## Mechanochemical methods towards sustainable phosphorus

## chemistry: From nanomaterials to molecules

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For Dad, Mom, and Uncle Terry

"Far and away the best prize that life offers is the chance to work hard at work worth doing."

-Theodore Roosevelt

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#### Abstract

Phosphorus is essential to human life, as it is present as a linker in the backbone of our DNA, in the fertilizers that assist in growing the food that feeds us, or in novel ligands and materials that catalyse reactions in a variety of industries. However, despite its importance, the industrial conversion of phosphate rock (PR) towards value-added chemicals suffers from many drawbacks, including high material and energy demand, its reliance on corrosive and toxic intermediates, and the non-renewable nature of phosphate rock itself. Mechanochemistry has already proven effective in organic, inorganic and materials chemistry. The ability to perform chemistry in the absence of bulk solvent, at room temperature, and with shorter reaction times, has made mechanochemical techniques a cornerstone of Green Chemistry research. Additionally, scalability is also showing direct viability using planetary milling, accelerated aging and twinscrew extrusion (TSE).

This Thesis outlines the application of mechanochemistry *i.e.* chemical reactivity induced by mechanical forces such as impact or shear, towards the simpler and more effective synthesis of phosphorus-containing nanomaterials. The first research project demonstrated the use of phosphorus pentoxide ( $P_4O_{10}$ ) as a solid-state phosphorylating agent for the functionalization of cellulose nanocrystals and synthetic polymers as novel and sustainable flame-retardants. The subsequent projects shifted focus toward the use of sodium phosphide ( $Na_3P$ ) for the development of heterogeneous water splitting catalysts. Initially, we developed a bottom-up synthesis of ultrasmall nickel phosphide nanoparticles as cocatalysts for the hydrogen evolution reaction (HER). Subsequently,  $Na_3P$  was used for the bottom-up synthesis of phosphorus-linked carbon nitrides as tunable, metal-free photocatalysts for HER. Alongside the novel reactivity presented throughout this Thesis, we additionally include sustainability metrics for all projects, presenting the quantitative improvement in sustainability of mechanochemical techniques compared to traditional solution-based ones.

#### Resumé

Le phosphore est essentiel à la vie humaine, puisqu'il sert de lien dans le squelette notre ADN, qu'il est présent dans les engrais qui aident à cultiver les aliments qui nous nourrissent, ou dans de nouveaux ligands et matériaux qui catalysent les réactions dans une variété d'industries. Cependant, malgré son importance, la conversion industrielle de la roche phosphatée (RP) vers des produits chimiques à valeur ajoutée souffre de nombreux inconvénients, notamment du fait du gaspillage qu'elle induit, tant en termes de matière qu'en énergie, de sa dépendance à des intermédiaires corrosifs et toxiques et de la nature non renouvelable de la roche phosphatée ellemême. La mécanochimie a déjà prouvé son efficacité en chimie organique, inorganique et des matériaux. La capacité d'effectuer la chimie en l'absence de solvant, à température ambiante et avec des temps de réaction plus courts, a fait des techniques mécanochimiques une pierre angulaire de la recherche en chimie verte. De plus, des travaux de mise à l'échelle montrent également une viabilité directe en utilisant le broyage planétaire, le vieillissement accéléré et l'extrusion à double vis (EDV).

Cette Thèse décrit l'application de la mécanochimie, c'est-à-dire la réactivité chimique induite par des forces mécaniques telles que l'impact ou le cisaillement, vers la synthèse plus simple et plus efficace de nanomatériaux contenant du phosphore. Le premier projet de recherche a mis en l'œuvre l'utilisation du pentoxyde de phosphore (P4O<sub>10</sub>) comme agent de phosphorylation à l'état solide pour la fonctionnalisation des nanocristaux de cellulose et des polymères synthétiques comme retardateurs de flamme nouveaux et durables. Les projets ultérieurs se sont concentrés sur l'utilisation du phosphure de sodium (Na<sub>3</sub>P) pour le développement de catalyseurs

hétérogènes de séparation de l'eau. Initialement, nous avons développé une synthèse ascendante de nanoparticules de phosphure de nickel ultrapetites comme cocatalyseurs pour la réaction de dégagement d'hydrogène (RDH). Par la suite, Na<sub>3</sub>P a été utilisé pour la synthèse ascendante de nitrures de carbone liés au phosphore en tant que photocatalyseurs accordables et sans métal pour RDH. Parallèlement à la nouvelle réactivité présentée tout au long de cette Thèse, nous incluons en outre des métriques de durabilité pour tous les projets, présentant l'amélioration quantitative de la durabilité des techniques mécanochimiques par rapport aux techniques traditionnelles basées sur des solutions.

### Acknowledgements

This journey has been made even more exciting and fruitful thanks to the wonderful people I've been able to work alongside and get to know. The often-understated side effect of being cosupervised is the additional friendships that develop. First, I am forever grateful to my supervisors, Audrey and Tomislav. Your combined mentorship, patience and support has completely changed my life. You have both given me a complete love of science, especially chemistry as well as the importance of community, and lifelong friendships. From the Moores lab, many thanks to all my lab mates over the years, past and present. Madhu, Alain, Michael Malca, Luis, Alex, Julio, Aude, Tony, Thomas, Michael Ferguson, Austin, Galen, Sarah, Tracy and Jasmine for being both my motivators and friends. Special thanks especially to Madhu, Alain, Michael Malca, and Luis for being my introduction to the community in the Moores Lab and each helping to foster and improve both my love and pursuit of science. A huge thank you also to the undergraduate students I've had both the opportunity and joy of working with and mentoring: Lucius, Georgia, and Monika. You have all done incredibly well, taught me much and have made me both a better chemist, leader, and teacher as a result.

I can't forget my extended scientific family from down the hall, the Friščić lab, helping to forge my love of crystalline materials as well as the fuel and motivation to follow my (many) wild ideas over the years. Many thanks to Patrick, Igor, Davin, Ghada, Dayaker and Cristina for being some of the first people I met in those early days up on the fourth floor of Otto Maass (I am sure to have missed people in those early days, apologies). Additionally, many thanks to Jean-Louis Do, my brother Hatem, Mihails (or as I knew him, "Misha"), Sandra, Filip, Mario, Tristan, Joe, Atanassios, Athena, Ivana, Dan, Cameron, Lori, Thomas, Luzia, Dylan, Jogi, Yong, Galen, Farshid, Linda, Yonger and Toni. Many of you, in both labs, have experienced a large piece of my joy, pain and frustration over the years and have always been a welcome support, listening ear or company for a coffee break. You are all my second family.

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To my friends and housemates for much of the journey, Dave and Sam, thank you for giving me a true home away from home. The many nights of chatting after a long day, board games, and socials helped keep me sane and show that there was always something to be excited about, outside of the lab.

To my mom and dad, thank you for the ever-present love and support, despite the physical distance. Thank you for teaching me the value of insane work ethic, being a person of integrity and always loving people, regardless of my goal in life has certainly played a major role in why I am here today. Thank you for always being there to pick up the phone when I needed it, given me those escape trips away to the cottage or Kitchener when I needed them, and the surprise care packages I would never expect. I love you both immensely.

For those who know me personally, living with Cerebral Palsy has never been an easy thing, and has certainly placed challenges in my path, even during my PhD. Yet, despite the uncertainty, I knew I wanted to be a scientist even before I could stand up straight or walk (in my case...3 steps at 5 years old). I hope this Thesis proves that regardless of challenges in life, with

the right support group, (like the one shown above) and the right mentors and attitude, those seemingly unreachable goals will become a possibility for future generations.

I think 5-year-old Blaine would be proud of me for this one...

#### **Contribution to Original Knowledge**

The results contained in this Thesis aimed to expand upon the use of mechanochemical methods towards phosphorus chemistries. The development of mechanochemical methods in inorganic chemistry have seen a resurgence in the last two decades and as such, this Thesis aimed to investigate and broaden solid-state phosphorus chemistry when applied to polymer and biomass functionalization, metal phosphide nanomaterials and novel organophosphorus compounds, either synthetically challenging or completely inaccessible *via* traditional solution-based methods. These advancements have been accomplished thanks to the application and use of solid, metastable phosphorus reagents, such as phosphorus pentoxide, sodium phosphide and sodium phosphaethynolate. Phosphorus pentoxide was applied towards the post-synthetic modification of polymers and biomass, typically a challenge due to their limited solubilities in a variety of solvents, which in turn were investigated as novel flame-retardant materials. The application of mechanochemistry allowed for comparable or improved substitution values with minimal loss of overall molecular weight. In the field of nanocatalyst design, sodium phosphide was successfully employed in the synthesis of photocatalysts for water splitting, both metal phosphide nanoparticles and phosphorus-bridged carbon nitride materials. In the case of metal phosphide nanoparticle synthesis, the mechanochemical methods consistently produced particles with diameters only a few nanometers across, a size which is a considerable challenge to achieve via solution-based techniques. Phosphorus-bridged carbon nitrides present their own challenges, as techniques typically require high temperatures and pressures to be successful. The pairing of metastable sodium phosphide with mechanochemical techniques allowed for the controlled synthesis of Pdoped carbon nitrides after only 90 minutes at room temperature.

#### **Contribution of the Authors**

All sections of this Thesis were written and edited by Blaine G. Fiss, with additional editing done by both Audrey Moores and Tomislav Friščić.

# Chapters 1 and 2: Introduction and inorganic metathesis and reduction reactivity in mechanochemistry

This chapter was written entirely by B. G. Fiss and edited by A. Moores and T. Friščić. Excerpts are taken from a broader scoped review published as Fiss, B. G.; Richard, A. J.; Douglas, G.; Kojic, M.; Friščić, T.; Moores, A., "Mechanochemical methods for the transfer of electrons and exchange of ions: Inorganic reactivity from organometallics to nanoparticles" *Chem. Soc. Rev.*, **2021**, *50*, 8279-8318. Copyright 2021 Royal Society of Chemistry.

# Chapter 3: Mechanochemical post-synthetic phosphorylation of cellulose nanocrystals and synthetic polymers

Synthetic work, data collection, analysis and the writing of this chapter was conducted by B. G. Fiss. L. Hatherly assisted in conducting experiments and collecting and analysing data. R. S. Stein assisted in gathering <sup>31</sup>P MAS NMR data. A. Moores and T. Friščić edited this work. This chapter is reprinted with permission from Fiss, B. G.; Hatherly, L.; Stein, R. S.; Friščić, T.; Moores, A., Mechanochemical Phosphorylation of Polymers and Synthesis of Flame-Retardant Cellulose Nanocrystals, *ACS Sustainable Chem. Eng.*, **2019**, 7, 8, 787951-7959. Copyright 2019 American Chemical Society.

Chapters 4 and 5: Application of sodium phosphide towards more sustainable metal phosphide and carbon phosphanitride nanomaterials for photocatalytic water splitting

Synthetic work, data collection, analysis and the writing of this Chapter was conducted by B. G. Fiss. G. Douglas assisted in conducting experiments and collecting and analysing data. Dr. Nhu Nang Vu assisted in gathering photocatalytic data and in the synthesis of the graphitic carbon nitride support for the nickel phosphide nanoparticles. Jorge Beccera gathered and analysed hydrogen evolution, photocatalytic and photoluminescence data for the phosphanitride materials. The Chapter was edited additionally by A. Moores and T. Friščić. Chapter 4 is reprinted with permission from Fiss, B. G.; Vu, N.-N.; Douglas, G.; Do, T.-O.; Friščić, T.; Moores, A., Solvent-free mechanochemical synthesis of ultrasmall nickel phosphide nanoparticles and their application as a catalyst for the hydrogen evolution reaction (HER), *ACS Sustainable Chem. Eng.*, **2020**, 8, 12014-12024. Copyright 2020 American Chemical Society. Excerpts from Chapter 5 are taken from Fiss, B. G.; Douglas, G.; Ferguson, M.; Becerra Sanchez, J.; Valdez, A.; Do, T.-O.; Friščić, T.; Moores, A., Mechanochemical synthesis of structurally well-defined graphitic phosphorus-linked carbon nitride (g-PCN) with water splitting activity, *ChemRxiv*, **2022**, DOI: 10.26434/chemrxiv-2022-15cwv-v2 (Online June 2, 2022).

### List of Abbreviations

ADHP: Ammonium dihydrogen phosphate AHA: Sodium 6-aminohexanoate ATR: Attenuated total reflectance BASF: Badische Anilin und Soda Fabrik

CASTEP: Cambridge Serial Total Energy Package
CB: Conduction band
CN: Carbon nitride
CNC: Cellulose nanocrystals
COF: Covalent-organic frameworks
CrI: Crystallinity index
CT: Computed tomography
DABCO: 1,4-diazabicyclo[2.2.2]octane
DFT: Density functional theory
DME: Dimethoxyethane
DMF: <i>N</i> , <i>N</i> -dimethylformamide
DMSO: Dimethylsulfoxide
D <sub>s</sub> : Degree of substitution
DSC: Differential scanning calorimetry
EBPR: Enhanced biological phosphorus recovery
EDX: Energy-dispersive x-ray
EELS: Electron energy loss spectroscopy
Eg: Band gap energy
EIS: Electrochemical impedance spectroscopy
ESM: Eggshell membrane
FLP: Frustrated Lewis pair
FTIR: Fourier Transform infrared
FRM: Flame-retardant materials

FTO: Fluoride doped tin oxide

GC: Gas chromatograph

g-C<sub>3</sub>N<sub>4</sub>: Graphitic carbon nitride

GIAO: Gauge independent atomic orbital

GIPAW: Gauge-inducing projector augmented waves

g-PCN: Phosphorus-bridged carbon nitride

HAADF: High-angle annular dark-field

HER: Hydrogen evolution reaction

HEMM: High-energy mechanical milling

HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol

HMPA: Hexamethylphosphoramide

HTC: Hydrothermal carbonization

HTHP: High temperature, high pressure

ILAG: Ion- and liquid-assisted grinding

IL-AG: Ionic liquid assisted grinding

IUPAC: International Union of Pure and Applied Chemistry

JCPDS: Joint Committee on Powder Diffraction Standards

LAH: Lithium aluminum hydride

MAS: Magic angle spinning

mPEG: Methyl ester of poly(ethylene) glycol

mPEG-NH<sub>2</sub>: Poly(ethylene glycol)-methyl-ether-amine

MOF: Metal-organic framework

MstCl: Mesityl chloride

NMR: Nuclear magnetic resonance NP: Nanoparticle MI: Mass intensity MSR: Mechanically-induced self-sustaining reaction MstCl: Methanesulfonyl chloride **OA:** Oleylamine **OER:** Oxygen evolution reaction P<sub>4</sub>: White phosphorus PAO: Polyphosphate accumulating organism PBE: Perdew-Burke-Ernzerhof PC: Photocatalytic P-CNC: Phosphorylated cellulose nanocrystals PEG: Poly(ethylene glycol) PL: Photoluminesence POLAG: Polymer assisted grinding PR: Phosphate Rock PULCON: Pulse length-based concentration determination PVA: Poly(vinyl alcohol) PVC: Poly(vinyl chloride) PXRD : Powder x-ray diffraction PyAOP: (7-azabenzotriazol-1-yloxy)tripyrrolidinophosphonium hexafluorophosphate **RIR:** Relative intensity ratio ssNMR: solid-state nuclear magnetic resonance

STEM: Scanning transmission electron microscopy
TBA: Tetrabutyl ammonium
TCD: Thermal conductivity detector
TEA: Tetraethylamine
TEM: Transmission electron microscopy
TEOA: Triethanol amine
TGA: Thermogravimetric analysis
TGCN: Triazine-based graphitic carbon nitride
THF: Tetrahydrofuran
TMEDA: Tetramethylethylenediamine
TMP: Transition metal phosphide
TOP: Trioctylphosphine
TOPO: Trioctylphosphine oxide
TPP: Triphenylphosphine
TPPO: Triphenylphosphine oxide
TriMP: Trimetaphosphate
TRPL: Time-resolved photoluminesence
UV-DRS: Ultraviolet-visible diffuse reflectance spectroscopy
UV-Vis: Ultraviolet-visible
VB: Valence band
XRD: X-ray diffraction
XPS: X-ray photoelectron spectroscopy

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Figure 1.3. Proposed mechanism for mechanochemical Kabachnik-Fields reaction. Reprinted with permission from C. Fiore, I. Sovic, S. Lukin, I. Halasz, K. Martina, F. Delogu, *et al.*, *ACS Sustainable Chem. Eng.* 2020, 8, 51, 18889–18902. Copyright 2020, American Chemical Society.

**Figure 2.1.** (a) Heat flow for the Al+B blend -0 to 6 h milling as measured in DTA with a constant heating rate of 10 K min<sup>-1</sup> and (b) the magnified view for 2 to 6 h milling where transformation temperatures are indicated.

**Figure 2.2.** (Left) Mg/V<sub>2</sub>O<sub>5</sub>/C system: PXRD patterns of the (a) initial materials, (b) combusted products for the initial stoichiometric mixture, (c) combusted products for the system with 10 wt. % extra carbon, (d) combusted products for the system with 15 wt. % extra carbon, and (e) product of (d) after chemical leaching. (Center) Mg/Nb<sub>2</sub>O<sub>5</sub>/C system: PXRD patterns of the (a) initial materials, (b) combusted products for the initial stoichiometric mixture, (c) product of (b) after chemical leaching. (Right) Mg/Ta<sub>2</sub>O<sub>5</sub>/C system: PXRD patterns of the (a) initial materials, (b) combusted products for the initial stoichiometric mixture, (c) product of (b) after chemical leaching. (Bight) Mg/Ta<sub>2</sub>O<sub>5</sub>/C system: PXRD patterns of the (a) initial materials, (b) combusted products for the initial stoichiometric mixture, (c) product of (b) after chemical leaching.

**Figure 2.3.** PXRD pattern of stoichiometric (a) blended Nb<sub>2</sub>O<sub>5</sub>(o)-SiO<sub>2</sub>-Mg powders and (b) of those mechanically milled for 3 h after the DSC analyses. DSC curves of stoichiometric (c) blended Nb<sub>2</sub>O<sub>5</sub>(o)-SiO<sub>2</sub>-Mg powders and (d) of those mechanically milled for 3 hours.

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Scheme 3.2. Overview of previous phosphorylation techniques, in comparison with this work.

Chart 3.1. Additives tested for their assistance in the phosphorylation of cellulose nanocrystals.

**Figure 3.1.** <sup>31</sup>P MAS NMR spectrum of mechanochemically phosphorylated CNC with the assistance of a) urea compared to b) phosphorus pentoxide. Spinning sidebands are denoted with an asterisk.

**Figure 3.2.** Visual appearance of 1 wt. % suspensions in DI water of: a) untreated CNC material; b) CNC phosphorylated in solution using urea and phosphoric acid and c) CNC phosphorylated mechanochemically, by milling with urea and phosphorus pentoxide. The change is colour is due to partial depolymerization of the CNC substrate.

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**Scheme 4.1.** Select examples of nickel phosphide nanoparticle synthesis, both in solution, as well as mechanochemically.

**Figure 4.1.** TEM images (a) and b)) and histogram of particle size distribution (c) of nickel phosphide nanoparticles made using 5 equivalents of heptadecylamine ligand, using a 3:2 ratio of NiCl<sub>2</sub> and Na<sub>3</sub>P (Ni<sub>x</sub>P<sub>y</sub>-5-C17).

**Figure 4.2.** XPS focused scans of a) nickel 2p, b) phosphorus 2p, c) oxygen 1s and d) carbon 1s orbitals of freshly made of nickel phosphide nanoparticles made using 3 equivalents of nickel chloride, 2 equivalents of sodium phosphide and 5 equivalents of heptadecylamine ligand ( $Ni_xP_y$ -5-C17).

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**Figure 4.5.** Schematic representation of the electron transfer behaviour between the  $g-C_3N_4$  support and the Ni<sub>2</sub>P catalyst. Effect of electron transfer a) with and b) without ligand exchange, preventing formation of hindering carbon layer.

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**Scheme 5.1.** Key examples of phosphanitride and phosphorus-containing graphitic carbon nitride presented by a) Antonietti b) Epshteyn c) Strobel d) Wang and e) the presented work.

**Figure 5.1** PXRD patterns of graphite, reference code YOPTUU (lime), phosphorus-containing g-C<sub>3</sub>N<sub>4</sub> (green), g-PCN (teal), g-PCN200 (blue) and g-PCN300 (purple).

**Figure 5.2.** Comparison of XPS data for: a) C 1s; b) N 1s; and c) P 2p scans of g-PCN, and d) C 1s; e) N 1s; and f) P 2p scans of g-PCN300.

**Figure 5.3.** STEM-HAADF images (left) and EELS maps (right) for the characteristic elements presented on graphitic carbon networks. a)  $g-C_3N_4$  network without any thermal treatment or phosphorus bridges is compared with; b) g-PCN (no annealing); c) g-PCN200 (annealing at 200 °C); and d) g-PCN300 (annealing at 300 °C) Dotted white circles denote localized regions of high phosphorus density.

**Figure 5.4.** a) UV-Vis DRS b) photoluminescence c) lifetime d) photocurrent and e) Nyquist plots of g-C<sub>3</sub>N<sub>4</sub> (green), g-PCN (teal), g-PCN200 (blue) and g-PCN300 (purple).

**Figure 5.5.** a) CASTEP-optimized structure; b) <sup>31</sup>P MAS NMR at 13 kHz of g-PCN300. Red lines denote shifts calculated using CASTEP-optimized structure. The asterisks denote spinning sidebands; c) From the bottom up: Simulated PXRD patterns of the g-C<sub>3</sub>N<sub>4</sub> structure from Cooper, Bojdys and coworkers.; g-PCN<sub>opt</sub>; g-PCN<sub>shift</sub> and g-PCN300. Asterisk indicates unidentified reflection.

**Figure 5.6.** a) Catalytic activity of varied photocatlyst, b) varied mass loading of g-PCN, c) reaction time and d) loading of Pt cocatlyst.

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**Figure 8.2.** <sup>31</sup>P MAS NMR of solution phosphorylated cellulose nanocrystals with urea. Asterisks denote spinning sidebands.

**Figure 8.3.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated cellulose nanocrystals without the assistance of urea. Asterisks denote spinning sidebands.

**Figure 8.4.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated cellulose nanocrystals with the assistance of urea. Asterisks denote spinning sidebands.

**Figure 8.5.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated poly(vinyl alcohol) (P-PVA). Asterisks denote spinning sidebands.

**Figure 8.6.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated poly(vinyl chloride) (P-PVC). Asterisks denote spinning sidebands.

**Figure 8.7.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated poly(ethylene glycol) (P-PEG). Asterisks denote spinning sidebands.

**Figure 8.8.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated poly(ethylene glycol) methyl ester (P-mPEG). Asterisks denote spinning sidebands.

**Figure 8.9.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated Kraft lignin. Asterisks denote spinning sidebands.

Figure 8.10. Survey scan of heterogeneously phosphorylated CNC from solution.

Figure 8.11. Phosphorus focused scan of heterogeneously phosphorylated CNC from solution.

Figure 8.12. Carbon focused scan of heterogeneously phosphorylated CNC from solution.

Figure 8.13. Survey scan of homogeneously phosphorylated CNC from solution.

Figure 8.14. Phosphorus focused scan of homogeneously phosphorylated CNC from solution.

Figure 8.15. Carbon focused scan of homogeneously phosphorylated CNC from solution.

Figure 8.16. Survey scan of CNC mechanochemically phosphorylated in a MM 400 mill.

**Figure 8.17.** Phosphorus focused scan of CNC mechanochemically phosphorylated in a MM 400 mill.

Figure 8.18. Carbon focused scan of CNC mechanochemically phosphorylated in a MM 400 mill.

Figure 8.19. Oxygen focused scan of CNC mechanochemically phosphorylated in a MM 400 mill.

Figure 8.20. Nitrogen focused scan of CNC mechanochemically phosphorylated in a MM 400 mill.

**Figure 8.21.** FTIR of CNC phosphorylated in solution with the assistance of molten urea (red) compared to untreated CNC (blue).

**Figure 8.22.** FTIR of CNC phosphorylated in solution without urea (red) compared to untreated CNC (blue).

**Figure 8.23.** FTIR of CNC phosphorylated in Retsch MM400 mill with urea (red) compared to untreated CNC (blue).

Figure 8.24. Comparative PXRD patterns of untreated and phosphorylated cellulose nanocrystals.

Figure 8.25. TEM image of untreated CNC stained with uranyl acetate.

Figure 8.26. TEM image of CNC following phosphorylation in solution, assisted by urea.

Figure 8.27. TEM image of CNC following phosphorylation by ball-milling, assisted by urea.

Figure 8.28. TGA of CNC phosphorylated only with phosphorus pentoxide (red) compared to untreated CNC (blue).

Figure 8.29. TGA of CNC milled only with urea (red) compared to untreated CNC (blue).

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**Figure 8.31.** TGA of CNC phosphorylated with the assistance of urea in MM 400 mill (red) compared to untreated CNC (blue).

**Figure 9.1.** Preparation of CN-Ni<sub>x</sub>P<sub>y</sub> sample.

Figure 9.2. Schematic preparation of protonated g-C<sub>3</sub>N<sub>4</sub>.

Figure 9.3. Schematic illustration of the cation exchange of Ni<sub>x</sub>P<sub>y</sub> nanoparticles.

Figure 9.4. Schematic preparation of CNH-Ex-300 and CNH-Im-300 samples.

**Figure 9.5.** Schematic illustration of the photocatalytic test. Reactions were conducted using 50 mg of photocatalyst, in 100 mL of  $H_2O$  under simulated sunlight conditions of 100 mW cm<sup>-2</sup> for 3 hours.

**Figure 9.6.** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 2 equivalents of pentadecylamine ligand ( $Ni_xP_y$ -2-C15).

**Figure 9.7.** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 5 equivalents of pentadecylamine ligand ( $Ni_xP_y$ -5-C15).

**Figure 9.8.** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 2 equivalents of hexadecylamine ligand ( $Ni_xP_y$ -2-C16).

**Figure 9.9.** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 5 equivalents of hexadecylamine ligand ( $Ni_xP_y$ -5-C16).

**Figure 9.10.** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 2 equivalents of heptadecylamine ligand ( $Ni_xP_y$ -2-Cl7).

**Figure 9.11.** TEM images of NixPy nanoparticles made mechanochemically using 3 molar equivalents of NiCl2, 2 molar equivalents of Na3P and 10 equivalents of oleylamine ligand (NixPy-10-OAm).

**Figure 9.12** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 2 equivalents of TOP ligand ( $Ni_xP_y$ -2-TOP).

**Figure 9.13** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 5 equivalents of TOP ligand ( $Ni_xP_y$ -5-TOP).

**Figure 9.14** EDX Analysis of  $Ni_3P_2$  nanoparticles prepared with 10 equivalents of oleylamine ligand ( $Ni_xP_y$ -10-OAm).

**Figure 9.15** XPS spectra for the a) phosphorus 2p orbital focused scan and b) Ni 2p orbital scans for freshly made of nickel phosphide nanoparticles made using 5 equivalents of tris-*n*-octylphosphine ligand ( $Ni_xP_y$ -5-TOP).

**Figure 9.16** XPS Survey scan of as-made  $Ni_xP_y$  nanoparticles made with 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 5 molar equivalents of heptadecylamine (Ni<sub>x</sub>P<sub>y</sub>-5-C17).

