL Acetic acid, 10g PG, 50 mL Water, 50 mL Ethanol.
PEG Quantity (g)	PG Quantity (g)	Additional component	
		Component	Quantity
2	10	Polyacrylic acid	2g
2	10	Triton-X	$800~\mu\mathrm{L}$
2	10	Triton-X	$400~\mu\mathrm{L}$
0	10	-	-
	PEG Quantity (g) 2 2 2 2 0	PEG Quantity (g) PG Quantity (g) 2 10 2 10 2 10 2 10 0 10	PEG Quantity (g)PG Quantity (g)Additional compo2IOComponent210Polyacrylic acid210Triton-X210Component210Ition-X010Ition-X

Table C.2: Additional paste formulations

Table C.3: Photovoltaic parameters corresponding to additional paste formulations

Paste	Thickness (μm)	$\eta~(\%)$	V_{oc} (V)	$J_{\it sc}~(mA/cm^2)$	FF
V1	13.78	2.51	0.72	5.21	66.71
V2	10.07	3.82	0.76	7.05	71.61
V3	12.14	3.08	0.73	6.65	63.24
U9	15.77	4.5	0.72	8.53	73.33

Appendix D

Additional information to Chapter 6

Figure D.1 presents the X-ray diffraction (XRD) patterns of powder obtained before and after hydrothermal treatment and shows presence of CuS (JCPDS #007-1392) and ZnS (JCPDS #005-0566). Crystallization of ZnS seems to be favored at high temperature/high pressure during hydrothermal treatment (180 °C, 8 hours). Table D.1 presents the elemental ratios of Cu, Zn, and S in powders before and after hydrothermal treatment.

	$\mathrm{Cu/Zn}$	S/Zn	S/(Cu+Zn)
Before hydrothermal	1.43	1.03	0.42
After hydrothermal	1.92	1.40	0.48

Table D.1: Molar ratios in precursor powders before and after hydrothermal treatment



Figure D.1: XRD patterns of precursor metal sulfide powders before and after hydrothermal treatment.