**Figure 9.17** XPS Survey scan of as-made  $Ni_xP_y$  nanoparticles made with 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 5 molar equivalents of heptadecylamine on a 2.5 gram scale in a planetary mill ( $Ni_xP_y$ -5-C17).

**Figure 9.18** XPS spectra for the a) phosphorus 2p orbital focused scan and b) Ni 2p orbital scans for as-made Ni<sub>x</sub>P<sub>y</sub> nanoparticles made with 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 5 molar equivalents of heptadecylamine on a 2.5 gram scale in a planetary mill (Ni<sub>x</sub>P<sub>y</sub>-5-C17).

**Figure 9.19.** PXRD diffractograms of  $Ni_3P_2$  nanoparticles prepared with 5 equivalents of heptadecylamine ligand using mechanochemical methods, compared to simulated patterns for various phosphide phases, as well as reactants and by-products.

**Figure 9.20.** PXRD diffractograms of Ni<sub>2</sub>P, Ni<sub>5</sub>P<sub>4</sub> and NiP<sub>3</sub> nanoparticles as well as the effect of washing procedure on ligand removal.

**Figure 9.21.** FTIR of freshly made  $Ni_xP_y$  nanocatalyst made with 3 equivalents of NiCl<sub>2</sub>, 2 equivalents of Na<sub>3</sub>P and 5 equivalents of heptadecylamine ligand (Ni<sub>x</sub>P<sub>y</sub>-5-C17).

**Figure 9.22.** FTIR of freshly made  $Ni_xP_y$  nanocatalyst made with 3 equivalents of NiCl<sub>2</sub>, 2 equivalents of Na<sub>3</sub>P following ligand exchange with tetraethylammonium ligand and mounting onto g-C<sub>3</sub>N<sub>4</sub> support (CNH-Im-300).

**Figure 9.23.** TGA of freshly made  $Ni_xP_y$  nanocatalyst made with 3 equivalents of NiCl<sub>2</sub>, 2 equivalents of Na<sub>3</sub>P and 5 equivalents of heptadecylamine ligand (Ni<sub>x</sub>P<sub>y</sub>-5-C17).

**Figure 9.24.** TGA of  $Ni_xP_y$  nanocatalyst made with 3 equivalents of  $NiCl_2$ , 2 equivalents of  $Na_3P$  following ligand exchange with tetraethylammonium ligand and mounting onto g-C<sub>3</sub>N<sub>4</sub> support (CNH-Im-300).

**Figure 10.1.** FTIR-ATR of furnace synthesized P@CN reference material (green), g-PCN (teal) g-PCN200 (blue) and g-PCN300 (purple).

Figure 10.2. TGA of g-PCN under N<sub>2</sub> from 30 to 800 °C.

Figure 10.3. XPS scan of a) C 1s b) N 1s and c) P 2p for furnace made P@CN.

Figure 10.4. XPS scan of a) C 1s b) N 1s and c) P 2p for g-PCN200.

Figure 10.5. Mott-Schottky plots of a) g-C<sub>3</sub>N<sub>4</sub> b) g-PCN c) g-PCN200 and d) g-PCN300.

Chart 10.1. Structure scope of GIAO analysis using Gaussian 16.

Figure 10.6. <sup>31</sup>P MAS NMR of a) g-PCN and b) g-PCN200. Asterisks denote spinning sidebands.

### **1. Introduction**

#### 1.1 Brief history of phosphorus chemistry

The history of phosphorus chemistry is intimately linked to alchemy and the pursuit towards the transmutation of other elements into gold. Henning Brandt made the connection that if urine was golden in colour, that gold could be isolated directly from urine. In 1669 Brandt set out to isolate gold from urine by first concentrating it down by distillation, followed by heating the residue in a furnace in the presence of charcoal (coke).<sup>1</sup> While Brandt was unsuccessful in obtaining gold, the solid he was able to isolate glowed on its own, without any external light source or photoexcitation. This led Brandt to refer to it as the "light-bearer", more commonly known as the white allotrope of the element phosphorus (P<sub>4</sub>). From being a key component to the backbone of both DNA and RNA, in fertilizers to feed humanity, as well as in ligands, flame-retardants, or catalysts in both fundamental and applied chemistries, phosphorus is critical to human existence and wellbeing. Since Brandt's discovery of white phosphorus upon its extraction from urine through boiling with coke, the process of isolating phosphorus from urine was later improved upon by Boyle through the addition of silica (sand) and cooking the concentrated residue in a furnace for twelve hours,<sup>2</sup> which most closely mimics the modern conversion of phosphate ores into P<sub>4</sub>. While Brandt is often credited with the initial discovery of white phosphorus, Boyle is largely regarded as being the one to first publish his process to generate white phosphorus. In both cases, Brandt and Boyle had unknowingly concentrated sodium metaphosphate from human urine and either reduced it directly to white phosphorus in the presence of carbon (in the case of Brandt) or by first converting it into phosphorus pentoxide (P<sub>4</sub>O<sub>10</sub>) through a ring-closing reaction in the presence of silica, followed by subsequent reduction to white phosphorus at high temperature (in the case of Boyle). Since that first publication in 1680, other scientists from France and Germany adopted Boyle's method, and began conducting experiments on the physical properties of this newly discovered element, such as the loss of the luminescent properties of white phosphorus when the element was exposed to air, by Lemery.<sup>3</sup> Since that time, the application of phosphorus in modern society has become paramount to the existence of humanity. The largest use of phosphate feedstocks (82 % of all mined phosphate) is for the production of phosphate fertilizers<sup>4-6</sup> to feed the ever growing human population.<sup>7</sup> Additional uses of phosphorus range from sustainable flame-retardant materials<sup>8</sup> to modern pharmaceutical design.<sup>9,10</sup>

#### 1.2 Historical and modern techniques used for mechanochemistry

#### **1.2.1 Brief History of Mechanochemical Techniques**

Ancient civilizations have depended on the use of solid-state techniques, which would today be termed "mechanochemical", for the development and processing of medicines, dyes, and minerals. One of the earliest known examples, dating from 315 BCE, is highlighted in a book titled "On Stones" written by Theophrastus, a disciple of Aristotle.<sup>11</sup> The experiment describes the conversion of the mineral cinnabarite, a form of mercury sulfide into elemental mercury through grinding using a copper mortar and pestle.

Particularly worth highlighting is the work of Michael Faraday in 1820, where he described the mechanochemical reduction of silver chloride in the presence of reducing metals such as tin, iron, and copper.<sup>12</sup> These initial reports lay the subsequent groundwork for a series of experiments that are considered to be the turning point towards modern mechanochemistry. In 1892, M. Carey Lea investigated the mechanochemical reduction in silver salts,<sup>13</sup> motivated partially by his passion for photography. He noted that the photographic plates used in traditional cameras at that time could be selectively developed by applying pressure with a glass rod prior to chemical treatment.<sup>14</sup>

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Carey Lea's work was one of the first early demonstrations of how varying the applied pressure during a mechanochemical reaction could have varying effects on the result. At the same time as Carey Lea was conducting his research on the reduction of silver halides, the Belgian chemist Walthère Spring was conducting his own experiments in Liége.<sup>15</sup> Driven by his interest in mineral formation in the Earth's crust, Spring had become interested in reactivity induced by pressure and shear forces, and developed a 6000-atmosphere press for his initial experiments. These experiments, reported in 1880, focused on the combination of copper and sulfur elemental powders to make the corresponding sulfide, or the reduction of mercuric chloride with copper,<sup>16</sup> mimicking the initial work of Theophrastus. These initial reports, along with his more well-known metathesis reaction of barium sulfate and sodium carbonates, and the report of several metal arsenides made under sequential pulverization and pellet formation in 1883, laid the eventual groundwork for the popularization of mechanochemical studies.

Since those early applications, several key discoveries around solid-state reactivity, later to become known as mechanochemistry, have occurred. For example, the term "mechanochemistry" that describes the specific chemical activation of materials through mechanical force was first coined by Ostwald in 1919, when he classified the various types of chemistry such as thermochemistry, photochemistry, electrochemistry, mechanochemistry and more.<sup>17</sup>

#### **1.2.2 Modern mechanochemical equipment and techniques**

While the mortar and pestle represent probably the most accessible of the tools available to budding mechanochemists, the degree of control over the applied forces and grinding motion is difficult to reproduce. Thus, modern mechanochemistry (and the bulk of the work presented in this Thesis) is predominantly done through the help of vibrational mills (Figure 1.1b), a technique

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allowing the mechanochemists to vary the size, or material, of both the milling jar and milling media (Figure 1.1c) while optimizing chemical reactions. Alternatively, mechanochemical reactions can be done on a kilogram scale using a planetary mill (Figure 1.1d). Planetary mills operate wherein a base plate is rotated in one direction while each individual milling jar holder rotates in the opposite direction (Figure 1.1e). In an effort to further upscale mechanochemical processes, with the potential for industrial integration, mechanochemists have also investigated the use of "continuous flow" technologies in order to mimic the current trend of flow chemistry in solution-based practices.<sup>18</sup> A variety of groups have begun using twin screw extrusion (TSE), a technology widely used in the polymer industry,<sup>19</sup> as a solid-state, continuous flow process.<sup>20-35</sup>



**Figure 1.1.** Equipment for mechanochemical reactions (a) mortar and pestle (b) vibrational mill and (c) small-scale milling jars and balls (d) planetary mill external and (e) internal (f) twin-screw extruder (TSE) allowing for continuous processing.

Alongside the improvements on mechanochemical equipment, various techniques have developed over the years to improve reactivity, selectivity and crystallinity of the products, something highly sought after, especially in the pharmaceutical industry for cocrystal development.<sup>36</sup> One such technique employs the use of additives and has proven to be highly effective for a variety of applications. Liquid-assisted grinding (LAG) refers to the use of a small, often sub- or near-stoichiometric amounts of a liquid, measured through  $\eta$  – the ratio of added

liquid volume (in microlitres) to the total weight of reactants (in milligrams). The use of LAG, compared to neat grinding, has been found to often give differing reactivity,<sup>37,38</sup> or assist in the formation of a crystalline product. For chemists to quantitatively compare one LAG reaction to the next, an effective range of  $\eta$ -values has been developed through empirical studies on cocrystallization reactions. Specifically, reactions conducted with  $\eta$ -values in the range of approximately 0-2  $\mu$ L/mg are being classified as LAG, those in the  $\eta$ -range of ca. 2-12  $\mu$ L/mg classified as slurry systems, and those in which  $\eta$  is even larger typically represent homogeneous solution reactions (Figure 1.2). Other additives beyond liquids have also been employed to modify mechanochemical milling reactions, with differing effects depending on the system chosen. For example, ion- and liquid-assisted grinding (ILAG) pairs together a small amount of a liquid with an inert salt. Other additives, such as polymers (in case of POLAG),<sup>39</sup> and even ionic liquids (in case of IL-AG),<sup>40</sup> have demonstrated effectiveness, primarily in their use within the crystal engineering community.



**Figure 1.2.** Schematic showing the range of  $\eta$  values, from neat grinding at 0 mL mg<sup>-1</sup> to  $\eta > 12$  mL mg<sup>-1</sup> for solution chemistry.

In addition to mechanochemical methods, the use of a technique known as accelerated aging provides an additional low-energy, readily scalable route towards new materials. This technique typically involves either the mixing or mechanochemical activation of a reaction mixture, followed by leaving the resulting mixture to age for a period, either under mild conditions, upon exposure

to increased heat and/or solvent vapours. The accelerated aging technique has shown utility in obtaining materials and phases which are traditionally not seen by grinding alone, such as products or phases which are either kinetically favoured or are considered metastable.<sup>41</sup>

## **1.3** In situ analysis and mechanistic understanding of mechanochemical reactions

In contrast to solution approaches, where the reactants, intermediates and products are diluted by the presence of a large amount of solvent, in mechanochemical neat and liquid-assisted reactions the concentrations of substances participating in reactions are much higher. As previously highlighted, the use of liquid or solid additives in the form of liquid-assisted grinding or ion- and liquid-assisted grinding can improve mass or heat transfer, although the exact role of additives in LAG and ILAG is still largely unknown. A recent study by Hasa, Jones and coworkers, presented the variable role of liquid additives in the formation of molecular cocrystal solids, stating that unpredictable behaviour was also seen with some additives, leading to physical mixtures of the two components in certain cases.<sup>42</sup> As a result, the development of *in situ* analytical techniques has become paramount in being able to decipher mechanochemical reactivity. To date, the two most predominant analytical approaches for in situ mechanochemical analyses have been synchrotron X-ray diffraction, and Raman spectroscopy.<sup>43-50</sup> These techniques have also been used for the understanding of mechanochemical reaction mechanisms in an ex situ fashion, however this approach to analysis has the drawback of disturbing the mechanochemical process for each sampling. Short-lived intermediates, key to a fuller understanding of mechanochemical reaction mechanisms, may be missed or decay over the lifetime of an ex situ measurement.

# 1.4 Current standard practices for making phosphorus containing molecules and materials

In nature, phosphorus appears in its +5 oxidation state, as phosphate rock (PR), which consists of a variety of mineral species, including calcium hydroxyapatites, fluorapatites and carbonatoapatites,.<sup>4,51</sup> The purity is typically denoted by the concentration of  $P_4O_{10}$  present in the material after purification, which can range anywhere from 25 to 40 %.<sup>7</sup> Due to the poor solubility of PR minerals, further processing is required to obtain usable feedstocks for products such as phosphate-based fertilizers, flame-retardant materials, pharmaceuticals, value-added chemicals and more. There are two major processes to convert phosphate rock into usable intermediates, either in the form of elemental white phosphorus, through what is known as the thermal or Wöhler process (Scheme 1.1a), or phosphoric acid obtained through a wet acid treatment (Scheme 1.1b).

- a)  $4 \operatorname{Ca}_{5}(\operatorname{PO}_{4})_{3}F + 18 \operatorname{SiO}_{2} + 30 \operatorname{C} \longrightarrow 3 \operatorname{P}_{4} + 30 \operatorname{CO} + 18 \operatorname{CaSiO}_{3} + 2 \operatorname{CaF}_{2}$
- **b)**  $Ca_5(PO_4)_3F + 5H_2SO_4 + 5nH_2O \longrightarrow 3H_3PO_4 + 5CaSO_4nH_2O + HF (n = 0, 0.5, or 2)$

Scheme 1.1. Wöhler process (a) and wet acid process (b) used in the industrial preparation of phosphorus precursors.



**Figure 1.3.** Overview of phosphate rock processing through both the wet and thermal processes, towards value-added chemicals. Adapted from 1. Jupp, A. R.; Beijer, S.; Narain, G. C.; Schipper, W.; Slootweg, J. C., Phosphorus recovery and recycling - closing the loop. *Chem. Soc. Rev.* **2021**, *50* (1), 87-101. Copyright Royal Society of Chemistry 2021.

In the Wöhler process, which very closely resembles Brandt's and Boyle's initial isolation of the element, fluorapatite is reacted at high temperature with coke and silica in electric furnaces up to 1500 °C, producing white phosphorus vapours which can be condensed and collected alongside carbon monoxide, calcium silicates, and calcium fluoride byproducts. Globally, this process consumes 12-15 MWh per tonne of phosphorus produced.<sup>52</sup> The reductive heating liberates P<sub>2</sub> gas, which is then condensed under water to isolate white phosphorus (P<sub>4</sub>). The condensed white phosphorus can be subsequently reacted with chlorine gas, to obtain the commonly used +3 and +5 oxidation states of phosphorus chlorides (Figure 1.3). Interestingly, despite the prevalent use of the chlorination step at the industrial scale, many organophosphorus compounds rarely retain their P-Cl bonds, as the strong leaving group nature of the chloride anion means that chlorinated phosphorus reagents make excellent electrophiles for subsequent attack by nucleophilic reagents,
such as Grignard reagents, or other organo-metallated species. As such, the thermal route from  $P_4$  to chlorophosphines presents waste challenges. The waste produced by the thermal process is closely related to the high energy demand of the process as well as the fluctuation of the redox state of phosphorus as it is converted from PR to white phosphorus, and then chlorinated back to oxidized species.

In the wet process, which is more widely used at the industrial scale than the thermal process, phosphate rock is reacted with sulfuric acid at high temperature, to generate calcium sulfates and phosphoric acid, which is then be distilled away (Scheme 1.1b) and further processed, if needed, into value-added phosphorus precursors.<sup>53</sup> Roughly 92 % of phosphoric acid generated in this way is then turned over to produce fertilizers.<sup>54</sup> Apart from sulfuric acid, a smaller number of manufacturing plants have also treated PR with either nitric or hydrochloric acid to produce nitro phosphates or acidified phosphate rock, respectively. There are however, considerable amounts of waste associated with both these processes. For example, major challenges of the Wöhler process are high energy losses and production of large amounts of waste phosphogypsum, which equates to approximately five tonnes for every tonne of P<sub>4</sub>O<sub>10</sub> produced.<sup>7</sup> Such large amounts of waste byproducts have led a variety of research groups to begin investigating more sustainable and industrially relevant routes towards both P(III) and P(V)-based starting materials.

## 1.5 Applications and challenges toward sustainable phosphorus chemistry

In the late 1990s, Paul Anastas and John Warner developed the 12 Principles of Green Chemistry (Table 1.1).<sup>55</sup> Despite the understanding of the detrimental effects of chemical waste and processes on the environment, as well as on human and animal health, guidelines to aid in reducing the impact of chemistry on the environment had yet to be developed. Within the phosphorus industry specifically, research groups are investigating the direct activation of white phosphorus, often

using transition metals,<sup>56</sup> and main group elements,<sup>57</sup> to avoid the high temperature reduction of

PR. Additionally, the substitution of phosphites and phosphoric acid for phosphorus chlorides

removes the need for phosphorus oxidation by chlorine gas.<sup>58</sup>

 Table 1.1. 12 Principles of Green Chemistry.

Prevention	It is better to prevent waste than to treat or clean up waste after it has been created.					
Atom Economy	Synthetic methods should be designed to maximize incorporation of all materials used in the process into the final product.					
Less Hazardous Chemical Syntheses	Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.					
Designing Safer Chemicals	Chemical products should be designed to preserve efficacy of function whil reducing toxicity.					
Safer Solvents and Auxiliaries	The use of auxiliary substances (e.g., solvents, separation agents, etc.) show be made unnecessary wherever possible and, innocuous when used.					
Design for Energy Efficiency	economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.					
Use of Renewable Feedstocks	A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.					
Reduce Derivatives	temporary modification of physical/chemical processes) should be minimized or avoided, if possible, because such steps require additional reagents and can generate waste.					
Catalysis	Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.					
Design for Degradation	Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.					
Real-time analysis for Pollution Prevention	Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.					
Inherently Safer Chemistry for Accident Prevention	Substances and the form of a substance used in a chemical process should chosen to minimize the potential for chemical accidents, including releases explosions, and fires.					

#### 1.5.1 Novel low coordinate phosphorus reagents and the direct use of P4

Novel reactivity of nucleophilic phosphorus centres allows for the removal of the need for chlorine gas in phosphorus processing. For example, the direct reaction between sodium metal and red phosphorus, which can be considered the parallel reaction to more current research on the direct functionalization of white phosphorus, allows for direct reduction of an air-stable phosphorus allotrope to a more reactive P(-III) starting material. Early examples of alkali metal activation include the seminal work of Brandsma and Trofimov throughout the 1990s, on the activation of

red phosphorus with superbasic solutions of KOH in DMSO or HMPA, or the use of Na in ammonia (Scheme 1.2).<sup>59,60</sup>



Scheme 1.2. Activation of red phosphorus under superbasic conditions.

More recent studies have demonstrated the broad versatility of red phosphorus activation, including the formation of soluble polyphosphide species through nucleophilic activation.<sup>61</sup> Reaction with alkali metals, either in the presence of liquid ammonia or through a mixture of DME and 5 mol % naphthalene, can provide access to suspensions of MP<sub>x</sub>, with variation in *x* being dependent on the initial stoichiometries used in the reaction. Similarly, researchers have investigated the direct oxidation of white phosphorus (P<sub>4</sub>) to phosphines to avoid the use of chlorine gas. Towards this goal, excellent reviews have been published on the use of both early<sup>56</sup> and late<sup>62</sup> transition metals for the activation of P<sub>4</sub>. The use of main group centered electrophiles for the oxidation of P<sub>4</sub> at room temperature has also shown potential as a benign route to access monophosphines.<sup>63</sup> A selected example, is the reaction of P<sub>4</sub> with group 14 reactants, which has been explored by Inoue,<sup>64</sup> and Wolf,<sup>65</sup> and represents an elegant approach for room temperature activation of P<sub>4</sub> using small molecule tin reagents (Scheme 1.3).



Scheme 1.3. Selected examples of low temperature, ambient activation of  $P_4$  at a tin atom presented by the a) Inoue and b) Wolf groups.

Alkali metal phosphides, such as sodium or lithium phosphide, can be reacted directly with organohalide reagents, or further reacted with either a cyclic carbonate or CO gas to achieve a P(-I) derivative affording NaOCP, as demonstrated by the Lecker, Goicoechia, and Grützmacher groups (Scheme 1.4a).<sup>66,67</sup> Due to their structural similarity to isocyanates, phosphaethynolates and their derivatives have shown to be broadly applicable, allowing for direct, often wasteminimized, and low-temperature access to organophosphorus compounds (Scheme 1.4).

$$P + 3 \text{ Na} \xrightarrow{0.05 \text{ mol \%}}_{\text{DME, 12 h, Ar}} \text{ Na}_{3}P \xrightarrow{1) \text{ Ice bath, } tert-butanol}_{2) 1 h, RT} \xrightarrow{1) \text{ NaOCP}}_{3) \circ 0^{\circ}\text{C over 1 h}} \text{ NaOCP}$$

Scheme 1.4. Synthesis of sodium phosphaethynolate dioxane adduct using sodium phosphide  $(Na_3P)$  as an initial activation of red phosphorus.

Cummins and coworkers have also shown the applicability of an anthracene-backed phosphinidene transfer reagent, first employed by their group to isolate a kinetically-stabilized  $P_2$  analogue through photodimerization.<sup>68</sup> This reagent has been studied mechanistically to understand the nature and limit of dissociation,<sup>69,70</sup> and has also been applied towards the formation of  $P_2S$ ,<sup>71</sup> novel heterocycles,<sup>69</sup> and Frustrated Lewis Pair (FLP) stabilized NPO-a heavier structural analogue to NO<sub>2</sub>.<sup>72</sup>

#### 1.5.2 Direct use of phosphates, phosphonates, phosphinates and phosphine oxides

# 1.5.2.1 Activation of (poly)phosphates

Recent reviews by the groups of Jessen and Cummins<sup>73,74</sup> have demonstrated the application of cyclometaphosphates and polyphosphates for the direct functionalization of bioactive molecules, and as viable nucleophiles for the formation of a wide variety of P-C bonds. The unique propensity of polyphosphates for hydrolysis, combined with their versatility, as well as appearance in

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bacteria,<sup>75</sup> all highlight the potential of polyphosphates as components for the formation of new phosphorus-containing materials. As early as 1966, chemists had attempted the direct phosphorylation of alcohols using trimetaphosphate (TriMP) under alkaline conditions.<sup>76</sup> However, low yields left the field laying largely untouched until the seminal work by Mohamady and Taylor in 2016, who used a combination of methylsulfonyl chloride (MstCl) and 1,4-diazabicyclo[2.2.2]octane (DABCO) to activate TriMP into a more reactive species for triphosphorylation of nucleobases or other hydroxyl-bearing nucleophiles (Scheme 1.5a). However, the method is complicated by variability of MstCl to DABCO, and requires an initial excess of TriMP to achieve high yields.<sup>77</sup>

Cummins and coworkers expanded versatility of modified TriMP as a viable triphosphorylating agent using the synthetic procedure involving addition of a phosphonium salt as a leaving group (Scheme 1.5b), through addition of a common peptide coupling reagent, PyAOP ( $[(H_8C_4N)_3PON_4C_5H_3][PF_6]$ ). The resulting modified TriMP reagent showed broad reactivity towards carbon, nitrogen, and oxygen nucleophiles, as well as Wittig reactivity, allowing for a broader range of polyphosphorylation substrates, as the phosphonium leaving group could be released as a neutral phosphoramide byproduct.



Cummins and coworkers, 2019

**Scheme 1.5.** a) Application of TriMP by Taylor and coworkers in 2016 towards polyphosphorylations and b) expansion of TriMP versatility as an electrophile through addition of a PyAOP salt by Cummins and coworkers in 2019.

In 2018, the same group demonstrated the direct reduction of trimetaphosphate in excess trichlorosilane to afford the tetrabutyl ammonium (TBA) salt of bis(trichlorosilyl) phosphide,<sup>78</sup> a solid phosphane intermediate, in that way showing the potential of this method to directly upgrade PR into viable phosphorus reagents. This also allowed for access to phosphane from a PR analogue, while being an atom-economical reagent, avoiding the traditional dependence on the use of P<sub>4</sub> to access phosphane (Scheme 1.6).



Scheme 1.6. Synthesis of isolable trichlorosilylphosphide through the reduction of TriMP in excess trichlorosilane.

#### 1.5.2.2 Activation of phosphonates and phosphinates

One of the driving areas of research towards circular phosphorus chemistry is the direct application of P(V) feedstocks (Chart 1.1). This is due to the similarity of compounds such as

phosphates to natural PR feedstocks, as well as waste phosphorus currently under investigation for recycling strategies.



Chart 1.1. Examples of commonly investigated P(V) feedstocks.

Work conducted by the Montchamp lab has demonstrated the versatility of phosphanates and phosphinates in place of traditionally used P-Cl based reagents. Compared to the direct activation through P<sub>4</sub>, the use of the expanded class of P(V) molecules as starting materials has the benefit of improved atom economy, as the incorporation of each phosphorus atom from the tetrahedron of P<sub>4</sub> becomes increasingly difficult after the initial strain of the molecule is reduced. Hypophosphites  $[(OR)P(O)H_2]$  are industrially produced through the reaction of P<sub>4</sub> with concentrated NaOH, also producing phosphane gas (Scheme 1.7).<sup>79</sup> They already serve as viable reductants, due to their tendency to decompose in the presence of excess base to produce hydrogen gas, and are typically employed in the electroless plating process (Kaigen).

$$P_4 + 3 \text{ NaOH} + 3 H_2 O \longrightarrow 3 \text{ NaH}_2 PO_2 + PH_3$$

Scheme 1.7. Industrial synthesis of sodium hypophosphite and phosphane from P4.

However, due to the low oxidation state and reactivity of P-H bonds, hypophosphites have potential as chlorine-free reagents to access P-C bonds. Transition metal catalysed strategies (*e.g.* Hirao coupling) allow for a variety of coupling reactions.<sup>80</sup>



**Scheme 1.8.** Selected examples of transition metal catalysed phosphite couplings using (a, b) palladium and c) copper. The seminal work of Hirao and colleagues in 1980 presented the palladium-catalyzed phosphorylation of aryl halides (Scheme 1.8a). Phosphites have additionally been employed towards sustainable aryl phosphorylation reactions driven by either photochemical or electrochemical means.<sup>81</sup> Of note, are recent reports by Wang and coworkers in 2019, as well as by Xu and coworkers in 2021, who demonstrated catalyst- and base-free aryl phosphorylations using an electrochemical method (Scheme 1.9).<sup>81,82</sup>



Scheme 1.9. Selected examples of electrochemical aryl phosphorylation with phosphites.

#### 1.5.2.3 Phosphorus reduction, recycling, and the use of phosphine oxides

As previously mentioned in this Chapter, interest in developing a truly sustainable and circular phosphorus economy has inspired investigation of methods for recycling phosphate waste streams and consequent methods to reduce phosphates, phosphinates and phosphine oxides into more usable derivatives. These efforts have so far followed two directions, the first being the actual capture and concentration of phosphate waste streams into usable phosphate feedstocks, and the second being the development of sustainable methods towards the reduction of these feedstocks (including the industrial reduction of phosphine oxides back to phosphines) into usable starting materials. The use of triphenylphosphine (TPP) is ubiquitous with several reactions used at industrial scales (*e.g.* Appel, Wittig, Arbuzov, Mitsunobu reactions), with triphenylphosphine oxide (TPPO) being the predominant waste product, with no clear further industrial application. The current state-of-the-art process developed by BASF has been reported to employ two-steps, in which TPPO is first chlorinated to the dichlorotriphenylphosphine, followed by reduction using either Al, Mg or Fe metal at 130 °C. This process produces stoichiometric quantities of CO<sub>2</sub> in the first step, and leads to the precipitation of metal chloride salts in the second (Scheme 1.10a).<sup>83</sup>

Scheme 1.10. Overview of methodologies for the reduction of phosphine oxides and phosphates to their corresponding reduced species.

In 2018, Tyler and coworkers demonstrated an elegant, gram-scale method to reduce a variety of oxidized phosphorus species into their corresponding phosphines.<sup>84</sup> The authors noted that typically, LiAlH<sub>4</sub> was the reagent of choice when conducting a typical phosphine oxide reduction at laboratory or process scale. However, the formation of aluminum alkoxides as the dominant byproducts in the presences of lithium salts tended to cause the reaction mixture to gel. Such gelation of the reaction mixture led to purification challenges in most cases, as well as insufficient conversion due to limited mass transfer as the reaction progressed. Alternatively, they presented the use of *in situ* generated allane gas (AlH<sub>3</sub>) as a cleaner, more effective reductant for a wider variety of phosphine oxides (Scheme 1.10b), including tricyclohexyl phosphine oxide, which typically showed lower conversions when treated using traditional techniques.

Electrochemical methods have also been employed towards more atom-economical recovery of phosphines, especially in cases where chiral phosphines, or uniquely designed ligands are used. The report by Nocera and coworkers in 2018 demonstrated the direct, four electron

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reduction of TPPO to TPP through the assistive use of excess aryl borates.<sup>85</sup> While triparamethoxyborate showed the best Faradayic efficiencies, there was little to no selectivity between the desired TPP and the over-reduced four electron product PHPh<sub>2</sub> (Scheme 1.10c). Subsequently, Sevov and coworkers advanced further this methodology, improving on the yield and selectivity, reducing the equivalency of secondary base and Lewis acid, as well as demonstrating the effectiveness of the process in flow, recovering up to 55 g of phosphine in a single batch (Scheme 1.10d).<sup>86</sup> The use of a mixed TMEDA/AlCl<sub>3</sub> system allows for coordination of the phosphoryl bond, favouring P-O dissociation and thus reduction towards TPP.

All examples of phosphorus chemistry discussed so far have been solution based. Mechanochemistry has also shown potential for the application of novel and more sustainable phosphorus reactants. In 2022, Cummins and coworkers demonstrated the reduction of extended phosphates in the presence of sodium hydride under mechanochemical conditions.<sup>87</sup> This hydride phosphorylation, which worked both with crystalline trimetaphosphate, as well as cyclic phosphates isolated from bacteria, demonstrated the power of mechanochemical techniques for the direct use of normally insoluble polyphosphates toward synthetically viable hypophosphites, without the need for extensive heating or the use of bulk solvent. The additional use of phosphates sequestered in microbes shows the potential for mechanochemical processing techniques to be applied in tandem with Enhanced Biological Phosphorus Removal (EBPR) techniques used in wastewater treatment plants, which will be discussed in more detail later in this section.

To date, one of the more promising routes towards a cyclic and ultimately sustainable phosphorus economy has been the recycling of available phosphorus from waste streams. Such efforts have recently been highlighted in a variety of reviews including one by the Slootweg group,<sup>88</sup> who have further pointed out the dwindling resources of available PR, and highlighted

the potential of recycling waste phosphates from human waste streams. To mirror Brandt's original isolation of white phosphorus, efforts are being made towards the recovery of phosphates separated from wastewater treatment facilities.<sup>88</sup> Initial concentration of the aqueous phase at wastewater treatment plants is conducted using EBPR, where microbes, generally classified as polyphosphate accumulating organisms (PAOs), are used to sequester phosphorus into a biomass-enriched feedstock.<sup>89</sup> Phosphate can also be recovered through chemical precipitation techniques, isolated as various metal phosphates, including calcium, iron or magnesium phosphates<sup>90</sup> as well as struvite (MgNH<sub>4</sub>PO<sub>4</sub>· 6H<sub>2</sub>O).<sup>91</sup>

The organic phase remaining in wastewater treatment, more commonly referred to as sewage sludge, is generally relegated to landfill storage, co-incinerated in the cement industry, or generally applied in agriculture.<sup>88</sup> While chemical and thermal methods do exist for the treatment of this sludge,<sup>92</sup> yield is highly dependent on the pH or temperature used in these processes, and work is ongoing to improve such methods towards a circular phosphorus economy.

#### 1.5.3 Mechanochemistry for the formation of P-C bonds

Despite its potential, the mechanochemical formation of P-C bonds is a largely under-investigated research field. A more recent report of such work is the development of a mechanochemical approach to conduct the Kabachnik-Fields reaction (Scheme 1.11a), which is a known route for imine phosphination.<sup>93</sup>



**Scheme 1.11.** a) General procedure for a mechanochemical Kabachnik-Fields reaction and b) radical-based mechanochemical dehydrogenative phosphination.

Colacino and coworkers demonstrated a methodology applicable to both alkyl and aryl amines, giving quantitative yields with both activated and deactivated aldehydes, and with both aryl phosphinates and alkyl phosphinites. Interestingly, the authors also proposed a catalytic role for the zirconia jar in the mechanochemical one-pot coupling (Figure 1.3).



**Figure 1.3.** Proposed mechanism for mechanochemical Kabachnik-Fields reaction. Reprinted with permission from C. Fiore, I. Sovic, S. Lukin, I. Halasz, K. Martina, F. Delogu, *et al.*, *ACS Sustainable Chem. Eng.* **2020**, 8, 51, 18889–18902. Copyright 2020, American Chemical Society.

Apart from this example, there appears to be only one other case of mechanochemical P-C bond formation, specifically through manganese-catalysed, radical-driven phosphonite coupling (Scheme 1.11b).<sup>94</sup> Mechanochemical approaches for phosphorylation of organic molecules have been reported, for example the phosphorylation of  $\beta$ -D glucans using sodium phosphate.<sup>95</sup> Additionally, mechanochemistry has been shown to be effective for the solvent-free formation of phosphonium salts either as final products.<sup>96,97</sup> or as intermediates towards the Wittig reaction.<sup>98,99</sup>

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# Mechanochemical methods toward inorganic reactivity and new materials design

The development of efficient and novel mechanochemical reactivity relies heavily on *in situ* understanding and detailed mechanistic studies. To this end, as previously discussed in the first Chapter, *in situ* methodologies have helped in understanding reaction pathways, and metastable intermediates. While *in situ* PXRD and Raman have largely been applied to cocrystal formation,<sup>1-4</sup> these techniques are still largely in their infancy when being applied to inorganic reactions. Notably, two common mechanisms, formally the transfer of electrons from one species to another (reduction), or ions exchanged between starting materials to give the desired product (salt metathesis), have seen the most prevalence in the inorganic mechanochemical community. This subsequent Chapter will aim to highlight research whose mechanisms have been driven by reduction or metathesis, and how these mechanistic trends relate to research presented throughout this Thesis.

# 2. Inorganic metathesis and reduction reactivity in mechanochemistry and select examples of main group materials synthesis

# 2.1 General mechanistic principles for metathesis and reduction reactions

As with any reaction pathway whether it is conducted in solution or solid-state, competing reactivity can occur between thermodynamically and kinetically favoured products. However, mechanochemical reactions occur far from equilibrium states and as such there is still an ongoing effort to highlight the finer details of this newly emerging field, but certain parallels can be drawn to help with our beginning to understand. Work presented by Chamorro and McQueen proposes a conceptual framework for such inorganic reaction, dividing this reactivity into three major categories.<sup>5</sup> The first one relies on controlling the position of equilibrium in a solid-state grinding reaction, using Chatelier's principle. This approach to mechanochemical synthesis is illustrated by processes directed through the removal of one of the reaction products either through phase separation (e.g. gas release), appearance of a highly stable product or byproduct (e.g. formation of NaCl), or by successive chemical transformations of a side product. The second category for mechanochemical inorganic reactions are mechanochemical self-propagating reactions (MSRs) pioneered by Takacs,<sup>6</sup> characterised by a highly exothermic reaction profile, potentially also including the ignition of the reaction mixture, resulting from a brief period of mechanical activation. The self-propagating nature of ion metathesis and redox reactions based on this design provides access to noticeably short reaction times. MSR processes have been extensively explored in making bulk chalcogenide and pnictogenide materials.<sup>7</sup> Boldyreva and coworkers have also

done extensive work in developing mathematical models to describe the mixing and milling of binary powder systems.<sup>8-10</sup>

The third class of reactivity involves the kinetic control of product formation, facilitated by the formation of easily accessible intermediates.<sup>11</sup> In this way, room temperature mechanochemical techniques can allow for the isolation of low-temperature, diffusion limited intermediates and products. The Neilson group has previously investigated the mechanistic pathways of kinetic product formation for low temperature, solid-state reactions. Namely, their work on the solid-state formation of pyrite and disulfide phases has employed *in situ* PXRD to monitor phase formation during a thermal solid-state reaction.<sup>12,13</sup> This work highlighted both the ability to observe new phase formation, as well as to trap kinetic products simply by controlling the temperature ramp.

# 2.2 Nanoparticle design

#### 2.2.1. Metal boride NPs

Murty and coworkers demonstrated a route to nanocrystalline Al borides *via* a two-step route from elemental precursors, pairing a mechanical alloying stage with an annealing stage under inert atmosphere.<sup>14</sup> Mechanical action played a significant role in determining the phase selectivity of the final product and, depending on how long the blended powders were milled for, a different ratio of crystalline product phases was achieved. Increased milling times showed a reduction in particle size and an increase in lattice strain and dislocation density of Al (Table 2.1).

**Table 2.1.** Microstructural evolution (crystallite size and particle size) during milling of the Al+B powder blend (1200 RPM, 10:1 BPR).

Milling Time / h	Crystallite size of Al, <i>d /</i> nm	Particle size, D₅₀ / μm	Lattice strain of Al, ε / %	Dislocation density of Al, ρ / x10 <sup>16</sup> m <sup>-2</sup>		
2	44 ± 10	13 ± 3	$0.26 \pm 0.02$	5.7		
4	30 ± 8	9 ± 4	$0.33 \pm 0.03$	10.6		
6	17 ± 9	4 ± 2	0.41 ± 0.05	23.3		

This mechanically induced change in the physical crystal properties reflects the changes observed in the annealing onset temperatures of the two pure Al borides phases, AlB<sub>2</sub> and AlB<sub>12</sub>. Differential thermal analysis (DTA) was used to monitor the heat flow of the powder blends over time (Figure 2.1). The two most notable differences found between the milled and non-milled blends are the disappearance of signal corresponding to the Al melting point, and the reduction in onset temperatures when milling is applied to the powder blends.



**Figure 2.1.** (a) Heat flow for the Al+B blend - 0 to 6 h milling as measured in DTA with a constant heating rate of 10 K min<sup>-1</sup> and (b) the magnified view for 2 to 6 h milling where transformation temperatures are indicated.

Variation in milling times influenced the onset annealing temperatures of the aluminum borides. The blended powders were annealed to the two onset temperatures  $T_1$  and  $T_2$  and held at each for 2 or 4 h for each of the three milling times. From the PXRD data and *via* the relative intensity ratio (RIR) method, the fraction of crystal phases was calculated for each sample (Table 2.2).

Milling time / h	Phase fraction after 2 h of annealed at onset temperature T <sub>1</sub> /% Phase fraction af h of annealed at o			n after 4 at onset T <sub>1</sub> / %	Phase h of ai tem	e fraction nnealed a perature	after 2 at onset T <sub>2</sub> / %	Phase h o onset	fraction f anneale tempera /%	after 4 ed at iture T <sub>2</sub>		
	AI	AIB <sub>2</sub>	AIB <sub>12</sub>	AI	AIB <sub>2</sub>	AIB <sub>12</sub>	AI	AIB <sub>2</sub>	AIB <sub>12</sub>	AI	AIB <sub>2</sub>	AIB <sub>12</sub>
2	78	13	9	49	35	16	58	19	23	42	15	43
4	64	20	16	38	45	17	40	12	48	31	10	59
6	34	37	29	15	57	28	23	9	68	-	-	100

Table 2.2. Fraction of phases obtained by RIR method after annealing.

Based on the pre-annealing milling time chosen, it was determined that final phases could be made selectively. For example, the fraction of pure aluminum decreased strongly with

increasing milling time and the fraction of the more favourable AlB<sub>12</sub> product increased with increasing milling time, with quantitative conversion achieved after 6 hours of milling at 1200 rpm and 4 hours of annealing at 1460 K. The synthesises of nanostructured metal borides, and of boride-based metal alloys, conducted under mechanochemical reaction conditions have been extensively studied. Nanostructured boride-based metal alloys have a notable presence as materials with magnetic applications.<sup>15,16</sup> Binary metal boride compounds have been synthesised mechanochemically using a variety of different metals such as cerium, ytterbium, iridium and zirconium.<sup>17-20</sup>

#### 2.2.2 Metal carbide NPs

Published in 2019 by Sayagués and coworkers VC, NbC, and TaC NPs were synthesised through a magnesiomechanic reduction reaction.<sup>21</sup> The desired nanocomposite precursor, either  $V_2O_5$ , orthorhombic Nb<sub>2</sub>O<sub>5</sub>, or Ta<sub>2</sub>O<sub>5</sub>, were milled with graphite and Mg in a planetary ball mill under pure argon gas. The combustion resulting from mechanical milling is known as a mechanically induced self-sustaining reaction. The moment of combustion was tracked by *in situ* pressure sensors for each of the three reaction systems. Combustion times were recorded at 10, just before 10, and at 23 minutes for the vanadium, niobium and tantalum systems, respectively. Milled powders were subsequently acid treated with 1M HCl to leach out the MgO byproduct.

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**Figure 2.2.** (Left)  $Mg/V_2O_5/C$  system: PXRD patterns of the (a) initial materials, (b) combusted products for the initial stoichiometric mixture, (c) combusted products for the system with 10 wt. % extra carbon, (d) combusted products for the system with 15 wt. % extra carbon, and (e) product of (d) after chemical leaching. (Center)  $Mg/Nb_2O_5/C$  system: PXRD patterns of the (a) initial materials, (b) combusted products for the initial stoichiometric mixture, (c) product of (b) after chemical leaching. (Right)  $Mg/Ta_2O_5/C$  system: PXRD patterns of the (a) initial materials, (b) combusted products for the initial materials, (c) product of (b) after chemical leaching.

Mixtures for all three systems were taken and compared to the patterns of the as-milled material and the material after acid leaching (Figure 2.2).

For each of the three systems, milled samples showed characteristic X-ray reflections of the desired carbides, in contrast to the PXRD patterns of physical mixtures of reactants. Furthermore, the X-ray reflections of MgO completely disappeared following the leaching process. For each of the three systems the elemental mappings from HAADF-STEM images were consistent with the production of new carbide phases detected by PXRD, displaying good elemental overlap between carbon and the complementary element of each carbide.

TEM images, not shown, captured irregular and polydisperse particle sizes between 70 and 100 nm for the vanadium carbides, around 50 nm for the niobium carbide, and about 20 - 40 nm for the Ta carbide, all observed as agglomerates.

The (111) plane spacings were measured at high magnification and found to match the expected crystallographic plane spacing values for each carbide. Other carbide NPs and nanocomposites, synthesised through similar magnesiomechanic reduction pathways, have been published both more recently and at least a decade prior to the publication of this review.<sup>22,23</sup>

#### 2.2.3 Metal silicide NPs

In 2019, Öveçoğlu and coworkers mechanochemically synthesised NbSi<sub>2</sub> NPs *via* a magnesiomechanic reduction.<sup>24</sup> Nb<sub>2</sub>O<sub>5</sub>, Mg, and SiO<sub>2</sub> were blended and added in stoichiometric amounts using a stainless steel apparatus, under an argon atmosphere. The mixtures were milled in a vibratory mill at ~18 Hz with a ball-to-powder weight ratio of 10:1 until a combustion occurred and MSR products were observed. After the reaction, excess Mg and MgO byproduct phases were removed by acid washing and sonication for 15 min. The leached powders were subsequently washed and dried at 110 °C over five hours. Since Nb<sub>2</sub>O<sub>5</sub> has two different room temperature polymorphs, orthorhombic (o) and monoclinic (m), a pair of reactions with phase pure niobium oxides were both run. It was found that the Nb<sub>2</sub>O<sub>5</sub>(m) reactant produced no observable reaction and no change in crystallinity, as measured by PXRD, even after seven hours of milling. The Nb<sub>2</sub>O<sub>5</sub>(o) reagent however produced an observable reaction and a change in mixture crystallinity after five hours of milling (Figure 2.3). PXRD patterns of the pre-milled but blended mixtures and of the same mixtures milled for 3 hours, along with respective differential scanning calorimetry (DSC) plots, clearly demonstrated a chemical change to the solid mixture.

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**Figure 2.3.** PXRD pattern of stoichiometric (a) blended  $Nb_2O_5(o)$ -SiO<sub>2</sub>-Mg powders and (b) of those mechanically milled for 3 h after the DSC analyses. DSC curves of stoichiometric (c) blended  $Nb_2O_5(o)$ -SiO<sub>2</sub>-Mg powders and (d) of those mechanically milled for 3 hours.

Since the resulting powders presented a mix of phases, optimization of the desired NbSi<sub>2</sub> phase was done by adding excess Mg reductant and extra milling. Indeed NbSi<sub>2</sub> is commonly studied as a high temperature protective coating material because it has the highest hardness value and shear deformation resistance amongst the mix of Nb silicide phases produced in the MSR reaction.<sup>25</sup> Additionally, some of the Nb silicide phases such as  $\beta$ -Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Si are meta-stable phases and only appear at high temperature, making them less valuable than the room temperature stable phases such as NbSi<sub>2</sub>.

TEM imaging showed that the NbSi<sub>2</sub> particles were encased in shells of SiO<sub>2</sub>. The particles were irregularly shaped and polydispersed (Figure 2.4). Histograms for core diameters and shell widths of the milled and leached particles made with excess magnesium showed an average core size of 61 nm in a range of 30 - 380 nm, and an average shell width of 7.5 nm in a range of 3 - 20 nm.



**Figure 2.4.** (a, b) TEM images of mechanochemically synthesised and leached  $Nb_2O_5(o)$ –SiO<sub>2</sub>–Mg powders with excess Mg amount of 3.5 mol; I histogram of core size range with nonlinear curve fit (Gauss); (d) histogram of thickness range of SiO<sub>2</sub> layer with nonlinear curve fit (Gauss).

Mixed metal NP mechanosynthesis with uncommon and even rare earth metals have been reported. Typically, a magnesiomechanic or calciomechanic route was employed to reduce precursor metal oxides into mixed metal nanostructures with a washable MgO or a CaO byproduct. Examples of the variety of metals used in these mechanochemical reactions include samarium, praseodymium, yttrium, lanthanum, bismuth, manganese, and zirconium.<sup>26-28</sup>

# 2.2.4 Metal Nitride Nanomaterials

Owing to their potential in advanced electronic<sup>29</sup> and photocatalytic applications,<sup>30,31</sup> metal nitrides and their varied synthetic routes<sup>32</sup> have seen an increase in research interest. The mechanochemical synthesis of metal nitrides has been achieved *via* mechanical activation of a variety of metal powders in a N<sub>2</sub> or NH<sub>3</sub> atmosphere,<sup>33-36</sup> or other small molecule N sources.<sup>37-40</sup>

#### Gallium

While several mechanochemical synthesis methods have been explored for bulk metal nitrides, such as ball milling elemental metal powders under  $N_2$  or  $NH_3$  gases and milling metal compounds

with reactive nitrides such as Li<sub>3</sub>N or N containing organic compounds, fewer examples are seen for the mechanochemical synthesis of metal nitride nanomaterials.<sup>41</sup>

Preliminary work done by the McCormick and coworkers detailed the mechanochemical synthesis of GaN nanocrystals through a solid-state double displacement reaction. Stoichiometric amounts of  $Ga_2O_3$  and  $Mg_3N_2$  powders were milled using a mixer mill and then annealed and washed to remove the unwanted MgO byproduct, resulting in irregularly shaped, hexagonal GaN nanocrystals with a wide size distribution of 4 to 20 nm. Using  $Ca_3N_2$  as an alternative nitride precursor, PXRD patterns showed GaN nanocrystal formation in milled and pre-annealed samples, but the product could not be isolated after annealing and washing. Such inability to isolate GaN is likely due to the dissolution of GaN by Ca (OH)<sub>2</sub> formed from the reaction of the CaO byproduct in water.<sup>42</sup>

## Molybdenum

 $Mo_2N$  powder was synthesised through high energy ball-milling of elemental Mo powder under  $NH_3$  at room temperature. Both milling speed and milling time were found to influence particle formation and rate of conversion to  $Mo_2N$ . At a milling speed of 1300 rpm, PXRD analysis confirmed that the solid-gas reaction begins after 3 hours of milling and was nearly complete after 30 hours of milling. When the milling speed was reduced to 1000 rpm, keeping all other parameters the same, the reaction started after 10 hours and was approximately 60 % complete after 30 hours. For the sample milled at 1300 rpm for 30 hours, particles with a variety of diameters near the nanomaterial size boundary were synthesised, with an average of around 100 nm.<sup>43</sup>

#### Hafnium

HfN NPs were synthesised using a mechanochemical method, through high energy ball milling under argon gas, of partially hydrated HfCl<sub>4</sub> and Mg powders. The milled precursor powders were

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subsequently annealed under N<sub>2</sub> gas and then washed with HCl to remove the MgO byproduct, resulting in the formation of HfN NPs with an average size between 10 and 30 nm. While the electron diffraction pattern confirmed the formation of HfN, XPS showed there was an oxide layer of less than 4 nm that passivated the surface of the HfN NPs. Thermogravimetric analysis (TGA) determined that Hf hydride intermediates formed during milling prevented Hf from being fully oxidized, allowing for its nitridation into HfN.<sup>44</sup>

#### Zirconium

Cubic ZrN (c-ZrN) nanopowders were synthesised through a mechanochemical reaction between ZrCl<sub>4</sub> and Li<sub>3</sub>N powders, as seen in Scheme 2.1.

4 
$$Li_3N$$
 + 3  $ZrCl_4$   $\longrightarrow$  3  $ZrN$  + 12  $LiCl$  + 1/<sub>2</sub>  $N_2$ 

Scheme 2.1. Reaction scheme for the mechanochemical synthesis of zirconium nitride.

The reaction was found to initiate after 7 minutes of milling under argon and finished completely within a few seconds. DSC and *in situ* temperature measurements of the reaction vial suggested that the reaction was self-propagating, due to the release of a large amount of heat upon reaction. By increasing the milling time, the ignition temperature decreased and once the ignition temperature fell below the local temperature generated by the collision of the steel milling balls, the reaction takes place. The 30 hour milled products were washed with ethanol, hydrochloric acid, and distilled water, to remove the LiCl byproduct. PXRD analysis suggested the average grain size of the c-ZrN nanopowders to be 40 nm and that grain size did not decrease with extended milling time. SEM images confirmed NP formation, as the average particle size was also 40 nm with a distribution ranging from 20 to 80 nm.<sup>45</sup>

#### Iron

In 2020, Baek and coworkers presented a mild mechanochemical method to synthesise  $NH_{3}$ .<sup>46</sup> Upon milling Fe powder under 1 bar of N<sub>2</sub>, surface defects produced on the surface of the Fe powder allowed for the dissociation of N<sub>2</sub> into Fe-N\* species, which could undergo subsequent hydrogenation to  $NH_{3}$ . The authors noted that despite surface amorphization during the initial nitrogenation, surface analysis revealed the formation of Fe<sub>3</sub>N<sub>4</sub>.

#### 2.2.5 Metal Phosphide Nanomaterials

Due to their high electrochemical performance, metal phosphides show promise for many applications, including as battery anode materials<sup>47,48</sup> and as catalysts for water splitting reactions.<sup>49</sup> While mechanochemical synthesis methods vary, many groups report milling of the precursor metal and red phosphorus to form the metal phosphide nanomaterial.<sup>50,51</sup>

#### Zinc

Park and Sohn synthesised tetragonal ZnP<sub>2</sub> and ZnP<sub>2</sub>@C nanocomposite through a high energy mechanical milling (HEMM) process without further heat or chemical treatment. Zn and red P powders were milled under argon at ambient temperature and pressure with a vibratory mill at 700 rpm for 12 hours to form ZnP<sub>2</sub> particles of a few hundred nanometers in size. When Zn and red P were milled with C, under the same conditions, approximately 200-300 nm sized ZnP<sub>2</sub>@C particles were observed through high resolution TEM (HRTEM) analysis, with 10 nm sized ZnP<sub>2</sub> nanocrystals uniformly dispersed in the amorphous C matrix. The ZnP<sub>2</sub>@C nanocomposite was studied for its electrochemical applications as an anode material for Li rechargeable batteries and showed a highly reversible reaction with Li, good cyclability and rate capability.<sup>52</sup>

## Vanadium

The Sohn group also synthesised hexagonal VP as another possible Li rechargeable battery anode material. During HEMM, the temperature can reach more than 200 °C and the pressure generated has been estimated to be in the order of 6 GPa, which is sufficient to transform the elemental precursors into transition metal phosphides.<sup>53</sup> The VP NPs were prepared *via* HEMM under argon for 6 hours, starting from V and red P powders. PXRD and HRTEM analysis confirmed that aggregates made of 10-20 nm sized VP NPs were formed. The nanomaterial exhibited excellent electrochemical performance, which was attributed to topotactic Li insertion and extraction in the VP electrode.





Another phase of vanadium phosphide, VP<sub>2</sub>, has been synthesised mechanochemically, also through ball milling of V and red P powders. After 50 hours of milling at 600 rpm, a poorly crystalline VP<sub>2</sub> phase was evident through XPRD. HRTEM revealed the sample contained mainly

amorphous grains and a few well crystalized 5-10 nm NPs. Heat treatment of the amorphous  $VP_2$  at 600 °C yielded a crystalline product with 10 times larger crystallite size. Both the amorphous and crystalline  $VP_2$  showed Li electrochemical reactivity, as negative electrodes for secondary Liion batteries, reversibly reacting with 3.5 Li and 2.5 Li per formula unit respectively.<sup>53</sup>

Hong and coworkers demonstrated an ambient temperature, mechanochemical synthesis of  $V_4P_7$  NPs as an anode material for rechargeable sodium ion batteries (SIBs). High energy mechanical milling under argon of stoichiometric amounts of vanadium and red phosphorus resulted in phase pure  $V_4P_7$  after 60 hours of milling at 300 rpm. TEM analysis showed approximately 100 nm aggregates were formed, made of several  $V_4P_7$  NPs with diameters ranging from several to tens of nanometers. The resultant SIB anode material showed excellent cycling behaviour.<sup>54</sup> In an earlier synthesis, the same group developed  $V_4P_7$  nanopowder through an identical HEMM procedure to form 50-100 nm NPs, which were then made into a  $V_4P_7$ @C nanocomposite for lithium ion battery anode material applications. TEM analysis confirmed that the  $V_4P_7$  NPs were composed of aggregated nanocrystallites around 5-20 nm in size (Figure 2.5).<sup>55</sup>

# Ruthenium

Ru<sub>2</sub>P NPs embedded in a carbon matrix (Ru<sub>2</sub>P-BM-C), applied as a highly efficient H<sub>2</sub> evolution reaction (HER) electrocatalyst, were synthesised *via* a solid-state ball milling assisted reaction. NaPO<sub>2</sub>H<sub>2</sub>, RuCl<sub>3</sub> and carbon black were first milled in a planetary ball mill at 600 rpm for 2 hours and then pyrolyzed at 600 °C for 2 hours under an inert N<sub>2</sub> atmosphere. TEM images showed that the Ru<sub>2</sub>P NPs were an average size of 5 nm, dispersed among the carbon matrix (Figure 2.6).



Figure 2.6. TEM images (a, b) and HRTEM image (c) of Ru<sub>2</sub>P NPs embedded in a carbon matrix.

Synthesis of Ru phosphides as an electrocatalyst for HER have been well explored, however Jin and coworkers detailed the first solid-state synthesis using mechanochemistry. Ru<sub>2</sub>P-BM-C showed a Pt-like HER performance overpotential of 36 mV at a current density of 10 mA cm<sup>-2</sup> in 1 M KOH.<sup>56</sup>

#### Cobalt

Xia and coworkers detailed the mechanochemical synthesis of Co<sub>2</sub>P NPs encapsulated in N-doped hollow carbon rods (Co<sub>2</sub>P/N-HCRs) for electrocatalytic applications. Citric acid, cobalt(II)acetate and diammonium phosphate were first ball milled at 700 rpm for 10 hours and then annealed under N<sub>2</sub> at 350 °C for 1 hour and at 750 °C for 3 hours, resulting in approximately 60 nm Co<sub>2</sub>P NPs embedded in N-doped, hollow carbon rods, 140 nm in diameter and 1 um in length (Figure 2.7). The Co<sub>2</sub>P/N-HCRs exhibited impressive electrocatalytic activity towards the O<sub>2</sub> reduction reaction (ORR), HER and O<sub>2</sub> evolution reaction (OER) with particularly high electrochemical durability towards the ORR when compared to commercially available Pt/C. Enhanced ORR performance was attributed to nitrogen integration into the carbon rods, which influenced the electroneutrality of the carbon atoms and facilitated O<sub>2</sub> adsorption. When compared to 20 % Pt/C, Co<sub>2</sub>P/N-HCRs

showed better stability and methanol tolerance, which is necessary for the application of ORR electrocatalysts. Stability was investigated through recording their I-t curves at 0.6 V.  $Co_2P/N$ -HCRs showed a current loss of 12.5 %, whereas 20 % Pt/C showed a more rapid current loss of 30.2 % over the same 50 000 second period.<sup>57</sup>



Figure 2.7. TEM Images of Co<sub>2</sub>P NPs encapsulated in N-doped hollow carbon rods.

#### Indium

InP NPs embedded in a hybrid conductive TiO<sub>2</sub>-C matrix (InP@TiO<sub>2</sub>-C) were synthesised *via* a two-step mechanochemical process. The first step involved ball milling of In<sub>2</sub>O<sub>3</sub>, titanium and red phosphorus under argon at 300 rpm for 10 hours to form both InP and TiO<sub>2</sub> NPs. After the secondary milling step, where the InP/TiO<sub>2</sub> product and elemental C were milled under the same conditions, InP@TiO<sub>2</sub>-C was synthesised. SEM analysis showed a uniform InP NP size distribution of approximately 50 nm within the TiO<sub>2</sub>-C matrix (Figure 2.8). Under the same milling

conditions, in a single step milling procedure, InP@TiO<sub>2</sub> and InP@C were synthesised as controls and both products showed a high level of size distribution through SEM analysis due to higher amounts of aggregation. All three were tested for performance as Li ion battery (LIB) anodes and the InP@TiO<sub>2</sub>-C nanocomposite showed superior performance in terms of the specific capacity, life span and rate performance.<sup>58</sup>



Figure 2.8. (a) SEM image and (b) HRTEM image of InP@TiO<sub>2</sub>-C.

#### Nickel

Our group had developed a solvent-free, mechanochemical synthesis of Ni<sub>2</sub>P NPs as HER cocatalysts. The procedure involved ball-milling stoichiometric amounts of NiCl<sub>2</sub> and Na<sub>3</sub>P powders with heptadecylamine as a surface capping ligand to control the size of the NPs (Scheme 2.2). Various amine and phosphine ligand types and amounts were tested for their influence on the final average size and size distribution of the NPs, with five equivalents of heptadecylamine yielding the smallest and most uniform Ni<sub>2</sub>P NPs. Ball-milling was performed under argon in sealed ZrO<sub>2</sub> jars for 90 minutes, then the samples were left to age for 18 hours prior to washing and drying the product (Scheme 2.2). For HER applications, a graphitic carbon nitride photocatalytic support was used, and the material generated 233.9  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> of H<sub>2</sub> after 3 hours with broad spectrum lighting and was able to be recycled without a decrease in reactivity.<sup>59</sup> To the
best of our knowledge, these are the smallest nickel phosphide nanoparticles produced through a bottom-up, solid-state approach without the need for excess solvent or high reaction temperatures.

2 Na<sub>3</sub>P + 3 NiCl<sub>2</sub> + 5 Alkyl amine 
$$2 \text{ Na}_3 \text{ P} + 3 \text{ NiCl}_2 + 5 \text{ Alkyl amine}$$
  $3/_2 \text{ Ni}_2\text{P} + 6 \text{ NaCl} + 1/_2 \text{P}$   
age 18 hrs, RT

Scheme 2.2. Reaction scheme for the mechanochemical Ni<sub>2</sub>P synthesis using Na<sub>3</sub>P as a solid phosphide source.

#### **2.2.6 Metal Arsenides**

#### *Gallium & Aluminum*

Currently, there are few examples for metal arsenide nanomaterials made using mechanochemistry through reduction or metathesis pathways. Early work done by Matteazzi and Farné detailed the synthesis of GaAs and AlAs by room temperature milling of elemental powders with a vibratory mill. A complete synthesis was seen for both the GaAs and AlAs samples within 2 and 5 hours, respectively, and the crystallite size from PXRD analysis was within 10-20 nm.<sup>60</sup> Without full characterization and images of these samples, it is unclear if metal arsenide NPs were formed. While work in the mechanochemical synthesis of metal arsenide nanomaterials is promising thus far, it is underdeveloped compared to solution methods.

#### Indium

InAs NPs were synthesised *via* a one-step mechanochemical procedure from elemental In and As. The precursors were milled at 500 rpm in a planetary mill under an argon atmosphere for 90 minutes to form InAs NPs containing cubic Zn-blende structure crystallites. PXRD and TEM analysis of the nanocrystals confirmed particles in the range of 3 to 50 nm in size. In this first attempt at synthesising InAs using mechanochemistry, most of the crystals showed defects, as a consequence of milling. The nanocrystals exhibited transverse optical (TO) and longitudinal optical (LO) phonon frequency modes at 215 cm<sup>-1</sup> and 243.4 cm<sup>-1</sup> through Raman spectroscopy

and a maximum emission peak at 930 nm through photoluminescence spectroscopy (Table 2.3). When compared to more extensively studied methods of InAs preparation, the mechanochemical synthesis of InAs NPs shows potential, but requires further investigation to minimize structural defects in the nanocrystals to be used for semiconductor material applications.<sup>61</sup>

**Table 2.3.** Properties of InAs NPs prepared by milling.

Size of crystallites (nm)		Microstrain	Raman shift (cm <sup>-1</sup> )		Emission wavelength
Rietveld	HRTEM	_	то	LO	(nm)
37 ± 13	3-15	0.72	215	243.4	930

#### 2.2.7 Metal Sulfides

The synthesis of chalcogenide (sulfide, selenide, and telluride) semiconductor nanomaterials has garnered growing interest as nano-sized semiconductor materials exhibit a wide variety of potential applications, primarily optical, thermoelectric, environmental, and biomedical in nature. Synthesised chalcogenide NPs possess many useful physical and chemical properties, namely, their optical properties that may be tuned by altering particle size. These unique optical properties allow for their potential as visible light absorbers and emitters in optoelectronic devices such as light-emitting diodes, solar cells, transistors and infrared detectors.<sup>62</sup> Other more recent applications of some chalcogenide nanomaterials include their application as heterogeneous photocatalysts.

#### Zinc, Cadmium and Cerium

Mechanochemically synthesised ZnS and CdS NPs have been investigated for their optical properties, specifically for solar cells and quantum dot applications.  $Ce_2S_3$  NPs are of high interest for their potential applications as photocatalysts and in hydrogen storage. The McCormick group synthesised ZnS, CdS and  $Ce_2S_3$  NPs from the corresponding metal chloride and commercial grade

CaS, in a hardened steel vial with steel balls using a SPEX 8000 mixer mill under a high-purity

argon atmosphere (Scheme 2.3).<sup>63</sup>



Scheme 2.3. Scope of metal sulfides made using alkali earth sulfides as a sulfur source.



Figure 2.9. TEM image of CdS quantum dots produced.

During mechanical milling solid-state displacement reactions between the metal chloride and alkali sulfide or alkaline earth sulfide resulted in the synthesis of the corresponding metal sulfide NPs.<sup>63</sup>

The separated NPs of ZnS and CdS (Figure 2.9) and  $Ce_2S_3$  were of sizes 8 nm, 4 nm, and 20 nm, respectively. A decrease in particle size was noted as a result of a structural change, observed for the CdS and  $Ce_2S_3$  particles. For the CdS particles, particle size decreased with decreasing milling ball size. Finally, it became evident that the addition of a diluent had minimal

effect on the sulfide particle size, however it was only possible to form separated single crystal NPs in samples milled with the presence of a diluent.

As a decrease in particle size was not observed for ZnS in previous experimental trials, the investigation of the synthesis of ZnS was continued by the same group.<sup>64</sup> Mechanical milling using a SPEX 8000 mixer/mill with a ball- to-powder mass ratio of 10:1, was carried out for ZnCl<sub>2</sub> with commercial grade CaS (Scheme 2.4).

 $ZnCl_2 + CaS \longrightarrow ZnS + CaCl_2$ 

Scheme 2.4. ZnS NPs made using metathesis reaction between ZnCl<sub>2</sub> and CaS as a sulfur source.

The resultant ZnS particles were 0.2 to 0.5  $\mu$ m in size and contained crystallites of approximately 12 nm. Following the addition of 71 vol % CaCl<sub>2</sub> as a diluent phase, isolated ZnS NPs of 16 nm in diameter were produced after approximately 80 hours of milling. The average NP size of the ZnS sample after milling was estimated to be approximately 16 nm, as calculated from the Scherrer equation. TEM analysis showed partially dispersed particles after 77 hours of milling (Figure 2.10).<sup>64</sup>



Figure 2.10. TEM micrograph of the ZnS NP sample milled for 77 hours.

To examine the effect of the CaS particle size on the size of the synthesised ZnS particles and the kinetics of the reaction, CaS particles of various sizes were synthesised. Subsequently, CaS particles, 10-50 nm in size, were synthesised by the mechanical alloying of elemental calcium and sulfur, together with 82 vol % CaCl<sub>2</sub> as a diluent. The addition of CaCl<sub>2</sub> was chosen to prevent combustion during milling. Using the synthesised CaS with 71 vol % CaCl<sub>2</sub> as the starting powder, discrete ZnS particles of approximately 7-9 nm in size were produced *via* milling with ZnCl<sub>2</sub>. The effects of milling time and annealing temperature on particle size were also investigated. Milling samples of ZnCl<sub>2</sub>, CaS, and 3.6 equivalents of CaCl<sub>2</sub> for varying lengths of time followed by annealing under an argon atmosphere at 350 °C for one hour. After annealing, the resultant particle sizes were 7 - 8 nm, and independent of milling time, showed no change in crystallite size after annealing for 3 hours. It was observed that the crystallite size increased as the annealing temperature was increased and eventually tapered off at approximately 7 nm for temperatures higher than 260 °C.

#### Lead

PbS nanocrystals were synthesised mechanochemically by Zorkovská and coworkers in 2013, milling lead(II)acetate hydrate with protein-rich eggshell membrane (ESM) using a tungsten carbide milling apparatus.<sup>65</sup> The 4 % cystine content found in the dried ESM powder act as a biobased sulfur source. The product formation was confirmed through PXRD analysis. The following year, Psotka and coworkers investigated the specific influence of L-cystine as both a sulfur source along with acting as a capping agent.<sup>66</sup> Analysis by PXRD (Figure 2.11) show only the presence of L-cystine after milling for 15 minutes. However, upon milling for 60 minutes, reflections corresponding to PbS begin to appear, with the reaction going to completion after 105 minutes of milling.



**Figure 2.11.** PXRD patterns for PbS nanocrystal formation, through the milling of lead(II)acetate hydrate with L-cystine as a S source and capping agent.

#### Bismuth

Bi<sub>2</sub>S<sub>3</sub>, as a nanocrystalline sulphide semiconductor, has amassed the interest of many, specifically for its photoelectrochemical applications, as it has a narrow band gap ( $E_g = 1.3 \text{ eV}$ ). It is also an attractive semiconductor material for applications in photovoltaic cells,<sup>67</sup> lithium ion batteries,<sup>68</sup> solar cells,<sup>69</sup> electrochemical hydrogen storage<sup>70</sup> and thermoelectric technologies<sup>71</sup> due to its environmentally favoured nature. Mechanochemical synthesis of nanocrystalline Bi<sub>2</sub>S<sub>3</sub>, from elements using high-energy milling in a planetary mill was investigated by Šatka and coworkers.<sup>72</sup> Their work demonstrated the mechanochemical synthesis of Bi<sub>2</sub>S<sub>3</sub> from elemental bismuth and sulfur powders in a 2:3 stoichiometric ratio, performed in a 250 mL tungsten carbide milling chamber and 50 10 mm diameter- balls, with a rotation speed of 500 rpm. Milling was performed for durations between 1 and 60 minutes under an argon atmosphere, to test the effect of milling time.

PXRD analysis showed good correlation to the Joint Committee on Powder Diffraction Standards (JCPDS) patterns and thus the crystallite sizes of the NPs produced could be calculated

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using the Scherrer formula, yielding  $Bi_2S_3$  particles of approximately 24 nm. It must be noted that the absolute value varies by approximately  $\pm 10$  % depending on the exact method of obtaining and correcting the PXRD reflection widths. The specific surface area of the NPs was also determined by low temperature N<sub>2</sub> adsorption measurements. The specific surface area notably increased with increasing milling time. The synthesised NPs showed no contamination by EDX analysis, and the surface morphology of the mechanochemically synthesised samples, showed agglomerated Bi<sub>2</sub>S<sub>3</sub> particles (Figure 2.12), correlating with the phenomenon that individual NPs have a susceptibility to form nanoparticle agglomerates during the milling process.<sup>73</sup>



Figure 2.12. SEM image of Bi<sub>2</sub>S<sub>3</sub> NPs, made by milling for 60 minutes.

Due to the large atomic number of bismuth, Bi<sub>2</sub>S<sub>3</sub> NPs are also suitable candidates for contrast agents in computed tomography (CT) and have demonstrated greater or similar effectiveness in comparison to currently employed iodinated CT compounds.<sup>74</sup> Although bismuth-based NPs have been presented as promising nanomaterials for CT contrast agents, the production of bismuth-based nanomaterials for this application has encountered numerous synthetic challenges.<sup>75</sup> These synthetic issues encompassed difficulty in size control including wide size

distributions and poor monodispersity as well as poor shape control.<sup>75</sup> Common hydrothermal approaches for the synthesis of  $Bi_2S_3$  NPs, warrants the use of higher temperatures, longer heating periods, inert atmospheres, and exhaustive amounts of hazardous organic solvents.<sup>74,76</sup> In addition to the synthetic hurdles mentioned, all of these syntheses require an additional ligand exchange to generate NPs that are readily suspended in water instead of organic solvent and thus produce nanomaterials viable for biomedical applications. More recently, our group demonstrated an alternative mechanochemical synthetic route in order to achieve effective control of shape and size for Bi<sub>2</sub>S<sub>3</sub> NPs using Bi(NO<sub>3</sub>)<sub>3</sub>·5(H<sub>2</sub>O) and L-cysteine (Figure 2.13).<sup>77</sup> Mechanical activation of the reaction was achieved via ball milling in a mixer or planetary ball mill for 90 minutes or by manual grinding using a mortar and pestle. Following activation, the NPs underwent an aging process, allowing the mixture to rest at ambient conditions between 12 and 24 hours. The Bi<sub>2</sub>S<sub>3</sub> particles were capped with three different capping ligands, namely oleylamine (OA), sodium 6aminohexanoate (AHA) and poly(ethylene glycol)-methyl-ether-amine (mPEG-NH<sub>2</sub>) in order to produce NPs that were readily suspended in organic solvent, aqueous media and directly biocompatible, respectively. The resultant  $Bi_2S_3$  NPs were found to have tunable diameters, averaging 2 to 8 nm, by manipulating reaction conditions.



Figure 2.13. Reaction Scheme for Bi<sub>2</sub>S<sub>3</sub> NPs capped with various ligands.

For the OA-capped synthesis, the Bi<sub>2</sub>S<sub>3</sub> NPs generated were readily suspendable in hexanes and toluene after brief sonication and remained stable in solution in ambient conditions for a week. Two different OA/Bi ratios were investigated and with both ratios, very small NPs were observed, with narrow size distributions, independent of the ligand to bismuth ratio. The OA/Bi ratios tested were 5:1 and 10:1 yielding NPs with average diameters of  $2.09 \pm 0.29$  and  $2.08 \pm 0.32$  nm, respectively. It was determined that increasing the ligand/Bi stoichiometric ratio from 5:1 to 10:1 resulted in no significant change in the OA surface coating. This was indicative of the saturation of the NP surface with organic ligand already occurring at the 5:1 stoichiometric ratio. TEM studies showed an average NP diameter of  $1.96 \pm 0.24$  nm for the NPs synthesised using a mortar and pestle. Following capping with OA, Bi<sub>2</sub>S<sub>3</sub> NPs of approximately 2 nm in diameter were achieved, yielding the smallest Bi<sub>2</sub>S<sub>3</sub> NPs ever reported.

Attempts to synthesise of AHA-capped Bi<sub>2</sub>S<sub>3</sub> NPs by the neat milling of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, L-cysteine, and AHA for 90 minutes in a vibrational mill, and subsequent aging for up to 5 days, showed no particle formation. Repeating the same synthesis with 50  $\mu$ L of water LAG for 90 minutes and aging for 24 hours produced particles ranging from 7.6 – 8.2 nm in diameter. AHAcapped NPs were significantly larger than those capped with OA possibly due to the difference in the relative sizes of the two capping ligands, with the aliphatic chain of AHA being 3 times shorter than that in OA. Additionally, switching from a mixer to a planetary mill resulted in a limited size change for the OA-capped particles (2.09 ± 0.29 nm to 1.88 ± 0.27 nm) however resulted in a significant decrease in the average diameter of the AHA-capped particles, from 7.9 nm to 3.0 nm (Figure 2.14).



Figure 2.14. TEM image and size distribution histogram of AHA-capped particles and OA-capped  $Bi_2S_3$  NPs, respectively.

Finally, water-soluble, and biocompatible Bi<sub>2</sub>S<sub>3</sub> NPs were synthesised through the same milling and aging process using PEG of various lengths as capping agents. PEG polymers have been studied as capping agents due to their ability to reduce surface protein adsorption, preventing NP recognition by the phagocyte system and thus increasing their circulation time *in vivo*.<sup>78</sup> Specifically, mPEG-NH<sub>2</sub>, was utilized and added into the reaction mixture before a regular AHA-capped Bi<sub>2</sub>S<sub>3</sub> NP synthesis. Analysis of TEM images of the mPEG-NH<sub>2</sub>-capped NPs revealed an average size of 3 nm in diameter. Their average size was approximately half the average size of the solely AHA-capped Bi<sub>2</sub>S<sub>3</sub> NPs synthesised under identical conditions, suggesting that capping with the mPEG-NH<sub>2</sub> polymer impedes increasing NP size. Overall, the effects of the ligand nature, the ligand/Bi ratio, and the mechanical grinding technique were thoroughly investigated, with the use of a planetary mill revealing potential for larger scale production of Bi<sub>2</sub>S<sub>3</sub> NPs for biomedical applications.

#### Copper

Among the various candidates for widely applicable semiconductor nanomaterials, Cu sulfide has gained momentum as a non-toxic alternative for a wide range of diverse applications, including but not limited to, photocatalysis, solar cells, energy storage devices and biomedical applications.<sup>79</sup> In a study conducted by Gock and coworkers,<sup>79</sup> the mechanochemical synthesis of CuS and Cu<sub>2</sub>S from elemental precursors was pursued. The effect of the morphology of the starting materials, their preparation method, as well as milling speed were investigated for their influence on the final particle size and morphology. Mixtures of Cu and S were milled in a 1:1 and 2:1 stoichiometric ratio, to synthesise CuS and Cu<sub>2</sub>S, respectively. The milling was conducted in air, using 18 10 mm tungsten carbide milling balls in a 47:1 ball-to-powder ratio with a rotation speed of 500 rpm and varied milling times from 10 seconds to 5 minutes. Four different types of copper and two different types of sulfur were used as reactants. Each was distinguishable in terms of morphology, specific surface area and particle size distribution.





Electrolytic types of copper which possess a needle-like morphology exhibited higher specific surface area values but smaller grain size. Meanwhile, the copper prepared in a different manner had spherical morphology, lower specific surface area and larger grain size, hence

corresponding to the higher reactivity of the first group. Regarding sulfur, the morphology of the two types used was not significantly different and its structure can be easily distorted and thus did not play as significant a role in determining final particle morphology. The morphology of the prepared copper sulfides were investigated by SEM.<sup>79</sup> Due to the high energy milling process used to prepare the powders, the NPs are highly agglomerated. This is a common mechanochemical phenomenon.<sup>79</sup> The prepared CuS appeared to be more agglomerated than the Cu<sub>2</sub>S NPs, as the agglomerated Cu<sub>2</sub>S particles contained smaller grains (Figure 2.15).

For both CuS and Cu<sub>2</sub>S NP syntheses, using a gas pressure and temperature measuring (GTM) system it was found that an explosion occurred when electrolytic copper was the copper source, while atomized copper showed no such behaviour. When using atomized copper powder, a constant increase of the temperature and the pressure was observed during the entire milling process for approximately 5 minutes.

Furthermore, PXRD patterns showed the rapid and successful synthesis of CuS using the electrolytic Cu, and a much slower progress reaction, when the other type of copper was used. The PXRD patterns further confirm the observation that the ultrafast explosive progress of the reaction is dependent upon the copper used. A trend between mean particle size and the shape of the pressure peak observed during the explosion was also identified. It was observed that the larger and narrower the peak shape, the smaller the crystallites produced. Mixed metal copper sulfides have also been synthesised, both at benchtop<sup>80,81</sup> and industrial scales,<sup>82</sup> demonstrating the scalability of such methods.

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### 2.2.8 Metal Selenides

#### Iron

In 2019, Ulbrich and Campos reported the mechanosynthesis of  $\beta$ -FeSe nanostructures upon milling elemental precursors, obtaining the Fe<sub>1.0</sub>Se, Fe<sub>1.25</sub>Se and Fe<sub>1.5</sub>Se phases through controlling the initial ratios of iron and selenium.<sup>83</sup> PXRD patterns of the resulting powders demonstrated an increase in  $\beta$ -FeSe phase upon aging the samples anywhere from 3 weeks to a year (Figure 2.16).



**Figure 2.16.** Phase progression upon aging determined by PXRD analysis for a)  $Fe_{1.0}Se$  b)  $Fe_{1.25}Se$  and c)  $Fe_{1.5}Se$  mechanochemically synthesised from Fe and Se powders.

#### Lead

As a binary IV – VI semiconductor, PbSe attracts attention for its potential in applications such as IR detectors and Pb<sup>2+</sup> ion-selective sensors.<sup>84</sup> Moreover, PbSe nanocrystals are of particular interest due to the strong quantum confinement exhibited because of the large Bohr radius of Pb. Gock and coworkers have also investigated the mechanochemical synthesis of Pb selenide NPs *via* high energy milling of lead and selenium powder in a laboratory planetary ball mill compared to its synthesis in an industrial eccentric vibratory mill.<sup>84</sup>

The mechanochemical synthesis of lead selenide from starting reactants, lead and selenium, was performed in a Pulverisette 6 laboratory mill subjected to an argon atmosphere at room temperature. Milling was conducted using a 250 mL tungsten carbide milling jar, 50 10 mm diameter balls at a rotational speed of 300 rpm testing milling times between 20 seconds and 15 minutes. In order to study the synthesis of PbSe in an industrial setting, the same reaction process was performed using an ESM 654 industrial eccentric vibratory mill, in an Ar atmosphere at room temperature. A tungsten carbide milling chamber was filled with 37 mm diameter balls to a combined mass of 17 kg, 100 g of starting element mixture and a rotational speed of 960 rpm milling between 6 and 20 minutes.<sup>84</sup>

PXRD reflections were compared to the patterns of the JCPDS patterns. Calculation of the sizes of the synthesised PbSe nanocrystallites was accomplished using the Williamson Hall analysis for deducing the particle size broadening and microstrain broadening, giving an average crystallite size of 37 nm. The Williamson Hall method operates on the principle that size broadening values and strain broadening values vary significantly with respect to Bragg angle and can be used to deduce the mean size and strain of particles in an approximate fashion. Additionally, specific surface area values were determined using low temperature N<sub>2</sub> adsorption techniques. An

increase in specific surface area with reaction time was observed and was concluded to be due to the agglomerate pores being more accessible with increased milling time. The reaction progress of the mechanochemically synthesised PbSe was observed to have an approximate completion time of 5 minutes.

The majority of the PbSe nanocrystals observed *via* SEM were well separated from the agglomerates as a result of the ultrasonic suspension. TEM images showed that the synthesised PbSe nanocrystals are idiomorphic, hence appear to be characteristically crystalline and predominantly exhibit a cubic crystallographic form. PbSe NPs ranged in diameter from a few nanometers to 80 nm, with the average size of 37 nm corresponding to the value calculated using PXRD data.

The degree of conversion from the respective elements to PbSe was found to be 97 % after 6 minutes of synthesis in the industrial ball mill. However, the size of the PbSe NPs synthesised in the industrial mill did not reach the nanoscale. The mean particle size values were determined to be 8 and 14 microns and correlated with the size of the stable aggregates formed. Nonetheless, it was concluded that mechanochemical synthesis of PbSe NPs in both the laboratory and industrial mills, was relatively efficient and fast with reaction times of 5 and 6 minutes, respectively.

#### Tin

SnSe<sub>2</sub>, has been investigated for its potential to be applied in the design of thermoelectric cooling materials but can also be applied in film electrodes, infrared optoelectronic devices, and solar cells. Šepelák and coworkers have studied a dry one-step mechanochemical synthesis of SnSe<sub>2</sub> NPs.<sup>85</sup> Different properties of the synthesised NPs that were investigated include crystalline structure, morphology, surface area as well as optical properties.

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The mechanochemical synthesis of  $SnSe_2$  was performed *via* high energy milling of tin and Se powders in a Pulverisette 6 planetary ball mill, with 31 10 mm diameter- balls, a 250 mL tungsten carbide milling chamber, tin and selenium powders, an argon milling atmosphere, and a milling time between 30 to 100 minutes. Interestingly, the specific surface area increasing with milling time of the synthesis. For specific surface area, the maximum value of 1.39 m<sup>2</sup> g<sup>-1</sup> was achieved for the SnSe<sub>2</sub> sample generated after 100 minutes of milling thus further suggesting the completion of reaction at that time. The TEM study of the synthesised SnSe<sub>2</sub> established that the sample is comprised of a hexagonal SnSe<sub>2</sub> phase and the morphology of the SnSe<sub>2</sub> nanocrystals is bipyramidal-hexagonal with particle sizes ranging from a few nm to greater than 100 nm (Figure 2.17).<sup>85</sup>



Figure 2.17. TEM image of SnSe<sub>2</sub> nanocrystals.

Indirect and direct band-gap values of 1.0 eV and 1.25 eV, respectively, were derived from UV-Vis-NIR measurements obtained for these samples (Figure 2.18).



Figure 2.18. UV-Vis-NIR optical absorption spectrum of synthesised SnSe<sub>2</sub> nanocrystals.

#### Bismuth

BiSe and Bi<sub>2</sub>Se<sub>3</sub> have been synthesised mechanochemically from elemental precursors using a tungsten carbide milling assembly.<sup>86,87</sup> Analysis by PXRD revealed that both phases are obtained after only 10 minutes of milling in a planetary mill, using bismuth and selenium powders in appropriate stoichiometric ratios. Mixed metal Cu/In/Ga diselenides have also been previously synthesised through the mechanochemical combination of elemental precursors.<sup>88</sup>

#### **2.2.8 Metal Tellurides**

#### Cadmium

Telluride-based inorganic materials have been investigated for the application of their corresponding nanomaterials in electrical and optoelectric devices.<sup>89</sup> For example, there has been significant recent interest in spectroscopic and structural studies on CdTe NPs.<sup>90, 91</sup> The majority of the work involving CdTe NPs involved preparation in either aqueous solution using thiol-based stabilizing agents,<sup>92</sup> or in high-boiling coordinating solvents.<sup>93</sup> Reagents used for such approaches

are characterised by notable toxicity, encouraging investigation of mechanochemical techniques that would avoid the need for organic capping reagents, while facilitating a more economically feasible route for large-scale CdTe NP production.<sup>89</sup>

Mechanosynthesis of CdTe was performed using high-purity cadmium and tellurium powders, milling for various time intervals using a ball-to-powder mass ratio of 20:1. PXRD analysis showed reaction completion after 8 hours of milling, due to the disappearance of key reflections for cadmium and tellurium powders, and the appearance of reflections consistent with cubic CdTe. Broadening of X-ray reflections with increased milling time was also observed due to particle size reduction with increased milling time. Using the Scherrer equation, the average particle size of uncapped CdTe NPs changes from 23 nm to 3.5 nm, upon milling for 4.5 hours and 50 hours, respectively. TEM micrographs of the uncapped, aggregated CdTe NPs (Figure 2.19) showed lattice fringe distances consistent with cubic CdTe, confirming the results of PXRD analysis.<sup>89</sup>



Figure 2.19. TEM images of the uncapped CdTe nanocrystals for milling time a) 4.5 hours and b) 20 hours.

Upon suspending the capped CdTe NPs in hexanes, the resultant colour of the solutions ranged from red, blue, green, or yellow depending on the diameter of CdTe NPs.<sup>89</sup> The capped CdTe nanocrystals were dispersed in hexane, and the solution exhibited a yellow/blue colour. After 4.5 hours of milling, NPs in solution exhibited a size range 3-12 nm, while 50 hours of milling

produced significantly smaller particles in the size range 1-6 nm, supporting the hypothesis that longer milling times produced smaller particles (Figures 2.20a,b).<sup>89</sup>



Figure 2.20. TEM images of the capped CdTe nanocrystals for milling time a) 4.5 hours and b) 50 hours.

Analysis of UV-vis spectra revealed that uncapped CdTe nanocrystals absorb in the ultraviolet wavelength range, with a large shift of the band gap from 1.475 eV (bulk) to 4.71 eV (CdTe NPs) explained by the quantum confinement effect for nanocrystals of approximately 2 nm in size. Following the capping of the CdTe NPs using the polarizing organic ligand (TOPO), the CdTe nanocrystals dispersed within solution displayed a varying colourization (ranging from yellow to blue), depending on the milling time employed. Regarding the capped CdTe NPs synthesised, their UV-Vis absorption shifted to the visible range (500–700 nm), consistent with behaviour of CdTe nanocrystals obtained by other, non-mechanochemical methods.<sup>89</sup>

#### Nickel

de Campos and coworkers expanded the synthesis of metal tellurides through the mechanochemical synthesis of nickel tellurides from elemental precursors. In 2020, their combination of nickel and tellurium powders in 3:1 and 3:2 molar ratios, furnished the Ni<sub>75</sub>Te<sub>25</sub> and Ni<sub>60</sub>Te<sub>40</sub> phases respectively.<sup>94</sup> PXRD, TEM and selected area electron diffraction (SAED) confirmed the formation of both desired Ni<sub>3-x</sub>Te<sub>2</sub> phases. Later that year, the same group reported the mechanochemical synthesis of nanocrystalline NiTe<sub>2</sub> using a similar methodology.<sup>95</sup>

#### Cobalt

The mechanochemical synthesis of  $\beta$ -CoTe was reported in 2021, by milling of cobalt and tellurium powders.<sup>96</sup> Sample analysis by PXRD indicated a CoTe phase as the major product after 6 hours of milling, with iron contamination arising from abrasion of the milling assembly becoming noticeable after 12 hours (Figure 2.21).



**Figure 2.21.** PXRD patterns showing product evolution over time. Coloured tick marks represent Bragg reflections for  $\beta$ -CoTe (red), Fe (blue), Co (magenta), and CoO (black).

Analysis of the resulting powders by TEM revealed aggregates of smaller crystallites on

the order of several hundred nanometers (Figure 2.22).



Figure 2.22. TEM image of aggregated CoTe nanocrystallites, formed after 15 hours of milling Co and Te powders together.

## 2.3 Main group complexes of Groups 13–15 (p-block)

Though underrepresented, mechanochemical metathesis and reduction chemistry leading to pblock centred complexes has shown unique potential. Brennessel, Hanusa and coworkers have employed the potassium salt of the allyl anion to obtain the corresponding *tris*-allyl aluminum analogue by milling with AlBr<sub>3</sub> (Figure 2.23).<sup>97</sup>



**Figure 2.23.** Crystal structure of  $[Al((1,3-SiMe_3)_2C_3H_3)_3]$  obtained from grinding 3 molar equivalents of  $K[(1,3-SiMe_3)_2C_3H_3]$  with 1 equivalent of AlBr<sub>3</sub>.

The mechanochemical synthesis of similar tin complexes was accomplished by milling of  $SnCl_2$ and  $K(1,3-SiMe_3)_2C_3H_3$  in a 1:3 ratio for 5 minutes at 600 rpm.<sup>98</sup> The proposed mechanism

suggests that a Sn(II) metallate is formed initially, which subsequently reduces another equivalent of  $SnCl_2$  in the presence of another equivalent of the allyl ligand (Scheme 2.5).

$$4 \text{ K}[A'] + 2 \text{ SnCl}_{2}$$

$$\bigotimes_{i=2}^{5 \text{ min}} \bigotimes_{i=2 \text{ KCl}}^{5 \text{ min}} \bigotimes_{i=1}^{6 \text{ min}} (\text{KSnA'}_{3}] + \text{SnCl}_{2} + \text{K}[A']$$

$$\{[\text{KSnA'}_{3}] + \text{SnCl}_{2} + \text{K}[A'] \}$$

$$\sum_{i=1}^{6 \text{ min}} (\text{SnA'}_{4}] + \text{Sn}^{0} + 2 \text{ KCl}$$

$$3$$

Scheme 2.5. Proposed pathway for generating  $[Sn((1,3-SiMe_3)_2C_3H_3)_4]$  obtained from grinding 4 molar equivalents of  $K[(1,3-SiMe_3)_2C_3H_3]$  with 2 molar equivalents of  $SnCl_2$ .

Similar methodology was also used to synthesise complexes of heavier Group 15 elements

arsenic and antimony.<sup>99</sup> Specifically, tris-allylarsenic and tris-allylantimony complexes were

obtained by milling the corresponding pnictogen triiodide with the K(1,3-SiMe<sub>3</sub>)<sub>2</sub>C<sub>3</sub>H<sub>3</sub> salt for 5

minutes, giving both products in >80 % yields.

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# Application of phosphorus pentoxide (P<sub>4</sub>O<sub>10</sub>) as a solid-state phosphorylating agent towards biomass and synthetic polymer functionalization

Phosphorylation is a key process, both in biology for the formation and use of adenosine triphosphate (ATP) and the phosphate backbone of DNA and RNA, as well as in chemical processes for the development of flame-retardant materials. Traditionally, phosphorus-based flame-retardants require time-intensive monomer syntheses, or the application of phosphorus based small molecule additives, physically blended with the polymer of choice to achieve the desired effect. In the context of Green Chemistry, the risk of leaching organophosphorus fillers into landfills and ultimately the environment, or the use of solvent- and energy-intensive synthetic methods, are both areas of needed improvement. The goal of this first experimental Chapter was to investigate if ball milling could be used to phosphorylate polymers and biomass in a post-synthetic fashion, using a cheap and commercially available phosphate source, phosphorus pentoxide. The presented method avoided traditional limitations, such as the inability to produce high molecular weight polymers, as solubility was not a concern for mechanochemical techniques, as well as being generally applicable to both biomass-derived and synthetic polymer substrates.

# **3.** Mechanochemical post-synthetic phosphorylation of cellulose nanocrystals and synthetic polymers

# **3.1 Abstract**

Phosphorylated polymers are versatile materials for a broad range of applications from flameretardant coatings to bioactive scaffolds. Traditionally, they are synthesized in solution using corrosive concentrated phosphoric acid and energy-intensive drying techniques. In the past decade, mechanochemistry has proven to be a valuable tool for green chemists to conduct new transformations, with minimal waste, often solvent-free. This work presents the phosphorylation of cellulose nanocrystals, poly(ethylene glycol), poly(vinyl alcohol), poly(vinyl chloride) and lignin through mechanochemical processes with phosphorus pentoxide to produce reproducible phosphorylation for potential flame-retardant applications. Through <sup>31</sup>P MAS NMR, loadings of up to 3300 mmol kg<sup>-1</sup> were determined for cellulose nanocrystals, far superior to loadings in solution around 1600 mmol kg<sup>-1</sup>, and loadings of up to 4375 mmol kg<sup>-1</sup> were obtained for synthetic polymers such as poly(vinyl alcohol).

### **3.2 Introduction**

Chemical transformations of polymers which provide high functionality while preserving their chain structure are efficient and potentially green methods to access functional materials. They are particularly appealing towards the valorization of biomass, for instance cellulose, the most abundant natural polymer on the planet, and, as such, an ideal source of renewable materials and feedstocks,<sup>1,2</sup> but also in the context of polymer recycling or upgrading. Traditionally, the introduction of chemical functionalities to polymers backbones is achieved by pre-functionalization of monomers, followed by polymerization to form the targeted material.<sup>3</sup> The

alternative approach, *i.e.* direct functionalization of a pre-made polymer, is challenging, notably because of the complex challenges posed by polymer solubilization and poorer reactivity, inspiring the development of new functionalization methodologies. Recently, mechanochemistry<sup>4,5</sup> has emerged as a method of choice in organic chemistry<sup>6,7</sup> and materials synthesis<sup>5</sup> to circumvent issues related to solubility in common solvents, selectivity or separation, while cutting overall solvent waste generation and energy demand.<sup>8,9</sup> Mechanochemical methods have been successfully developed for the design of unique pharmaceutical cocrystals,<sup>10</sup> coordination polymers and metal-organic frameworks,<sup>5</sup> and have been applied in organic<sup>6,7,11-14</sup> and biomolecular synthesis.<sup>15</sup> Very recently, it was demonstrated that mechanochemistry could be used to functionalize polymers with Schiff base moieties post-production.<sup>16</sup> Our group also reported a ball milling method to effectively functionalize poly(ethylene glycol) (PEG) with 5 different functional groups without affecting the main chain,<sup>9</sup> and a mechanochemical/aging one for the deacetylation of chitin to chitosan while maintaining high-molecular weight.<sup>17</sup>

Phosphorylation is a key transformation to access biocompatible or flame-retardant materials (FMRs), a class of chemicals able to slow the ignition and progression of fire. Regulations imposing the use of such molecules in construction, furniture, electronics and textiles have had an overall positive effect on both the human and material costs associated with fires.<sup>18</sup> A recent example of the importance of such flame-retardant materials was the collapse of the Grenfell tower in the United Kingdom in 2017, where an older style of cladding with poor flame-retardant properties was used.<sup>19</sup> However, innovation in flame-retardant materials may have different, but equally significant, human and environmental toxicity consequences. Among flame-retardant molecules (FRM),<sup>20</sup> organohalides and organophosphates have raised the most concerns,<sup>21</sup> as they leach into the environment and are detected in the atmosphere, fresh water, soils and biota.<sup>20,22</sup>

Their lipophilic nature means they bioaccumulate,<sup>23</sup> and FRMs can be detected in human breast milk and may affect cognitive development.<sup>24</sup> Traditional FRMs are typically used in the form of secondary additives to a polymer melt, without covalent bonding between the polymer and the FRM. An alternative approach is direct phosphorylation of the polymer, which imparts flameretardant functionality to the polymer while limiting or even completely preventing the possibility of leaching toxic species. In such a design for FRMs, any phosphate leaching due to hydrolysis results in innocuous phosphate species, as opposed to more concerning organophosphates.<sup>25</sup> Therefore, phosphorylated polymers present an attractive alternative to traditional halogenated FRMs. Mechanistically, the origin of flame-retardant properties in phosphorylated polymers is different from that in commonly used halogenated counterparts, which are aimed towards preventing the degradation of polymer backbone by producing halogen-free radicals that scavenge the carbene, proton and hydroxyl radicals which are deleterious to the polymer chain.<sup>25</sup> In the case of phosphate ester FRMs, heat leads to hydrolysis of ester groups and the release of phosphoric acid on the polymer surface. The H<sub>3</sub>PO<sub>4</sub> released acts as a catalyst for the dehydration of cellulose chains,<sup>26</sup> charring the surface (Scheme 3.1) and leading to the formation of a thermally-resistant char coating capable of protecting the remaining internal material at temperatures of up to 600 °C.<sup>27-29</sup>



Scheme 3.1. Proposed mechanism of thermally stable char formation of phosphorylated cellulose.<sup>26</sup>

Here, we describe the direct phosphorylation of cellulose nanocrystals (CNCs) to form materials with potential use as FRMs, as well as a preliminary investigation of a solvent-free phosphorylation of selected synthetic polymers via mechanochemical methods. The CNCs are a high aspect ratio nano-sized crystalline form cellulose, and are typically synthesized through the acid hydrolysis of pulp with inorganic acids, most frequently sulfuric acid.<sup>2,30</sup> Some of the most notable features of CNCs are their chiral nematic, or liquid crystal, behaviour in aqueous suspensions; their mechanical strength, optical properties, and unique thixotropic behaviour at higher concentration; and an active surface covered in hydroxyl groups.<sup>30</sup> In the context of flameretardant materials, surface-phosphorylated CNCs (P-CNCs) have attracted attention due to their ability to form stable films that upon exposure to fire and/or high temperatures form a protective, thermally stable carbonaceous layer.<sup>31</sup> Classically, phosphorylated CNCs are obtained *via* direct treatment of pulp with inorganic phosphoric or phosphorus acids in solution.<sup>32,33</sup> However, the hydrogen bonding which occurs between individual nanocrystals causes them to aggregate above a critical concentration or when dried. In order to limit hydrogen bonding and improve phosphate ester incorporation, molten urea was used as a solvent by Nuessle in 1956<sup>34</sup> and applied to the synthesis of flame-retardant celluloses by Inagaki in 1976.<sup>35</sup> Alternatively, pre-made CNCs can also be used as starting materials and phosphorylated as described by Kokol *et al.*, either in aqueous phosphoric acid or using urea as a molten solvent (Scheme 3.2, Route 2).<sup>36</sup> Their work investigated the surface phosphate content through the commonly used conductometric titration.<sup>37</sup> This work inspired us to phosphorylate cellulose nanocrystals using mechanochemical ball-milling. Along with biological polymers such as cellulose, other organic polymers (e.g. poly(vinyl alcohol), PVA) have also been studied as substrates for the synthesis of FRMs through phosphorylation.<sup>29,38</sup>



**Scheme 3.2.** Overview of previous phosphorylation techniques,<sup>36</sup> in comparison with this work.

In this report, we describe a simple, clean, and previously unexplored route for direct phosphorylation of CNCs as well as synthetic polymers, poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA), poly(vinyl chloride) (PVC) and the methyl ester of poly(ethylene glycol) (mPEG) by ball-milling mechanochemistry. While this route enables us to avoid the use of elevated temperatures and organic solvents, it also permitted us to use a simple, solid-state reactant, phosphorus pentoxide, as a readily available, inexpensive phosphorylating reagent. We also show that the phosphorylated CNC and polymers prepared by mechanochemistry exhibit notable flame-retardant properties, demonstrating a potential clean, solvent-free route to halogen-free FRMs. As an additional point of interest, we also describe a methodology for quantitative evaluation of the degree of phosphorylation based on solid-state NMR. For this study, the formation of phosphate ester bonds was established by <sup>31</sup>P magic angle spinning solid-state nuclear magnetic resonance (MAS ssNMR), X-ray photoelectron spectroscopy (XPS), and Fourier transform infra-red attenuated total reflectance (FTIR-ATR) spectroscopy.

#### **3.3 Results and Discussion**

#### **3.3.1** Phosphorylation of CNC

We first focused on CNC as a starting polymer to develop a mechanochemical method of phosphorylation. The choice of phosphorus pentoxide ( $P_4O_{10}$ ) as the phosphorylation reagent was inspired by the early works from Touey<sup>38</sup> and Granja *et al.*, who used this reagent in conjunction

with phosphoric acid in solution-based methods.<sup>39</sup> More recently, P<sub>4</sub>O<sub>10</sub> has been employed in the phosphorylation of lignin in THF in a process involving refluxing for up to 8 hours.<sup>40</sup> Importantly, P<sub>4</sub>O<sub>10</sub> is a solid material, so handling is safer and easier, and it has a well-defined chemical composition, allowing greater stoichiometric control over the phosphorylation process in comparison to phosphoric acid.

To develop an effective mechanochemical methodology to phosphorylate CNCs using  $P_4O_{10}$ , we have explored milling with and without additives. Specifically, previous work has demonstrated that phosphorylation of cellulosic materials is sometimes enhanced by the presence of urea<sup>34,41</sup> which assists the disruption of hydrogen bonds between cellulose nanocrystals, preventing their aggregation.<sup>35,36,42</sup> Consequently, in addition to neat milling of CNC with  $P_4O_{10}$ , we also explored milling in the presence of urea, tetramethylurea, 2-imidazolidone, and the salt urea phosphate (Chart 3.1). The additives were chosen in order to explore possible effects of steric bulk, hydrogen bonding properties and solid-state structure of the phosphorylating agent (Chart 3.1).



2-Imidazolidone Urea phosphate salt

Chart 3.1. Additives tested for their assistance in the phosphorylation of cellulose nanocrystals.

Of particular importance in developing a mechanochemical route to polymer phosphorylation is the choice of material for milling balls and jars. Stainless steel, a popular material for mechanochemical organic transformations, had to be excluded because of its sensitivity to acids.

Preliminary studies also revealed that Teflon<sup>™</sup> equipment was unsuitable; its softness leads to contamination of the final product with the jar material. Consequently, zirconia, an inert and high-density material, was used in our work.

In a typical experiment, one equivalent of freeze-dried CNC (relative to glucose monomer), ten molar equivalents of urea and one molar equivalent of  $P_4O_{10}$  were loaded into a 10 mL milling jar along with one 10 mm zirconia ball and milled in a Retsch<sup>®</sup> MM400 shaker mill for 90 min at 30 Hz. After milling, the materials were investigated by X-ray powder diffraction to establish the degree of crystallinity, as well as by a combination of <sup>31</sup>P ssNMR spectroscopy, FTIR-ATR spectroscopy and X-ray photoelectron spectroscopy (XPS) to establish the degree of substitution (D<sub>s</sub>), *i.e.* the ratio of converted -OH groups to the total number of available hydroxyl functionalities, as well as the nature of phosphorus species introduced to the polymer.

# 3.3.2 Characterisation of phosphorylated CNCs by <sup>31</sup>P MAS NMR, XPS and FT-IR

Conventionally, the amount of phosphate half-ester groups introduced to a cellulosic polymer is determined through conductometric titration<sup>37</sup> against aqueous NaOH. However, as some of the materials prepared herein were not readily suspendable in deionized water, a solid-state methodology for quantitative determination of the degree of substitution of hydroxyl groups by phosphate esters ( $D_s$ ) was developed using <sup>31</sup>P MAS ssNMR spectroscopy. Notably, while both <sup>13</sup>C and <sup>31</sup>P MAS ssNMR spectroscopies have previously been applied to confirm presence of phosphate groups and measure the crystallinity of cellulosic materials,<sup>43-47</sup> these approaches were not used for quantitative measurement of phosphorylation. In order to achieve quantitative assessment of  $D_s via$  <sup>31</sup>P ssNMR spectroscopy, MAS spectra were acquired under spinning at 13 kHz with a recycle delay of 150 s (see Chapter 8 for details). Integrals of the phosphorylation signals were compared with those in the spectrum of a known mass of ammonium dihydrogen
phosphate acquired in a separate experiment. This external quantification method is analogous to the PULCON approach to external quantification in liquid-state NMR,<sup>48</sup> permitting us to measure the amount of phosphate species present. This information was used to determine the  $D_s$  using the methodology described by Eyley *et al.* for calculating the degree of substitution on the surface in relation to the total number of available surface hydroxyl groups (see Chapter 8 for details).<sup>49</sup>

Analysis of samples produced by milling, both with and without the assistance of urea as an additive, revealed the presence of a unique signal centred around 0.3 ppm (Figure 3.1), relative to an externally run ammonium dihydrogen phosphate standard (referenced to 0.8 ppm), corresponding to phosphate ester groups bound to the cellulose.<sup>39</sup> This signal was noted in all samples with or without the assistance of urea. Interestingly, a smaller signal was observed around -12 ppm, consistent with the formation of a polyphosphate.<sup>50</sup> No phosphorus pentoxide or phosphoric acid peaks were observed, thus proving the effectiveness of washing by centrifugation to remove any unbound phosphates.



**Figure 3.1.** <sup>31</sup>P MAS NMR spectrum of mechanochemically phosphorylated CNC with the assistance of a) urea compared to b) phosphorus pentoxide. Spinning sidebands are denoted with an asterisk.

Milling of CNC and P<sub>4</sub>O<sub>10</sub> leads to a material with an average phosphate loading of 950 mmol kg<sup>-1</sup>, equivalent to  $D_s = 8$  % (see Table 3.1, Entry 1). Milling in the presence of urea, however, led to an increase in phosphate loading to 3,300 mmol kg<sup>-1</sup>, corresponding to an increase in D<sub>s</sub> to 26 % (Table 3.1, Entry 2). However, replacing the urea with more sterically hindered derivatives, which exhibited a smaller number of N-H groups available for hydrogen bonding, led again to a drop in D<sub>s</sub>. Specifically, milling with 2-imidazolidone produced a CNC material with a phosphate loading of 170 mmol kg<sup>-1</sup> ( $D_s = 1.4$  %, see Table 3.1, Entry 3), while tetramethylurea produced a phosphate loading of 660 mmol kg<sup>-1</sup> ( $D_s = 5.3$  %, see Table 3.1, Entry 4). Furthermore, milling CNC with one molar equivalent of urea phosphate salt led to a material with a very low D<sub>s</sub> of 0.08 %. This result reveals that the urea phosphate salt is not an effective reagent for mechanochemical phosphorylation of the CNC and is also not likely to be an important species in the mechanochemical reaction of CNC and  $P_4O_{10}$ . Overall, among the additives explored, urea is the most effective in facilitating the mechanochemical phosphorylation of CNC. We speculate that the notable effect of urea compared to other herein explored additives might be related to the presence of only a primary, non-substituted amide group. Importantly, the primary amide functionality is less sterically hindered and more acidic compared to secondary or tertiary amide groups of other explored additives. This should make urea a particularly suitable reagent for the formation of hydrogen bonds with in situ formed phosphoric acid, forming a stabilizing hydrogenbonded adduct and promoting phosphorylation, as presented in previous literature.<sup>34,41</sup> In contrast, the sterically more encumbered secondary and tertiary amide functionalities found in other additives would hinder hydrogen bond formation and lead to a lower degree of phosphorylation.

Table 3.1. Influence of various additives on the phosphate loading and degree of substitution  $(D_s)$  in CNC phosphorylation by milling with  $P_4O_{10}$ .<sup>a</sup>

CNC $P_2O_5$ (1 equiv.), Additive (10 equiv.)				
90 mins, 30 Hz, ZrO <sub>2</sub> jar				
10 mm ZrO <sub>2</sub> ball				
Entry	Additive	P loading / mmol kg <sup>-1</sup>	D <sub>s</sub> / %	
1	none	950 ± 250	8 ± 2	
2	urea	3300 ± 160	26 ± 1	
3	2-imidazolidone	170 ± 57	$1.4 \pm 0.5$	
4	tetramethylurea	660 ± 4	$5.34 \pm 0.03$	
5 <sup>b</sup>	urea phosphate salt	10 + 3	$0.08 \pm 0.03$	

a) mechanochemical reactions were conducted in a 10 mL zirconia jar, using a 10 mm diameter zirconia ball, milling at 30 Hz; all experiments were conducted in triplicate. b) used in equimolar amount to keep phosphate loading consistent, no phosphorus pentoxide used

The results of <sup>31</sup>P MAS NMR analysis were further validated by XPS spectroscopy. Analysis of the 2p<sup>3/2</sup> peak for phosphorus was first conducted on CNCs milled with 10 equivalents of urea and 1 equivalent of phosphorus pentoxide. A single peak was present at 134.4 eV, known for P-O-C type bonding (Figure 8.17).<sup>51</sup> The 1s peak of oxygen also showed a peak at 531.1 eV, consistent with P-O binding. (Figure 8.19) Interestingly, there was a small peak in the nitrogen spectrum at 400.6 eV (Figure 8.20) which has been previously documented for free amine groups.<sup>52</sup> This suggests that a minute amount of the urea binds to the materials surface during phosphorylation by milling.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy also evidenced the presence of a phosphate half-ester group in mechanochemically treated samples and showed proof of partial hydrolysis of the glycosidic bonds. The samples phosphorylated by milling with the assistance of urea displayed an absorption band at 1652 cm<sup>-1</sup>, which is indicative of a carbonyl stretching vibration. The presence of carbonyl moieties was further supported by the presence of an absorption band at 2895 cm<sup>-1</sup>, which corresponds to C-H stretching characteristic of aldehyde groups.<sup>53</sup> Such observations are consistent with the work of Suflet, who reported that the glycosidic bond can be cleaved and converted to the aldehyde under acidic conditions.<sup>42</sup> Mechanochemically synthesized samples also show new absorption bands at 975, 830 and 476 cm<sup>-</sup>

<sup>1</sup> (Figure 8.23). The most intense of these bands is at 975 cm<sup>-1</sup>, and is indicative of a P-OH stretch previously seen, while the 830 cm<sup>-1</sup> is close to that of previously described P-O-C bonds at 811 cm<sup>-1</sup>.<sup>42</sup>

To evaluate the efficiency of our method of phosphorylation by mechanochemical ballmilling we compared the properties of the resulting materials to products obtained following the two solution-based phosphorylation routes reported by Kokol *et al.* The first involved a suspension-based reaction in which CNCs are suspended in water and refluxed with phosphoric acid at 150 °C (Scheme 3.2, Route 1).<sup>36</sup> The second procedure using molten urea was also used as an additive, and involves first melting of urea at 140 °C, followed by dropwise addition of a 3 wt. % aqueous suspension of CNCs and a 85 % phosphoric acid solution, and heating at 150 °C for 30 min (Scheme 3.2, Route 2).<sup>35</sup>

#### 3.3.3 Crystallinity and aggregation of phosphorylated CNCs

Crystallinity and aggregation of CNCs in water suspension are key parameters directing their applicability. The crystallinity of mechanochemically phosphorylated CNCs was evaluated through PXRD analysis and was compared to that of a pristine CNC sample, as well as CNC samples modified through two solution-based phosphorylation techniques (Figure 8.24). The PXRD analysis reveals that the phosphorylation in solution has little influence on the crystallinity index (CrI) of CNC, with pristine material exhibiting a CrI of 62 %, milled CNC having a CrI of 48 % and samples obtained by phosphorylation in phosphoric acid, and in the presence of urea melt exhibiting CrI values of 59 % and 58 %, respectively. In contrast, phosphorylated CNC produced by milling with  $P_4O_{10}$  and urea showed a much lower CrI of 21 %. For comparison, we also explored the PXRD patterns for CNC samples milled only with  $P_4O_{10}$ , and only with urea, as well as samples where the additive chosen was tetramethylurea, 2-imidazolidone and urea

phosphate. Control samples milled with only  $P_4O_{10}$ , and only with urea revealed somewhat higher CrI values of 36 % and 49 %, respectively. Upon varying the additive to tetramethylurea, 2imidazolidone and urea phosphate, the CrI became 52 %, 47 % and 48 % respectively (Figure 8.24). Importantly, the loss in crystallinity upon mechanochemical phosphorylation was in all cases accompanied by the appearance of carbonyl C=O and C-H stretches in the FTIR-ATR spectra, indicating partial CNC depolymerization at the glycosidic bond. This observation was further supported by transmission electron microscopy (TEM) analysis of samples phosphorylated by milling, compared to those made using solution techniques (Figure 8.25-8.27). Notably, TEM images of CNC samples that were not treated showed significant differences in the dimensions of the resulting particles compared with those that were phosphorylated in solution or mechanochemically phosphorylated. Whereas the average length of CNC particles before treatment is around 133 nm, upon phosphorylation in solution it increases to 173 nm (Table 3.2, Entry 2). In contrast, mechanochemical phosphorylation in the presence of urea leads to a decrease in average particle length to 107 nm (Table 3.2, Entry 3). On the other hand, the average width of CNC particles following phosphorylation generally increased from ca. 7 to ca. 12 nm, regardless of whether the functionalization was conducted in solution or mechanochemically. (Table 3.2, Entries 2 & 3

s measureu t	y i Livi ioi unucated a	ind phospholylate	u CIVC, boui in solut
Entry	Sample	Length / nm	Width / nm
1	untreated CNC	133 ± 48	7 ± 2
2	solution method	173 ± 41	12 ± 4
3	mechanochemical	107 ± 46	12 ± 2

Table 3.2. Dimensions measured by TEM for untreated and phosphorylated CNC, both in solution and by milling.

By milling the CNC, thus rendering them largely amorphous, a larger number of free hydroxyl groups become available to functionalize as more surface is exposed, leading to more effective phosphorylation. Despite the loss of crystallinity, the P-CNC made using mechanochemical

milling is still suspendable up to 1 wt. % in water (Figure 3.2), which is typical for applications of cellulose nanocrystals. Notably, this opens the possibility to use mechanochemically functionalized CNC in producing surface coatings. Over the course of two weeks, the aqueous suspensions made from mechanochemically modified CNC began to settle, while those in solution remained a stable colloid. However, this only should present a problem for long-term storage of the material in suspension, not the ability to produce surface coatings.



**Figure 3.2.** Visual appearance of 1 wt. % suspensions in DI water of: a) untreated CNC material; b) CNC phosphorylated in solution using urea and phosphoric acid and c) CNC phosphorylated mechanochemically, by milling with urea and phosphorus pentoxide. The change is colour is due to partial depolymerization of the CNC substrate.

#### 3.3.4 Thermal stability and flame-retardant properties of phosphorylated CNC

A preliminary assessment of the flame-retardant properties of the phosphorylated CNC samples was performed by thermogravimetric analysis (TGA) in a dynamic atmosphere of air. The TGA measurements provided two significant parameters for flame-retardant behaviour: the average mass loss and the inflection temperatures. Notably, a lower value of the average mass loss is indicative of better thermal stability suitable for use as a flame retardant, while a lower value of the inflection temperature is also beneficial for use of a material as a flame retardant, indicating earlier formation of the protective char coating.<sup>54</sup> Table 3.3 provides a comparison between the

phosphate loading, D<sub>s</sub>, average mass loss and inflection temperature for selected materials prepared herein, and material reported in relevant prior literature.<sup>36</sup> Pristine CNC samples exhibited an almost complete mass loss up to 500 °C, with an inflection temperature of roughly 303 °C (Table 3.3, Entry 1). In the case of Espinosa's work, Kraft pulp underwent phosphoric acid hydrolysis to produce phosphorylated CNC with a loading of 3.95 mmol kg<sup>-1</sup>, determined by conductometric titration (Table 3.3, Entry 2).<sup>55</sup> These samples have a mass loss of 87.8 % with a later inflection temperature of 325 °C. Due to this later inflection temperature, it is unclear whether these samples are protected through the formation of a protective char layer, which should form at earlier temperatures, or if they are flame-retardant through a different mechanism. Kokol et al. produced phosphorylated CNC by functionalizing without any additive and with the assistance of molten urea, using 85 % phosphoric acid as a phosphorylating agent heating under reflux. (Table 3.3, Entries 3-4). The sample phosphorylated without urea showed a mass loss range from 60-70 % compared to untreated with an inflection temperature at 230 °C, implying that some char could be forming at a lower temperature, protecting the material. The introduction of urea (Table 3.3, Entry 4) to their solution-based synthesis results in a phosphate loading less than half as much compared to the phosphorylated CNC made without any additive, with loadings of 1038 and 435 mmol kg<sup>-1</sup>, respectively. The inflection temperature of the samples treated with urea were also higher than those samples made with no additive, at 350 °C and 230 °C respectively. Mechanochemically produced P-CNC with urea (Table 3.3, Entry 7) afforded samples featuring good mass loss of 70 %, comparable to past work, with an excellent inflection point of 172 °C.

Entry	Method	P Loading / mmol kg <sup>-1</sup>	Ds* / %	Mass loss / %	Inflection Temp. / °C
1	Untreated CNC	N/A	N/A	96 ± 1	302.9 ± 0.1
2	Espinosa et al.56	$3.95 \pm 0.80$	0.032 ± 0.006	87.8	325
3	Kokol <i>et al. (no</i> additive) <sup>36</sup>	$1038.0 \pm 0.8$	8.38 ± 0.01	60-70	230
4	Kokol <i>et al.</i> (molten urea) <sup>36</sup>	435 ± 7	$3.5 \pm 0.1$	45-55	350
5	No additive	1200 ± 550	10 ± 4	96 ± 2	493 ± 4
6	Molten urea	1600 ± 150	13 ± 1	63 ± 1	242 ± 1
	Mechanochemical				
7	phosphorylation	3300 ± 160	26 ± 1	70 ± 1	$172.0 \pm 0.1$

Table 3.3. Phosphate loadings and relative thermal stabilities of solution methods in comparison to this work.

\* D<sub>s</sub> values for literature references were calculated based on the provided information

To further confirm the potential for mechanochemically phosphorylated cellulose nanocrystals as FRMs, qualitative flame-retardant testing was conducted by exposing coated spruce wood substrates to the flame of a butane torch. The wood samples without any modification underwent ignition after 0.57 seconds of exposure to the torch (Figure 3.3a), while coating the sample with 1 wt. % unmodified CNC decreased the ignition time to 0.48 seconds (Figure 3.3b). However, treating the wood samples with mechanochemically phosphorylated CNC delayed the ignition to 1.35 seconds (Figure 3.3c), revealing a significant flame-retardant potential. This implies that the addition of a coating of CNC increases the ignition rate of the surface when exposed to a flame, most likely due to the increased surface area available from a CNC coating. After five seconds of exposure, the untreated sample and sample coated with untreated CNC had a local hotspot directly at the point of contact with the flame, while the sample treated with P-CNC showed a dispersion of the heat over the whole substrate surface. The fact that the addition of a 1 wt. % coating of P-CNC to the wood surface increased the ignition time 3-fold from 0.48 to 1.35 seconds shows that P-CNC produced through mechanochemical means can act as an effective flame-retardant coating for wood samples. Similar phosphorus or P-N containing coatings have shown ignition times ranging from 37 to 237 s,<sup>56</sup> showing room for improvement for this proof-of-concept study.



**Figure 3.3.** Qualitative testing of coatings for a) uncoated spruce b) spruce coated with 1 wt. % untreated CNC and c) spruce treated with 1 wt. % phosphorylated CNC by milling.

#### 3.3.5 Mechanochemical phosphorylation of synthetic polymers

The ability to effectively phosphorylate CNCs using phosphorus pentoxide under mechanochemical conditions lead us to conduct a preliminary investigation into applying this methodology to the phosphorylation of selected synthetic polymers, as well as Kraft lignin. As substrates for this study, we focused on poly(ethylene glycol) (PEG), poly(ethylene glycol methyl ester (mPEG), poly(vinyl alcohol) (PVA) and Kraft lignin. The polymer samples were milled in 10 mL zirconia jars using one zirconia ball of 10 mm diameter, and the resulting products after milling were washed with methanol and dried *in vacuo*. Phosphate loadings in the mechanochemically prepared materials were measured using <sup>31</sup>P MAS NMR spectroscopy, which revealed a phosphate loading of 210 mmol kg<sup>-1</sup> for and PEG (Table 3.4, Entry 2) and 207 mmol kg<sup>-1</sup> (Table 3.4, Entry 3) for mPEG. These values are lower than observed for cellulose, which is consistent with the availability of only 2 terminal hydroxyl groups per each polymer chain in PEG and mPEG. In contrast, mechanochemical phosphorylation of PVA resulted in much higher monophosphate loading of 4375 mmol kg<sup>-1</sup>, with different mono- and polyphosphate species observable using <sup>31</sup>P MAS ssNMR as signals at ca. -12 and -25 ppm (Table 3.4, Entry 4). A high

phosphate loading of 2186 mmol kg<sup>-1</sup> was also observed for PVC. Lignin showed phosphate loadings at 284 mmol kg<sup>-1</sup> most likely due to the large number of free hydroxyl groups, with smaller peaks corresponding to bis- and tris- polyphosphates (Table 3.4, Entry 6).

Entry	Starting polymer	Product	P Loading mmol kg <sup>-1</sup>
1	CNC	Phosphorylated CNC	3300 ± 160
2	$H\left[0, \mathcal{A}_{n}\right]_{n}^{O'}H$ M <sub>n</sub> : 2000	HO, HO, O, P, O O <sup>C</sup> OH n OH	210
3	$H_{3C}\left[0, \dots, H\right]_{n} H_{n}: 2000$	$H_3C \left[ O \right] \cap \left[ P \right] O \cap OH$	207
4	(OH) (Mn: 88 000	O <sub>≤P</sub> OH HÓ O ↓ ↓ n	4375
5	$\begin{bmatrix} CI \\ I \end{bmatrix}_n$	о <sub>р</sub> он но́ро т	2186
6 <sup>a</sup>	Kraft lignin	Phosphorylated lignin	284

Table 3.4. Mechanochemical phosphorylation of natural and man-made polymers.

Typical reaction conditions: Polymer (0.05 mmol, 180 mg) and  $P_2O_5$  (0.05 mmol, 12.8 mg) were loaded into a 10 mL ZrO<sub>2</sub> fitted with 1 ZrO<sub>2</sub> ball and milled for 90 min at 29.5 Hz. <sup>a</sup>: Equivalency of Kraft lignin done by mass, due to uncertainty of exact molecular weight

Although not all functional properties of mechanochemically phosphorylated synthetic polymers have been determined yet, these preliminary results demonstrate the general applicability of phosphorus pentoxide as a phosphorylating reagent under mechanochemical conditions.

# **3.4 Conclusions**

The application of mechanochemistry has already shown great promise in the field of materials science. In this Chapter, I expanded this repertoire by including the direct functionalization by phosphate esters of polymers as greener alternatives to traditional halogenated materials. By doing so through mechanochemical means, the process is further made greener by eliminating solvent waste, as well as a major pathway through which these materials can be leached into the environment. Quantitative <sup>31</sup>P MAS NMR allowed us to determine the amount of phosphate in the final product. In addition, <sup>31</sup>P MAS NMR and TGA demonstrated that the mechanochemical phosphorylation treatment is successful in rendering the cellulose nanocrystals more thermally

stable. Flame retardance was evaluated for wood coating, because of the accessibility of standard samples, yet experiments are underway for other applications to other hydrophilic surfaces.

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Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER)

# Investigation of sodium phosphide (Na<sub>3</sub>P) as a low-coordinate phosphorus source for solid-state mechanochemical, bottom-up nanoparticle synthesis

During the investigation of applying phosphorus pentoxide as a solid-state phosphorylating reagent, I also became interested in the application of sodium phosphide (Na<sub>3</sub>P) as a solid, easy to prepare, low oxidation state "P" source. Typically, sodium phosphide was employed as a steppingstone towards other low coordinate phosphorous reagents (*i.e.* NaPH<sub>2</sub>, solid source of PH<sub>3</sub>, NaOCP), but alkali metal phosphides had very rarely been used directly, largely due to their insolubility. We then set out to investigate whether sodium phosphide could be used directly as a nucleophilic reagent, readily amenable to mechanochemical reactions for the formation of metal phosphide nanomaterials. This direction provided a unique successor to the work conducted earlier by our group on the mechanochemical synthesis of binary bismuth sulfide nanoparticles, while further expanding the available landscape of reagents for phosphorus-centered mechanochemistry.

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# 4. Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER)

# 4.1 Abstract

The photocatalytic (PC) splitting of water into oxygen and hydrogen has attracted considerable attention in the last decade. Despite the promise of hydrogen gas as a new energy resource, the environmentally-friendly design of viable catalysts with good morphological and size control remains a continual challenge. Of the many classes of available catalysts, metal phosphides are a low-cost and potentially accessible option as catalysts for this reaction, compared to the traditionally used precious metal catalysts. However, the synthesis of metal phosphide nanomaterials currently involves the use of highly reactive phosphorus sources at high temperatures in organic solvents. Herein, we demonstrate the application of sodium phosphide as an excellent solid-state phosphorus source for the synthesis of nickel phosphide nanoparticles below 3 nm in diameter, a size range previously unheard of for mechanochemical synthesis of metal phosphides. These nanoparticles in turn showed success for the hydrogen evolution reaction, using graphitic carbon nitride as a photocatalytic support, generating 233.9 µmol g<sup>-1</sup> h<sup>-1</sup> of hydrogen, using broad spectrum light at room temperature after only 3 hours, as well as being readily recyclable and reusable, without any decrease in reactivity. This mechanochemical method shows a mass intensity (MI) value over 2.5 times lower than traditionally used solution-based methods, even after workup and washing of the product. Upon scaling up the reaction to a 2.5

Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) gram scale, we were able to further improve the MI to 3 times lower than traditional solvent based methods, while reducing the energy demand over 18-fold.

# **4.2 Introduction**

The research and use of metal-based quantum dots has shown great potential in applications ranging from medical imaging,<sup>1,2</sup> as optical materials<sup>3</sup> and catalysts, including water splitting,<sup>4</sup> for the production of hydrogen as an alternative fuel source.<sup>5</sup> Various environmentally and energy conscious methods have been employed to produce single atom or transition metal sulfide<sup>6</sup> catalysts to reduce overall cost compared to the traditionally employed supported platinum catalysts. In particular, transition metal phosphide nanoparticles (TMP NPs) have attracted attention as recoverable, cost effective catalysts for hydrogen evolution reaction (HER),<sup>7-10</sup> hydrodesulfurization,<sup>11-13</sup> hydrodenitrogenation,<sup>14,15</sup> hydrodeoxygenation<sup>16-19</sup> along with a recent example of photocatalytic C-C bond forming reactions.<sup>20</sup> Among these, the most promising have been metal phosphide nanoparticles based on earth-abundant metals such as iron, cobalt and nickel.<sup>9</sup> Two main synthetic approaches have been investigated for the synthesis of metal phosphide nanoparticles, specifically those based on nickel. First are methods involving the thermal decomposition of premade transition metal phosphine or phosphite complexes,<sup>21</sup> affording well defined metal phosphide NPs, as shown by the Brock<sup>13</sup> or Hu<sup>10</sup> groups. Second, ready-made zero valent metal nanoparticles are reacted with zero-valent phosphorus sources, such as white phosphorus (P<sub>4</sub>), as seen in the work of Mézailles and coworkers (Scheme 4.1).<sup>22</sup> However, both types of approaches employ phosphorus-containing compounds that are either hazardous, such as P4,<sup>21,23</sup> or require a large amount of energy input to activate them, such as trioctylphosphine (TOP).<sup>7,21,23,24</sup> While red phosphorus can also be employed as a precursor, its use requires significantly longer runtimes (20-40 hours),<sup>25,26</sup> often in a large excess of solvent.

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Mechanochemistry has been increasingly researched as an effective synthetic method to access a wide range of materials,<sup>27</sup> including polymers,<sup>28-31</sup> perovskites<sup>32</sup> and metal organic frameworks (MOFs).<sup>33-35</sup> Mechanochemistry is associated with sustainability benefits such as the reduced use of bulk solvent and lower input energy, being listed by IUPAC as one of the Top 10 chemical innovations towards a sustainable future.<sup>36</sup> The application of mechanochemistry to the area of main-group and phosphorus chemistry has been gaining gradual traction.<sup>37</sup> This includes the synthesis of regiospecific phosphazanes,<sup>38</sup> or sterically encumbered phosphazanes whose synthesis was only achieved using ball-milling techniques.<sup>39</sup> This background work gave a strong precedent for the application of mechanochemistry towards the activation of a simple, metastable phosphide source, namely Na<sub>3</sub>P, which was both easy to synthesize and handle under air-free conditions and yet, could be activated at room temperature. Alkali phosphides like sodium phosphide have long been known, both their fundamental study in main-group structure and bonding, as well as solid forms of phosphine gas by hydrolysis.<sup>40</sup> Early solid-state metathesis work indicated that light grinding of early transition metal halides (TaCl<sub>5</sub>, NbCl<sub>5</sub> and MoCl<sub>5</sub>) with sodium phosphide can lead to the formation of transition metal phosphides, but in these cases, only the bulk material was observed.<sup>41</sup> This early work, as well as the mechanosynthesis of bulk metal phosphides using elemental precursors, in which metal powders are milled together with red phosphorus over longer timescales (3-40 hours),<sup>42-44</sup> are appealing approaches to access these important materials. Yet the control over the structure of such materials at the nanoscale is absolutely essential, in particular for applications towards catalysis in which high surface area for better reactivity is crucial or applications relying on tuneable optical properties.<sup>45</sup>

Mechanochemistry has been proven a powerful means to access heterogeneous catalysts through more benign pathways,<sup>46,47</sup> including nanoparticles (NPs) of precious metals<sup>48</sup> or binary

Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) metal sulfide quantum dots.<sup>49-53</sup> Mechanochemical methods of metal sulfide synthesis were shown to allow access to a variety of NP shapes, such as nanorods of copper sulfide<sup>54</sup> and has even been shown to be a viable synthetic method towards the semi-industrial synthesis of quaternary metal sulfides for photovoltaic applications.<sup>55</sup> It has also been used to make bioinspired nanoparticle composites for both oxidation and water-splitting, employing titania supported proteins<sup>56</sup> and premade silver nanoparticles on a carbon nitride support with hemoglobin proteins respectively.<sup>57</sup> Good size and shape control is often obtained through the use of a bottom-up method, in which the NP precursors are milled with a suitable ligand, typically containing long alkyl chains.<sup>58</sup> Herein we describe a mechanochemical approach for the synthesis of ultrasmall nickel phosphide NPs using a novel bottom-up approach in the presence of long chain amines and their potential use as water-splitting cocatalysts paired with graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>).



Scheme 4.1. Select examples of nickel phosphide nanoparticle synthesis, both in solution, as well as mechanochemically.

# **4.3 Results and Discussion**

#### 4.3.1 Effect of ligand chain-length and ligand loading

The herein presented synthesis of nickel phosphide nanoparticles is based on a general approach involving milling of anhydrous nickel chloride, sodium phosphide and a capping ligand. In a typical experiment, the reaction components were milled together in a zirconia milling jar with a 10 mm zirconia ball for 90 minutes at 30 Hz. The samples were then left sealed and allowed to age at room temperature for 18 hours prior to washing via centrifugation and drying *in vacuo*.

Chapter 4 - Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) Characterization was conducted using Transmission Electron Microscopy (TEM), Energy-Dispersive X-Ray (EDX) Spectroscopy, X-ray Photoelectron Spectroscopy (XPS) and Powder Xray diffraction (PXRD) to evaluate the size, morphology and crystallinity of the nickel phosphide phases formed by milling. We tested two ligand parameters for their influence on the final size and stability of the produced particles: 1) the chain length of the alkyl amine ligands; 2) the binding strength of each ligand, by testing both traditionally used amines, as well as phosphines. The choice of amines was based on past successful experience in our group for the mechanochemical formation of Au and  $Bi_2S_3$  NPs.<sup>48,49</sup> In these examples, it was believed that the lability of the metalamine bond, contributed to growth control. Initial exploration of a shorter (C15) pentadecylamine ligands confirmed the ability to obtain nanoparticle material, albeit with broad particle size distributions of  $3.5 \pm 1.2$  and  $4.8 \pm 2.1$  nm when using 2 and 5 molar equivalents in the reaction respectively (Table 4.1, Entries 1 and 2; Figures 9.6 and 9.7). Increasing the chain length from C15 to C16, by using 2 or 5 molar equivalents of hexadecylamine produced nanoparticles of  $3.5 \pm$ 0.8 nm and  $5.4 \pm 1.3$  nm diameters, respectively (Table 4.1, Entries 3 and 4; Figures 9.8 and 9.9). The use of heptadecylamine, a C17-substituted amine, provided more consistent outcomes of the mechanochemical synthesis, giving particles with an average diameter of  $5.0 \pm 2.1$  nm and  $2.8 \pm$ 0.6 nm for 2 and 5 molar equivalents respectively (Table 4.1, Entries 5 and 6; Figures 9.10 and Figure 4.1). Traditionally used liquid ligands such as oleylamine (Table 4.1, Entry 7; Figure 9.11) and trioctylphosphine (TOP) (Table 4.1, Entries 8 and 9; Figure 9.12 and 9.13) were also tested. Milling with oleylamine produced discrete yet aggregated particles, with average particle size of  $3.0 \pm 0.8$  nm. When using TOP, a mixture of both small, aggregated particles, as well as larger, more discrete particles were seen, indicating slower rates of nucleation compared to heterogenous nucleation and particle growth. The presence of Ni(0) was also detected by XPS (Figure 9.18b)

Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) suggesting TOP was reducing the NiCl<sub>2</sub> at a faster rate compared to phosphide formation, also supported by the smaller shoulder as shown in the phosphorus focused scan compared to the samples made with alkyl amine ligands, for which the signal is more distinct (Figure 9.18a). In all cases using alkylamine ligands, particles showed the presence of both Ni and P, at binding energies of 7.5 and 2 keV respectively, as proven through EDX analysis (Figure 9.17). Since the use of 5 molar equivalents of heptadecylamine consistently gave particles with diameters below 3 nm, offering more available surface area for catalytic activity, we focused on this amine as the standard ligand in all subsequent tests.



**Figure 4.1.** TEM images (a) and b)) and histogram of particle size distribution (c) of nickel phosphide nanoparticles made using 5 equivalents of heptadecylamine ligand, using a 3:2 ratio of NiCl<sub>2</sub> and Na<sub>3</sub>P (Ni<sub>x</sub>P<sub>y</sub>-5-C17).

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Entry	Sample name	Ligand	Ligand equivalents	Particle size / nm
1	Ni <sub>x</sub> P <sub>y</sub> -2-C15	Pentadecylamine	2	3.5 ± 1.2
2	Ni <sub>x</sub> P <sub>y</sub> -5-C15	Pentadecylamine	5	4.8 ± 2.1 <sup>a</sup>
3	Ni <sub>x</sub> P <sub>y</sub> -2-C16	Hexadecylamine	2	$3.5 \pm 0.8$
4	Ni <sub>x</sub> P <sub>y</sub> -5-C16	Hexadecylamine	5	5.4 ± 1.3
5	Ni <sub>x</sub> P <sub>y</sub> -2-C17	Heptadecylamine	2	5.0 ± 2.1
6	Ni <sub>x</sub> P <sub>y</sub> -5-C17	Heptadecylamine	5	$2.8 \pm 0.6$
7	Ni <sub>x</sub> P <sub>y</sub> -10- OAm	Oleylamine	10	$3.0 \pm 0.8$
8	Ni <sub>x</sub> P <sub>y</sub> -2-TOP	TOP	2	Mix of aggregates and larger particles
9	Ni <sub>x</sub> P <sub>y</sub> -5-TOP	TOP	5	Mix of aggregates and larger particles

**Table 4.1.** Effect of alkyl amine chain length as well as ligand equivalency on final metal phosphide particle sizes.

a: A mixture of free and aggregated particles were noted by bright field TEM microscopy

The surface composition of  $Ni_{x}P_{y}$ -5-C17 was validated through XPS analysis. The survey scans showed the presence of oxygen, nickel, and phosphorus throughout the materials surface, which supports the formation of nickel phosphate, alongside residual sodium, and chlorine peaks. stemming from sodium chloride by-product still on the surface (Figure 9.19). The XPS analysis indicated a nickel phosphide phase with Ni–P covalent bonds. Notably, the observed binding energy of Ni 2p (852.88 eV, Figure 4.2a) is higher than that of Ni metal (852.6 eV) while the observed binding energy of P 2p (129.98 eV, Figure 4.2b) is red-shifted compared to that of the elemental P (around 130 eV), revealing a Ni<sup> $\delta+P^{\delta-}$ </sup> electronic state.<sup>59</sup> The nickel-focused scan also showed two additional signals at 856.28 and 873.88 eV, matching closely with previously reported peaks of Ni-O bonds, due to partial surface oxidation (Figure 4.2a).<sup>60</sup> This surface oxidation was also validated by the phosphorus-focused scan of the 2p orbital with a second maximum at 133.28 eV (Figure 4.2b).<sup>61</sup> Looking also to the oxygen 1s scan, two major peaks can be seen, the first at 531.38 eV has been well documented as the -OH signal for both hydroxyl and P-OH groups on the surface (Figure 4.2c).<sup>62,63</sup> The carbon focused 1s scan (Figure 4.2d) showed 3 distinct peaks, the first at 284.88 and 286.28 eV corresponding to the C-C and C-N bonds found in the surface Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) capping alkyl amine ligands. The last peak at 288.88 eV is indicative of a C=O bond, most likely due to surface absorbed CO<sub>2</sub> for their storage under ambient conditions.<sup>62</sup>



**Figure 4.2.** XPS focused scans of a) nickel 2p, b) phosphorus 2p, c) oxygen 1s and d) carbon 1s orbitals of freshly made of nickel phosphide nanoparticles made using 3 equivalents of nickel chloride, 2 equivalents of sodium phosphide and 5 equivalents of heptadecylamine ligand ( $Ni_xP_y$ -5-C17).

The surface functionalization of the nickel phosphide nanoparticles made by milling was also confirmed using ATR-FTIR. Specifically, analysis of the dried powder catalyst revealed a pair of bands at 2360 cm<sup>-1</sup> and 2340 cm<sup>-1</sup> indicative of C-H stretches found in the surface alkyl amine ligands, as well as a large distinct signal at 1057 cm<sup>-1</sup>, indicative of the P=O double bond vibration due to partial oxidation (Figure 9.24).<sup>64</sup>

The organic/inorganic ratio in the mechanochemically synthesized nickel phosphide NPs was investigated using TGA (Figure 9.26), revealing that 67 % was composed of inorganic matter while the rest was constituted of the ligand shell, shown in three distinct regions. The first from 25 to 225 °C can be attributed to the loss of surface water (13.5 % loss), the second from 225-375 °C

Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) which we hypothesize to be the thermal decomposition of the heptadecylamine ligand on the surface (8.5 % loss), thus coating the surface in a thin carbon layer. The final loss beyond 375 °C is the thermal decomposition of that subsequent carbon layer (10.9 % loss).

#### **4.3.2** Effect of varying the aging time on particle formation

Following our groups previous work on the mechanochemical synthesis of both gold and bismuth sulfide NPs,<sup>48,49</sup> it was noted that the impact and shear forces imposed by milling only worked to activate the precursors, while aging the samples allowed for the self-assembly of discrete NPs. We set out to investigate this effect for the synthesis of ultrasmall nickel phosphide NPs by following the same milling procedure, this time only aging for 1, 3 or 6 hours.

Visual analysis of the samples following milling, and aging showed black powders formed in all three cases, with no visual difference seen when varying the aging time. While further analysis by TEM showed the generation of some ultrasmall particles in each case, samples were largely made of bulk material, with the ultrasmall particles being a rarer exception (Figures 9.14-9.16). This supports the hypothesis that aging under air-free conditions for 18 hours ensures the consistent formation of ultrasmall, monodisperse particles.

### 4.3.3 Phase control and crystal structure

Analysis of mechanochemically prepared samples by PXRD did not reveal any Bragg reflections matching Ni<sub>2</sub>P patterns described in the literature (Figure 9.20)<sup>65</sup> The lack of crystallinity or X-ray reflections for a specific phase can be attributed to the minute size of particles overall, which can lead to significant broadening of diffraction signals, to the point where they become non-distinguishable from the background noise.<sup>49</sup>

Next, we explored how the stoichiometry of precursors would influence the final phase of NPs. Initially, our reactions focused on using a 3:2 molar ratio of NiCl<sub>2</sub> to sodium phosphide,

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Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) typically in the presence of 5 molar equivalents of our alkylamine capping ligand. However, other stoichiometric ratios were tested to investigate if specific, potentially more kinetically favoured phases of nickel phosphide NPs could be isolated. This investigation began with the testing of Ni:P stoichiometric ratios of 2:1 and 5:4, in the attempt to make the thermodynamically favored Ni<sub>2</sub>P as well as the catalytically relevant Ni<sub>5</sub>P<sub>4</sub> phases.<sup>66</sup> Upon milling together anhydrous NiCl<sub>2</sub> and Na<sub>3</sub>P in a 2:1 stoichiometry, a black powder was produced. The PXRD pattern for these samples was featureless, indicating the formation of an amorphous product (Figure 9.20). Apart from the samples originally tested with a 3:2 stoichiometric ratio of Ni:P, we also investigated how changes to the initial ratio of nickel and phosphide sources would affect the reaction. However, all subsequently tested samples showed no distinct Bragg reflections for either Ni<sub>2</sub>P, Ni<sub>5</sub>P<sub>4</sub>, or NiP<sub>3</sub> phases, indicating that changes to the initial reaction stoichiometry led to amorphous samples (Figure 9.23).

Information on the composition of the produced NPs was subsequently obtained *via* XPS, enabled by their diameters being below 3 nm. The survey scans of the nickel phosphide nanoparticles, both the small scale and gram scale mechanochemical syntheses, were used to determine the stoichiometries (Table 9.1). For the nickel phosphide made in the shaker mill, the determined stoichiometry was shown to be  $Ni_{2.3}PO_{6.3}$ . This supports our hypothesis that the formed cores have a  $Ni_2P$  stoichiometry, with a partially oxidized phosphate surface, while excess oxygen is seen as a result of surface adsorbed CO<sub>2</sub> and H<sub>2</sub>O.

## 4.3.4 Multigram-scale synthesis of Ni<sub>x</sub>P<sub>y</sub>-5-C17

We were successful in scaling up our synthesis using a planetary mill, up to a 2.5 gram scale. XPS analysis of the scaled-up product also showed the presence of Ni, P, O and C as seen before as well as Na and Cl, similar to the small-scale survey scan (Figure 9.20). The focused P 2p showed

Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) peak energies at 128.88 eV and 132.68 eV closely matching the energies seen for the small-scale synthesis (Figure 9.21a). This story was also true for the Ni 2p focused scan, with key peak energies at 855.08 eV, 861.28 eV, 872.68 eV and 881.28 eV (Figure 9.21b), with a very good agreement with our small scale XPS data. The stoichiometry was determined to be Ni<sub>1.9</sub>PO<sub>8</sub>, based on XPS survey data. The series of results we obtained from XPS on the NP phase strongly suggest that we have a Ni<sub>2</sub>P core, covered with a thin shell of partially oxidized material. For simplicity, from now on, we will call Ni<sub>x</sub>P<sub>v</sub>-5-C17 samples Ni<sub>2</sub>P.

#### 4.3.5 Deposition of mechanochemically synthesized Ni<sub>2</sub>P onto g-C<sub>3</sub>N<sub>4</sub> and characterization

An initial series of catalysts were synthesized through a direct mixing of Ni<sub>2</sub>P powder with g-C<sub>3</sub>N<sub>4</sub>, by combining 1 gram of bulk g-C<sub>3</sub>N<sub>4</sub>, with 0.03 grams of Ni<sub>2</sub>P powder in anhydrous ethanol for 30 minutes, followed by drying and annealing at either 300 °C (samples CN-NiP-300) or 400 °C (samples CN-NiP-400, Figure 9.1). A second series of hybrid catalysts was made by first conducting a ligand exchange on the Ni<sub>2</sub>P cocatalyst to make them more water soluble. This was done by first sonicating 300 mg of Ni<sub>2</sub>P powder in a tetraethylammonium hydroxide solution (1 g in 1:1 ethanol : water mixture, v/v) for 30 min before stirring for 24 h. The particles were then precipitated using 200 mL of acetone several times before resuspending in water Figure 9.3). This suspension was then added to a solution of g-C<sub>3</sub>N<sub>4</sub>, which has been protonated with 1 M HCl, (Figure 9.2) and stirred for 12 h before annealing the final product at 400 °C for 4 hours (Figure 9.4). Two varieties of composite catalyst were made using this method, the first, which was washed by centrifugation prior to annealing, with each annealing temperature listed at the end (for example, a sample centrifuged and then annealed at 300 °C is denoted CN-NiP-Ex-300, see Figure 9.4) with the second series being annealed directly after drying at 60 °C, without any centrifugation (denoted CN-NiP-Im-300 if annealed at 300 °C, see Figure 9.4). Once the Ni<sub>2</sub>P nanoparticles had Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) undergone ligand exchange and were mounted on the g-C<sub>3</sub>N<sub>4</sub> support, their morphology, surface chemistry and thermal stability were further investigated by TEM, XPS, ATR-FTIR and TGA. Analysis of the Ni<sub>2</sub>P onto g-C<sub>3</sub>N<sub>4</sub> composite photocatalyst by XPS revealed partial oxidation of the Ni<sub>2</sub>P NPs (Figure 4.3a-c), showing the presence of phosphorus in the form of surface phosphates as shown by the signal in the focused scan of the phosphorus 2p orbital at 133.38 eV (Figure 4.3b), similar to the as-made particles. The surface oxidation is likely due to exposure to air. The carbon focused scan also showed predominantly peaks which correspond to the g-C<sub>3</sub>N<sub>4</sub> photocatalyst support (Figure 4.3d).



Figure 4.3. XPS focused scans of a) nickel 2p, b) phosphorus 2p. c) oxygen 1s and d) carbon 1s orbitals of sample CN-NiP-Im-300.

The incorporation of the Ni<sub>2</sub>P NP cocatalyst was also evident in ATR-FTIR, although largely overshadowed by the stretches of the  $g-C_3N_4$  support (Figure 9.25). The resulting composite showed no significant thermal loss until 500 °C under a nitrogen atmosphere (Figure

Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) 9.27) with a final calculated residue after exposure up to 800 °C of 2.9 %, correlating well with the initial loading of 3 wt. % Ni<sub>2</sub>P cocatalyst.

To confirm the proximity of nickel, phosphorus, and oxygen in the cocatalyst, elemental mapping of the as-made and supported nickel phosphide was conducted using high-angle annular dark-field imaging (HAADF). Firstly, the freshly made Ni<sub>2</sub>P NP showed a good intermixing of nickel, phosphorus, and oxygen (Figure 4.4a). This data, paired with XPS data, supports the hypothesis that the nascent cocatalyst consists of a Ni<sub>2</sub>P core, partially coated with a nickel phosphate hydroxide shell, which has been previously shown to occur upon exposure of Ni<sub>2</sub>P to air.<sup>61</sup>



**Figure 4.4.** HAADF images of (A) as-made  $Ni_2P$  ( $Ni_xP_y$ -5-C17) showing a dark-field image (HAADF) in white as well as element-focused scans for nickel (red), phosphorus (green), and oxygen (blue) and (B) as-made CN-NiP-Im-300 showing a dark-field image (HAADF) as well as element-focused scans for nickel (red), phosphorus (green), and nitrogen (magenta).

Similar analysis was also conducted on CN-NiP-Im-300 to confirm the thorough incorporation of

Ni<sub>2</sub>P NPs within the photoactive g-C<sub>3</sub>N<sub>4</sub> support. Localized domains of Ni<sub>2</sub>P are visible throughout

the support (Figure 4.4b).

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# 4.3.6 Photocatalytic water-splitting using Ni<sub>2</sub>P onto g-C<sub>3</sub>N<sub>4</sub>

Next, we conducted hydrogen evolution tests by suspending 50 mg of the hybrid nanocatalyst and 5 g of triethanolamine in 100 mL of pure water in an oxygen-free closed reactor. The reactor was irradiated using 100 mW cm<sup>-2</sup> of simulated sunlight using a broad-spectrum xenon lamp and collecting the evolved hydrogen gas using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) to evaluate the hydrogen evolution efficacy of the catalyst (Figure 9.5). As seen in Figure 4.6, CN-bulk and CN-NiP-300 exhibited negligible rates of hydrogen evolution. As the temperature of the argon treatment increased to 400 °C (CN-NiP-400), a significant evolution rate of H<sub>2</sub> was obtained, reaching 34.7  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>. This result reveals the argon treatment temperature and, especially, the introduction of Ni<sub>2</sub>P NPs as cocatalyst are essential to activity. A possible mechanism of the photocatalytic H<sub>2</sub> production on Ni<sub>2</sub>P supported g-C<sub>3</sub>N<sub>4</sub> photocatalyst is proposed in Figure 4.5a. Under the light illumination, electrons and holes separate and accumulate respectively in the conduction band (CB) and the valence band (VB) of g-C<sub>3</sub>N<sub>4</sub>. Electrons transfer to Ni<sub>2</sub>P NP to initiate the H<sub>2</sub>O reduction and form H<sub>2</sub>, while the holes are consumed by TEOA. Due to an electronic structure similar to noble metals (e.g. Pt),<sup>67</sup> Ni<sub>2</sub>P NPs can act as sinks to effectively trap photogenerated electrons from g-C<sub>3</sub>N<sub>4</sub>, leading to enhanced charge separation. Moreover, the distinctive surface allows these NPs to be efficiently active sites for catalytic reduction of H<sub>2</sub>O into H<sub>2</sub>. As previously noted, XPS analysis revealed the nickel phosphide phase with  $Ni^{\delta \pm}P^{\delta}$  electronic state.<sup>59</sup> This is favorable for the formation of dualinteraction adsorption of H<sub>2</sub>O molecules onto the Ni<sub>2</sub>P NP surface, in which O and H atoms of the H<sub>2</sub>O molecule interact with Ni and P sites, respectively.<sup>68</sup> This dual-interaction adsorption weakens the H-O bonds, thereby facilitating their dissociation during the reduction.<sup>68</sup> The XPS analysis also indicated the formation of  $PO_4^{3-}$  groups, which can advance the transfer and coupling

Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) of protons.<sup>69</sup> Consequently, the photocatalytic H<sub>2</sub> production was significantly promoted in the introduction of partially oxidized Ni<sub>2</sub>P NPs. Interestingly, low temperature of the argon treatment (300 °C) afforded poor results. We hypothesized that the oxygen-free decomposition of heptadecylamine (capping agent used for the initial synthesis) produced at this temperature an amorphous carbon layer with a low degree of graphitization covering the Ni<sub>2</sub>P NP surface.<sup>70</sup> The low graphitization degree of this carbon layer made the electron transfer ineffective, as schematically shown in Figure 4.5b. When the temperature of treatment in Ar increased to 400 °C, the graphitization degree of the carbon layer was slightly improved, allowing few electrons to transfer through this layer to Ni<sub>2</sub>P NPs for the H<sub>2</sub>O reduction. As a result, CN-NiP-400 exhibited a small photoactivity. Thus, both CN-NiP-300 and CN-NiP-400 samples' activity was limited by the presence of heptadecylamine at the Ni<sub>2</sub>P surface which led to hard-to-control carbon layering. We thus explored ligand exchange prior to g-C<sub>3</sub>N<sub>4</sub> deposition as a means to avoid this problem.



**Figure 4.5.** Schematic representation of the electron transfer behaviour between the  $g-C_3N_4$  support and the Ni<sub>2</sub>P catalyst. Effect of electron transfer a) with and b) without ligand exchange, preventing formation of hindering carbon layer.

For the ligand exchanged series of hybrid catalysts (CN-NiP-Im-300 and CN-NiP-Ex-300), heptadecylamine was replaced by TEA cation, making Ni<sub>2</sub>P NPs soluble in water. This facilitates a uniform deposition of Ni<sub>2</sub>P NPs (negative charge) onto the protonated  $g-C_3N_4$  surface (positive charge). Moreover, TEA cation with low carbon content did not produce a hindering carbon layer

Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) during the argon treatment. Similar ligand exchanges have been shown to improve the hydrogen generation capabilities of both Au<sup>71</sup> and CoP nanocatalysts.<sup>72</sup> Therefore, an intimate interface between g-C<sub>3</sub>N<sub>4</sub> and Ni<sub>2</sub>P NPs was formed that induced an effective electron transfer (Figure 4.5a). CN-NiP-Ex-300 and CN-NiP-Im-300 showed enhanced H<sub>2</sub> evolution rates of 177.1  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> and 233.9  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>, respectively, which are much higher than that of samples obtained without prior ligand exchange (CN-NiP series) (Figure 4.6a). The higher H<sub>2</sub> evolution rate of CN-NiP-Im-300, as compared to CN-NiP-Ex-300, may also be due to the higher amount of deposited Ni<sub>2</sub>P NPs.



**Figure 4.6.** a) H<sub>2</sub> evolution rates of several prepared samples, b) H<sub>2</sub> evolution of CN- NiP-Im-300 for 3 cycles of 4 h. The photocatalytic activity of CN-NiP-Im-300 was tested for three cycles of 4 h to demonstrate the photostability. As shown in Figure 4.6b, there was no significant decay in the amount of H<sub>2</sub> evolved after 3 cycles, signifying the photocatalytic stability of CN-NiP-Im-300. To investigate the charge carrier behavior of CN and CN-NiP-Im-300, their transient photocurrent and electrochemical impedance spectroscopy (EIS) Nyquist plots were measured (Figure 4.7b). As shown in Figure 4.7a, the photocurrent of CN-NiP-Im-300 is higher than that of CN, revealing an efficient charge carrier generation and separation.<sup>73–76</sup> Additionally, CN-NiP-Im-300 exhibits a decrease in the impedance, signifying its enhanced charge transferability compared to CN.<sup>76–78</sup> The enhancement of charge carrier separation and transfer of CN-NiP-Im-300 results from the

Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) introduction of Ni<sub>2</sub>P NPs, which are the electron sinks and active sites for H<sub>2</sub> evolution, thereby improving the photoactivity.



**Figure 4.7.** a) Transient photocurrent and b) Electrochemical impedance spectroscopy (EIS) Nyquist plots of CN/FTO and CN-NiP-Im-300/FTO. (Inset Randles circuit used for EIS characterization;  $R_s$  – solution resistance;  $R_{ct}$  – polarization resistance;  $C_{ct}$  – double-layer capacitor).

Comparison of our catalyst system to similar systems which use the paired cocatalysts of earthabundant metal phosphide nanoparticles and g-C<sub>3</sub>N<sub>4</sub>, show competitive hydrogen production values for the Ni<sub>2</sub>P cocatalysts presented herein (Table 9.2). While the current state of the art is a paired 0.45 wt. % CoP@g-C<sub>3</sub>N<sub>4</sub>, producing up to 1074  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> of hydrogen (Table 9.2), various other earth abundant metal phosphides, such as iron or copper (Table 9.2, Entries 3 and 4) have also been employed with mild success. The effect of the support (Table 9.2, Entry 5) as well as the specific phase of nickel phosphide tested (Table 9.2, Entries 6-8) also support the hypothesis of Ni<sub>2</sub>P being the active cocatalyst phase. Interestingly, despite the presence of P-O peaks in the XPS data found in several literature examples, to the best of our knowledge, the influence of the specific amount of surface oxygen in metal phosphides is rarely corroborated systematically to the HER activity. Dreiss and coworkers had investigated the surface changes of nickel phosphide to a mixture of nickel phosphates and hydroxides under alkaline conditions, while still maintaining their efficacy for HER.<sup>79</sup> It is notable that Li and coworkers, and Ye and coworkers both showed that the external addition of K<sub>2</sub>HPO<sub>4</sub> boosted the catalytic activity of both Chapter 4 – Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER)

 $Co_2P@g-C_3N_4$  (Table 9.2, Entry 9)<sup>80</sup> and Pt@g-C\_3N\_4 respectively.<sup>81</sup> They demonstrated that the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> assisted in both the transport of protons to the active sites of the catalyst as well as increasing the onset potential, implying H<sub>2</sub>PO<sub>4</sub><sup>-</sup> plays an active role in the catalysis.<sup>81</sup> In order to further support the bifunctional nature of the surface of our cocatalyst, we sought to compare to other metal phosphate hydroxide systems. Work by Neppolian and coworkers demonstrated the use of a cobalt phosphate hydroxide catalyst with hydrogen production values very similar to our work (Table 9.2, Entry 10).<sup>82</sup> This supports the hypothesis that the surface phosphates seen in our catalysts may also have a bifunctional role, both to provide long term storage stability as well as reactivity of the cocatalyst. The ability to make nickel phosphide nanocatalysts with particle diameter sub 3 nm on a gram scale, all while having comparable hydrogen production values to similar systems which employ nickel phosphide made in solution, show the potential to further expand this mechanochemical methodology to other metal phosphide catalysts. In this proof of concept study, we also measured that our catalyst did not degrade over exposure to air for 2 weeks.

#### 4.3.7 Comparison of Mass Intensity (MI) and energy usage metrics

In order to support the use of mechanochemistry for the synthesis of TMP nanoparticles, we looked towards the use of both the Mass Intensity (MI) of each synthesis methodology, as well as the energy input required, per gram of product, to demonstrate the viability of mechanochemical methods towards future research in the design of metal phosphide nanomaterials. The Mass Intensity (MI) was calculated as previously reported,<sup>83</sup> shown in Eqn. (1).

Mass Intensity = Total Mass of Process/Mass of Product (1)

The use of both MI sustainability metrics as well as measuring the energy usage of each method, gave a quantitative comparison of both the small and large scale mechanochemical methods presented in this paper for the bottom-up synthesis of nickel phosphide. While similar metrics have

Chapter 4 - Solvent-Free Mechanochemical Synthesis of Ultrasmall Nickel Phosphide Nanoparticles and Their Application as a Catalyst for the Hydrogen Evolution Reaction (HER) been applied for the synthesis of pure metal nanoparticles or titanium dioxide,<sup>84</sup> to the best of our knowledge, no such analysis has been conducted for a bottom-up mechanochemical synthesis of NPs, however there are examples which show the cost and material benefit of such synthesis for metal-organic framework (MOF) synthesis.<sup>35,85,86</sup> Comparing first our small scale mechanochemical synthesis which produces roughly 100 milligrams to either the milligram synthesis by thermal decomposition of TOP or triphenylphosphite, there is a 2.4- to 18.6-fold decrease of the energy demand per gram of material. At the small scale, there is also a comparable decrease in the mass intensity from 9585 (Table 4.2, Entry 1) to 3593 (Table 4.2, Entry 4) for the decomposition of triphenylphosphite by solution methods, while being energetically competitive compared to the decomposition of both triphenylphosphite or TOP (Table 4.2, Entries 1 and 2). However, these benefits are compounded when scaled up using a planetary mill. Upon scaling up to 2.5 grams in a planetary mill the energy demand drops to 0.03 kWh g<sup>-1</sup> and the MI after washing drops to 101 (Table 4.2, Entry 5). This MI value is already more than 3 times lower than gram scale synthesis in solution (Table 4.2, Entry 3) as well as having an 18.7 time decrease in energy demand. These metrics help to further support the sustainability potential of future mechanochemical applications towards nanoparticle synthesis and provide a framework through which other nanoparticle syntheses can be evaluated.

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Entry	Method	MI (before washing)	MI (after washing)	Energy Input / kWh g <sup>-1</sup>
1	Thermal decomposition of triphenylphosphite <sup>87a</sup>	1501	9585	29.8
2	Thermal decomposition of TOP <sup>88b</sup>	95.54	1500	3.92
3	Hot injection of triphenylphosphite (1 gram scale) <sup>89c</sup>	76	331	0.562
4	Mechanochemical synthesis with Na <sub>3</sub> P in shaker mill (This work)	1	3593	1.60
5	Mechanochemical synthesis with Na <sub>3</sub> P in planetary mill (This work)	1	101	0.03

**Table 4.2.** Comparison of Mass Indices (MI) and energy demand of other synthetic methodologies to this presented work.

<sup>a</sup> These values were the best approximation based on 70 % mass yields as well as our energy measurements at similar temperatures

<sup>b</sup> The PIB used showed a max temperature of 290 °C, even after 2 hours

<sup>c</sup> These values were the best approximation based on 58 % mass yields in ESI as well as our energy measurements at similar temperatures

### **4.4** Conclusions

We report a simple and rapid synthesis of ultrasmall nickel phosphide nanoparticles suitable for photocatalytic applications, using a mechanochemical methodology that uses sodium phosphide as a readily accessible phosphorus source, while completely avoiding high temperatures and toxic organic solvents. Overall, increasing the length of the chain on the alkyl amine ligand resulted in a decrease in nanoparticle diameter to 2.8 nm, while preventing considerable sintering. The cocatalysts were then paired with a photoactive graphitic carbon nitride support after a simple ligand exchange and showed initial hydrogen production values of 233.9  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> after 3 hours using a broad-spectrum Xenon lamp at room temperature, owing to the unique bifunctional surface chemistry of nickel phosphate hydroxide. This preliminary investigation of the viability of mechanochemical activation and aging for the bottom-up synthesis of discrete nanoparticles will be further investigated to better understand the *in situ* growth kinetics of binary metal phosphides in the solid-state.
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## Application of sodium phosphide (Na<sub>3</sub>P) towards bottom-up mechanochemical synthesis of phosphorus-linked carbon nitrides

Following the initial success seen in the use of sodium phosphide for nanoparticle synthesis, my attention shifted to phosphorus-containing carbon nitrides. Heteroatom-containing carbon nitrides had shown improved reactivity for photochemical water splitting reactions. However, the exact structure and ability to pinpoint the location of phosphorus atom in modified carbon nitrides had potential for improvement over what was reported. Using a room-temperature mechanochemical synthesis between cyanuric chloride and sodium phosphide, paired with a 1 h anneal at 300 °C, I was able to obtain a layered, phosphorus linked triazine network (g-PCN300). The structure was supported through a combination of <sup>31</sup>P MAS NMR, PXRD and DFT calculations. The g-PCN series was investigated toward photocatalytic hydrogen evolution, with moderate activities of 122  $\mu$ mol H<sub>2</sub> g<sup>-1</sup> h<sup>-1</sup>.

# 5. Room temperature, solid-state access to phosphorus-linked triazine networks via mechanochemistry

### **5.1 Abstract**

Graphitic phosphorus-linked triazine network (g-PCN) materials are a unique class of carbon nitride materials with potential use as metal-free water-splitting photocatalysts, but remain difficult to access due to complicated synthetic procedures based on long reaction times, and annealing above 500 °C, while their structures are still ill-understood. Here, we reveal a mild, lower temperature approach for the synthesis of catalytically active g-PCN through combining a roomtemperature mechanochemical reaction of sodium phosphide and cyanuric chloride with only 1 hour annealing at 300 °C. This rapid, low-temperature procedure yields an effective water-splitting g-PCN photocatalyst, producing 122  $\mu$ mol H<sub>2</sub> h<sup>-1</sup> g<sup>-1</sup> under broad spectrum irradiation. Importantly, the layered structure of the mechanosynthesized g-PCN is sufficiently ordered to permit unprecedented structural characterisation for a g-PCN structure, through a combination of solid-state magic angle spinning, nuclear magnetic resonance spectroscopy (MAS NMR), X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM), supported by dispersion-corrected density functional theory (DFT) modelling. Modelling revealed an excellent match with experimental <sup>31</sup>P MAS NMR and PXRD data for the structure based on phosphorus-linked triazine network layers, making the mechanochemically synthesized material a unique example of a photocatalytically active and structurally characterized g-PCN material.

### **5.2 Introduction**

Over the last decade, photocatalytic water splitting has attracted much attention as a potentially sustainable route to hydrogen gas production. The scaling-up of the water splitting process is urgently needed as today, hydrogen gas is primarily obtained through the steam reforming of natural gas, an energy-intensive process producing carbon monoxide and dioxide as by-products.<sup>1</sup> Recent improvements in water splitting catalysis have led to the development of new cocatalysts and photoactive supports to further increase the rate of reaction. Much of this work has focused on the design of new earth-abundant cocatalysts such as metal oxides.<sup>2,3</sup> hydroxides.<sup>4,5</sup> sulfides.<sup>6,7</sup> phosphates<sup>8</sup> and phosphides.<sup>9-11</sup> In terms of photocatalytic supports, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has been one of the most promising candidates, due to its potential as a metal-free, heterogeneous photocatalyst, which is also readily modifiable towards different morphologies and dopants.<sup>12-14</sup> While g-C<sub>3</sub>N<sub>4</sub> has attracted interest as a metal-free semiconductor, outstanding challenges remain related to the understanding of its exact structure.<sup>15</sup> photophysical properties.<sup>16</sup>, <sup>17</sup> and a wide band gap<sup>18</sup> unsuitable for broad spectrum water splitting. Photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub> can be enhanced by doping with boron, oxygen,  $^{19,20}$  sulfur<sup>21,22</sup> or phosphorus heteroatoms,<sup>22-24</sup> in order to tune the band gap and improve exciton generation.<sup>12</sup> The Antonietti group (Scheme 1a) has detailed the successful application of g-C<sub>3</sub>N<sub>4</sub> for hydrogen production from water under visible light,<sup>25</sup> while other work explored the inclusion of phosphorus to afford phosphorus-doped graphitic carbon nitrides or carbon phosphanitride materials<sup>26</sup> applicable as photocatalysts for hydrogen evolution reaction (HER),<sup>27,28</sup> oxygen evolution reaction (OER),<sup>29,30</sup> and diverse photodegradation reactions.<sup>31-33</sup>

Typical approaches to phosphorus-containing graphitic carbon nitride rely on the hydrothermal carbonization (HTC) of triazine-containing precursors, such as melamine or

cyanuric chloride as carbon and nitrogen precursors, respectively and a phosphorus source, forming various polymeric carbon phosphanitrides. Alternatively, it was shown that thermal and high pressure treatment of specific small molecule precursors can afford extended C<sub>3</sub>N<sub>3</sub>P materials (Scheme 5.1b and 5.1c).<sup>34,35</sup> A microwave-based synthesis of phosphorus-doped graphitic carbon nitride nanosheets has been reported by Wang and coworkers in 2020 (Scheme 5.1d).<sup>36</sup> All these approaches, however, employ high-temperature furnace techniques, annealing for extensive periods of time, and rely on niche phosphorus sources such as pentafluorophosphate-containing ionic liquids.<sup>26</sup> or  $P(CN)_{3}$ .<sup>34,35</sup>, or utilize phosphorus sources which require high temperatures or long reaction times to activate, such as red phosphorus,<sup>37</sup> phytic acid,<sup>38</sup> ammonium hypophosphite and phosphates.<sup>36,39</sup> Finally, there has been very limited experimental work corroborating the structures of a phosphorus-linked carbon nitride materials, which is important for future rational design of materials. While first-principles calculations for the structure and electronic properties of C<sub>3</sub>N<sub>4-n</sub>P<sub>n</sub> were reported by Ding and Feng in 2004,<sup>40</sup> there is only one report correlating <sup>31</sup>P NMR data to DFT calculated chemical shifts and X-ray scattering data for phosphorus-linked triazine networks by Strobel and coworkers in 2019.<sup>35</sup> However, the reported synthesis required the use of a multi-anvil press, exerting 12 GPa over 19 h, followed by thermal treatment at 1000 °C for 30 min (Scheme 5.1c).



**Scheme 5.1.** Key examples of phosphanitride and phosphorus-containing graphitic carbon nitride presented by a) Antonietti b) Epshteyn c) Strobel d) Wang and e) the presented work.

Here, we demonstrate a significantly simpler, and milder synthesis (Scheme 5.1e) of a uniquely structurally well-defined phosphorus-linked carbon phosphanitride material that exhibits activity as a broad-spectrum water splitting photocatalyst. Our approach is based on combining mechanochemical ball milling crosslinking of cyanuric chloride with sodium phosphide (Na<sub>3</sub>P) as a simple phosphorus source, followed by room-temperature aging and brief (1 h) exposure to no more than 300 °C, under argon. Combining a range of solid-state analytical techniques with dispersion-corrected density-functional theory (DFT) modelling provided unambiguous confirmation of the structure, presenting a unique example of a carbon phosphanitride that can be obtained under mild conditions, is structurally well-characterized, and provides functional behavior as a photoactive support.

Our approach is based on mechanochemistry,<sup>41-45</sup> *i.e.* chemical reactivity induced and/or sustained by mechanical force in the form of milling, grinding or shear, a rapidly advancing approach for cleaner, solvent-free molecular and materials synthesis. Mechanochemistry has been applied across a wide range of organic,<sup>46-49</sup> inorganic,<sup>50-54</sup> and advanced materials syntheses, including metal-organic frameworks,<sup>55-57</sup> polymers,<sup>58-61</sup> cocrystals,<sup>62,63</sup> nanoparticle-based systems and more.<sup>64-69</sup> Recent reports by Takacs, Mandel and Borchardt have described the mechanosynthesis of heteroatom-bridged carbon nitride materials, for example by a mechanicallyinduced self-sustaining reaction<sup>70-72</sup> or between cyanuric chloride and CaC<sub>2</sub>.<sup>73</sup> Cyanuric chloride was also used as a triazine unit, alongside a variety of aromatic monomers, and AlCl<sub>3</sub> as an activating unit, in a mechanochemical Friedel-Crafts alkylation to form porous covalent triazine frameworks.<sup>74</sup> The use of mechanochemistry for the synthesis of phosphorus-doped carbon nitrides has, however, not yet been explored. Sodium phosphide has shown potential in lowtemperature access to unique low-valent phosphorus compounds,<sup>75</sup> as well as access to metal phosphide nanoparticles.<sup>76</sup> Consequently, we hypothesized that ball-milling of sodium phosphide (Na<sub>3</sub>P) together with cyanuric chloride as a commercially available triazine linker would provide room-temperature access to layered, phosphorus-linked triazine networks through a low temperature mechanochemical metathesis<sup>77</sup> reaction (Scheme 5.1d).

### **5.3 Results and Discussion**

The presented mechanosynthesis of phosphorus-linked triazine networks involved ball milling of equimolar quantities of Na<sub>3</sub>P with cyanuric chloride under an atmosphere of argon. In a typical experiment, the reactants were added to a zirconia-based milling assembly consisting of a 10 mL volume jar and two zirconia milling balls of 7 mm diameter, and the reaction mixture milled for 30 min at a frequency of 30 Hz, followed by aging for 24 h under argon. We have previously

demonstrated the synthesis of well-defined nanostructured materials simply by brief mechanical activation through ball milling, followed by aging at room temperature.<sup>78-80</sup> After aging, the jars were opened in air, the content taken up into a 3:1 v/v mixture of EtOH and deionized (DI) water, and the system separated by centrifugation, before drying *in vacuo* at 50 °C for 12 h prior to analysis. Attempts to obtain the same material by milling for shorter times or using a single zirconia ball of 10 mm diameter led to incomplete transformation, as evident by violent hydrolysis of unreacted Na<sub>3</sub>P upon washing of the final product. The effect of a post-synthetic annealing step was also investigated. The as-made carbon phosphanitride (g-PCN) material was placed into an alumina, boat-shaped crucible, wrapped loosely in aluminum foil and heated in a tube furnace under a flow of argon gas for 1 h at either 200 or 300 °C, producing samples denoted as g-PCN200 and g-PCN300, respectively. As a phosphorus-free reference, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was produced through a previously reported furnace-based method of thermally annealing melamine at 525 °C for 4 h.<sup>81</sup>



**Figure 5.1** PXRD patterns of graphite, reference code YOPTUU (lime), phosphorus-containing g-C<sub>3</sub>N<sub>4</sub> (green), g-PCN (teal), g-PCN200 (blue) and g-PCN300 (purple).

The crystallinity of the samples before annealing and during thermal treatment was evaluated by powder X-ray diffraction (PXRD). For the non-annealed samples, two broad Bragg reflections are

seen at approximately  $2\theta = 15^{\circ}$  and  $26^{\circ}$  (Figure 5.1, teal). The measured crystallinity index (CrI) for g-PCN before annealing was determined to be 21 %, showing a largely amorphous material being formed after the milling and aging process. Upon annealing at 200 °C, negligible change was noted in the PXRD pattern (Figure 5.1, blue). The most significant change was seen for the g-PCN300 sample, where annealing led to an increase in CrI to 33 %, as well as the appearance of novel X-ray reflections (Figure 5.1, purple), suggesting an increase in the ordering of the graphitic structure of the material. All materials also showed broad reflections similar to a phosphorus containing P@CN made through a previously reported furnace synthesis (Figure 5.1, green),<sup>82</sup> or graphite (Figure 5.1, lime),<sup>83</sup> further suggesting a layered structure of g-PCN.

The formation of a phosphorus-linked triazine was verified by X-ray photoelectron spectroscopy (XPS), solid-state magic angle spinning <sup>31</sup>P NMR (MAS NMR), and Fourier-transform infrared attenuated total reflectance (FTIR-ATR) spectroscopy, which also permitted the quantification and speciation of phosphorus loading. The C 1s-focused XPS scan of the g-PCN material showed three maxima at 248.4, 286.5, and 288.6 eV, confirming the presence of C=N, C-OH, and C=O species, respectively (Figure 5.2a).<sup>84</sup> The signal corresponding to C=N bonds confirmed the retention of the triazine linker following milling with Na<sub>3</sub>P and aging. The presence of the C-OH bonds suggests that upon centrifuging the g-PCN for a total of 15 min using a 3:1 EtOH:H<sub>2</sub>O (v/v) mixture, terminal chloride units on the pendant triazine fragments are hydrolysed to form hydroxyl moieties. Similarly, the presence of carbonyl absorption bands at ~1600 cm<sup>-1</sup>, which is seen in FTIR-ATR data (Figure 10.1), suggests the partial hydrolysis of the triazine ring to give amide functionalities. The focused N 1*s* scans (Figure 5.2b) further validate this hypothesis as two maxima at 398.9 and 399.9 eV are observed, which correspond to pyridinic and pyridine species for nitrogen. This suggests that unreacted terminal chlorides were still present on the edges

of the material after the reaction and have hydrolysed during work up. Focused scans of the P 2p signal showed a doublet consisting of two maxima centred at 129.8 eV, highlighting P-C bond character as well as a broader maximum centred at 133.2 eV, which highlights both the formation of bridging phosphorus centres between triazine rings, as well as their partial oxidation, which was quantified at 48 % upon desummation and integration of the XPS data (Figure 5.2c).



**Figure 5.2.** Comparison of XPS data for: a) C 1s; b) N 1s; and c) P 2p scans of g-PCN, and d) C 1s; e) N 1s; and f) P 2p scans of g-PCN300.

Comparing to furnace-made phosphorus-doped carbon nitride (P@CN),<sup>82</sup> the C 1*s* focused scans in XPS showed two signals, at 284.7 eV and 287.9 eV, corresponding to C=N/C-N and C=O bonds respectively (Figure 10.3a). The N 1*s* focused scans showed two major maxima at 397.4 eV and 398.7 eV, consistent with the majority of nitrogen being in the form of pyrrolic species, compared to pyridine-type nitrogen species that were observed in the furnace-made P@CN (Figure 10.3b). The P 2*p* scan showed only a doublet for P-O/P=O type bonds, centred at 133.4 eV (Figure 10.3c). Due to low crystallinity of the mechanochemically prepared samples, a subsequent annealing step under an argon atmosphere was conducted for 1 h at either 200 or 300 °C. Thermogravimetric analysis (TGA) confirmed that exposure to such temperatures does not lead to a significant mass loss upon heating in a nitrogen atmosphere (Figure 10.2). After annealing at 200 °C for 1 h under

argon, the C 1*s* XPS focused scans of the resulting phosphorus-linked triazine network (g-PCN200) showed three signals as before annealing, at 284.6, 286.6 and 288.5 eV. These signals correspond to bonds of the C=N/C-N, C-OH and C=O character, respectively (Figure 10.4a). Of note is the increase in the percentage of C-OH character after annealing at 200 °C, from 37 % to 63 % while the carbonyl character decreased from 35 % to 11 %. The N 1s scans showed a shift in the majority signal to favour pyrrolic N character on its surface up to 78 % following the anneal (Figure 10.4b). The P 2p focused scans also showed an increase of the P-O/P=O character upon annealing at 200 °C, from 27 to 89 % (Figure 10.4c).

Upon annealing at 300 °C for 1 h, the desummation of the C 1*s* scans revealed maxima at 284.7, 286.6, 288.5, and 292.5 eV (Figure 5.2d). The respective ratios of these signals demonstrate a decrease in the relative quantity of hydroxyl C-OH character from 37 % in g-PCN to 22 % in g-PCN300, implying a loss of terminal hydroxyl groups moieties and an increase in the relative abundance of graphitic nitride character. This decrease is also seen through a reduction in the carbonyl signal showing that partially hydrolysed triazine units further reduced upon annealing. This trend in sustained carbon nitride structure is further supported by a largely unchanged ratio of pyridinic-N and pyrrolic/pyridone-N character (Figure 5.2e), which showed a 55 % retention of pyridinic-N character in g-PCN300 compared to 58 % in g-PCN. The P 2*p*-focused scan (Figure 5.2f) showed a small increase in the degree of oxidation from 27 to 39 %, however the sample was still predominantly P-C in character, supporting the maintained integrity of the material after annealing.

Structural information for the phosphorus-linked triazine networks was also acquired through FTIR-ATR spectroscopy. Compared to  $g-C_3N_4$ , the mechanochemically synthesized g-PCN materials similarly show C-N heterocycle stretches in the 1200-1600 cm<sup>-1</sup> range (Figure

10.1).<sup>85</sup> For the sample annealed at 300 °C, g-PCN300, a band present at 1615 cm<sup>-1</sup> can be attributed to a C=N stretch, and the bands at ~810 cm<sup>-1</sup> can be matched to the vibrational fingerprint of the triazine unit,<sup>86</sup> further suggesting the graphitic structure was preserved after both ball milling and annealing. While the absorption band at 534 cm<sup>-1</sup> could also be associated with P-C bond character,<sup>34</sup> other phosphorus-related stretches may overlap with the strong C-N vibrations. Scanning transmission electron microscopy (STEM) analysis using a high angle annular dark field detector (HAADF) revealed that g-PCN200 and g-PCN300 featured a layered structure. This is remarkable since these types of properties are seen in g-C<sub>3</sub>N<sub>4</sub> typically when annealed at temperatures above 500 °C (Figure 5.3a).<sup>87</sup>

The intensity of HAADF signal is correlated to both the atomic number of their element, and the sample thickness.<sup>88,89</sup> Samples of increased intensity on the HAADF detector exhibit a higher relative thickness compared to the samples with a lower intensity. We obtained the relative thickness, *i.e.* the mean number of scattering events per incident electron which can be obtained in the low-loss region of an electron energy loss spectroscopy (EELS) spectrum, of g-PCN, g-PCN200 and g-PCN300. The relative thickness was found to increase from pristine g-C<sub>3</sub>N<sub>4</sub> at 0.34 to 0.90 for g-PCN, and relative thicknesses of 0.73 and 0.66 for g-PCN200 and g-PCN300, respectively, showing an inversed relationship of relative thickness to annealing temperature. This follows similarly reported trends, wherein graphitic carbon nitride films show a similar reduction in thickness as annealing temperature is increased from 150 °C up to 500 °C.<sup>90</sup>

The EELS analysis of g-PCN (prior to any annealing) showed an even distribution of carbon, nitrogen, and oxygen throughout the material, while phosphorus appeared localized to specific regions (Figure 5.3b). A similar localization of phosphorus was also seen on g-PCN200

(Figure 5.3c). However, upon increasing the annealing temperature to 300 °C, the distribution of phosphorus becomes more uniform (Figure 5.3d).



**Figure 5.3.** STEM-HAADF images (left) and EELS maps (right) for the characteristic elements presented on graphitic carbon networks. a)  $g-C_3N_4$  network without any thermal treatment or phosphorus bridges is compared with; b) g-PCN (no annealing); c) g-PCN200 (annealing at 200 °C); and d) g-PCN300 (annealing at 300 °C) Dotted white circles denote localized regions of high phosphorus density.

To better understand the photochemical properties of the mechanochemically-synthesized phosphorus-linked triazine networks, the samples were characterized by ultraviolet-visible diffuse reflectance spectroscopy (UV-DRS) and photoluminescence (PL) measurements. Pristine g-C<sub>3</sub>N<sub>4</sub> showed a typical semiconductor-like absorption maximum centred around 400 nm, originating from the charge transfer response of g-C<sub>3</sub>N<sub>4</sub> from the valence band (VB) populated by N 2p orbitals to the conduction band (CB) formed by C 2p orbitals.<sup>31,32,34</sup> For the mechanochemically-synthesized phosphorus-linked triazine networks, a red shift of the absorption band is seen in comparison to pristine g-C<sub>3</sub>N<sub>4</sub>. g-PCN samples, made by milling for 30 min and aging for 24 h showed a red-shifted maximum at 518 nm, suggesting a decrease in the band gap energy compared to g-C<sub>3</sub>N<sub>4</sub>. After annealing of the g-PCN material at either 200 °C or 300 °C, g-PCN200 and g-

PCN300, the absorption band is further broadened across the visible light range, with a maximum absorbance peak around 530 nm (Figure 5.4a).

In PL measurements a strong, broad signal is observed for pristine g-C<sub>3</sub>N<sub>4</sub>, and a much weaker signal for all g-PCN samples, with a minor increase in intensity seen as a function of annealing temperature (Figure 5.4b). These results imply that the generated exciton in the phosphorus-linked samples is recombining at a slower rate than g-C<sub>3</sub>N<sub>4</sub>, with bridging nitrogen, resulting in increased excited state lifetimes (Figure 5.4c). For pristine g-C<sub>3</sub>N<sub>4</sub>, a  $\tau$  value of 4.2 µs was noted, which gradually increased to 4.7, 41, and 39 µs for g-PCN, g-PCN200 and g-PCN300, respectively. This increase by an order of magnitude upon addition of phosphorus linkages and subsequent annealing suggests improved stability of the charged species, without the need for an additional cocatalyst.<sup>23,91</sup>

Chapter 5 – Mechanosynthesis of a well-defined graphitic phosphorus-linked carbon nitride (g-PCN) with water splitting activity



**Figure 5.4.** a) UV-Vis DRS b) photoluminescence c) lifetime d) photocurrent and e) Nyquist plots of g-C<sub>3</sub>N<sub>4</sub> (green), g-PCN (teal), g-PCN200 (blue) and g-PCN300 (purple).

The temporal photocurrent of g-PCN, g-PCN200, and g-PCN300 was then investigated to verify that the introduction of phosphorus into the triazine network improved the charge transport upon irradiation. The g-C<sub>3</sub>N<sub>4</sub> material, which is typically nitrogen-linked, showed a maximum photocurrent of 1  $\mu$ A (Figure 5.4d, green traces), g-PCN prior to any annealing featured a similar photocurrent performance (Figure 5.4d, teal trace). Upon annealing at 200 °C and 300 °C, the photocurrent increases to a maximum of 4  $\mu$ A and 5  $\mu$ A respectively (Figure 5.4d, blue and purple traces). Furthermore, the electrochemical impedance spectroscopy (EIS) (Figure 5.4e) showed a

decrease in the impedance for the materials where  $g-C_3N_4 > g-PCN > g-PCN200 > g-PCN300$ . This implies that incorporating phosphorus as the linking atom led to an enhancement of the photoelectrochemical properties. A lower arc radius, implying better charge transer,<sup>92,93</sup> was noted for the g-PCN series of materials compared to the native g-C<sub>3</sub>N<sub>4</sub>. These enhancements were furthered by annealing g-PCN at 200 and 300 °C. This effect could be seen in the improvement of the photocatalytic activity for the g-PCN series compared to g-C<sub>3</sub>N<sub>4</sub>. Finally, band structure was studied by Mott-Schottky technique (Figure 10.5, see Chapter 10 for details). All phosphoruscontaining samples exhibited a positive slope indicating an *n*-type semiconductor, characteristic of graphitic carbon nitride materials.<sup>94,95</sup> The conduction band of all as-prepared samples was determined from the x-intercept value, derived from the tangent line of the slope on the Mott-Schottky plot. Accordingly, the estimated value for g-C<sub>3</sub>N<sub>4</sub> was ~-1.10 V vs. Ag/AgCl which corresponds to previous literature reports.<sup>76,96</sup> For the nanocomposites a more negative band was observed (-1.30, -1.40 and -1.25 V for g-PCN, g-PCN200 and g-PCN300, respectively). Considering the broad visible light absorption of the nanocomposites and the estimated values from Mott-Schottky, it could be inferred that synthesized materials are suitable for HER due to their band positions, as it is more negative than H<sub>2</sub> standard reduction potential, 0 V vs NHE at pH 7 92,95,97

We then turned to <sup>31</sup>P MAS NMR techniques to gain more insights into the chemical structure of the synthesized materials, as reported by others.<sup>26,34,35,85</sup> The spectrum of g-PCN (Figure 10.6a) featured mostly a broad and noisy band centred on  $\delta_{P1} = 4.00$  ppm with a broad shoulder at  $\delta_{P2} = 26.65$  ppm, while g-PCN200 (Figure 10.6b) had several resonances in a more upfield region at  $\delta_{P1} = 0.84$  ppm,  $\delta_{P2} = -9.47$  ppm and  $\delta_{P3} = -20.96$  ppm. The g-PCN300 material exhibited the most easily interpreted spectrum with two peaks at  $\delta_{P1} = -12.8$ . ppm and  $\delta_{P2} = -24.7$ 

ppm. This trend indicates that annealing results in an overall chemical reduction of the phosphorus species inside the materials. This sharp resonance in the case of g-PCN300 is unprecedented for triazine-based, phosphorus-linked carbon nitrides, as often broad resonances are seen even upon materials treated at high temperature and pressure.<sup>35</sup>

Next, computational methods were employed to determine the species responsible for the individual signals found in the desummed <sup>31</sup>P MAS NMR spectra. Gaussian 16<sup>98</sup> was used to optimise the structure and calculate the <sup>31</sup>P chemical shielding tensors for a variety of phosphoruscontaining molecules serving as models in this context. These molecules were chosen to represent various stages of oligomerization of triazine rings bridged by phosphorus, III or V, and considered with either chloride or hydroxyl functionalities (Chart 10.1). They were treated as isolated molecules in the gas phase and were described by an atom-centred basis set (6-311+G(d,p)). The analysis of the trends in chemical shifts of this family of molecules confirms that likely phosphorus containing molecules formed in this reaction are being reduced upon annealing. Also, despite the cleanliness of the recorded spectra, it was difficult to attribute unambiguously the peaks to one single computed structure, as eight of them fell in the  $10 < \delta < -30$  ppm region (Table 10.1). To account for the pure product of the reaction, a perfectly repeating unit of g-PCN, we employed periodic DFT calculations. The <sup>31</sup>P chemical shifts for bulk g-PCN were calculated using the periodic plane-wave DFT code CASTEP, v20.11,99 following the work of Strobel and coworkers.35 whereby the bridging nitrogen atoms in the experimentally resolved structure of  $g-C_3N_4$ , reported by Cooper, Bojdys and coworkers,<sup>100</sup> were replaced with phosphorus (see details in Supplementary Information). Two unique phosphorus environments were seen in the DFT calculated structure of g-PCN. The environment termed P1 was calculated to have empty space above and below it, while the environment P2 is centred between triazine rings both above and below it (Figure 5.5a).

Importantly, in this work we obtained a planar geometry from full structural and cell optimizations, which is different from the previously observed buckling of the g-PCN sheets.<sup>35</sup> Two chemical shifts were obtained for the structure,  $\delta_{P1} = -11.83$  ppm and  $\delta_{P2} = -23.47$  ppm and correspond to the two different environments experienced by phosphorus atoms in the optimised structure. These numbers are in excellent agreement with the experimental data for g-PCN200 and g-PCN300. (Figure 5.5b, also Figure 10.5b).



**Figure 5.5.** a) CASTEP-optimized structure; b) <sup>31</sup>P MAS NMR at 13 kHz of g-PCN300. Red lines denote shifts calculated using CASTEP-optimized structure. The asterisks denote spinning sidebands; c) From the bottom up: Simulated PXRD patterns of the  $g-C_3N_4$  structure from Cooper, Bojdys and coworkers.<sup>100</sup>; g-PCN<sub>opt</sub>; g-PCN<sub>shift</sub> and g-PCN300. Asterisk indicates unidentified reflection.

Given the agreement between the calculated and experimental data for the optimized structure, we revisited the PXRD pattern of g-PCN300, which features sharp, distinct reflections over an amorphous background (Figure 5.5c, purple). The CASTEP simulated pattern for the optimized structure (Figure 5.5c, teal) exhibits X-ray reflections at 13.5 °, 23.3 °, 26.3 °, and 32.6 ° 2 $\theta$ , in good agreement with the experimental pattern for g-PCN300. We further improved on this

agreement applying a translational distortion of 1 % along the a-axis of the upper plane of the optimized structure (more positive in the c-axis). This provided more matching reflections at 23.3 °, 26.3 °, and 32.6 °  $2\theta$  (Figure 5.5c, blue). We also compared the pattern for g-PCN300 with the simulated pattern of the experimentally derived g-C<sub>3</sub>N<sub>4</sub> structure from Cooper, Bojdys and coworkers (Figure 5.5c, green), which revealed to be close, yet not matching, as expected from a non-phosphorus-containing structure with a similar reflection at  $2\theta$  of 26.9 °.

As previously highlighted by our team<sup>76</sup> and others,<sup>78,101,102</sup> the use of sustainability metrics is paramount in demonstrating the benefit in energy-waste reduction that mechanochemical techniques have over the traditionally used high-temperature solid-state techniques, often employed for layered carbon nitride based materials. Our group had previously shown that comparing the energy demand of a Retsch MM400 vibrational mill in comparison to tube furnace and solution-based routes to nickel phosphide nanoparticles<sup>76</sup> can also be employed in the present study (Table 5.1). A furnace-based synthesis of g-C<sub>3</sub>N<sub>4</sub> conducted on a 2 g scale used 1.87 kWh g<sup>-1</sup> after 4 h, while the presented work, at only a 250 mg scale was shown to use only 1.07 kWh g<sup>-1</sup>, even after combining both the energy draw during the milling step and after annealing in a tube furnace at 300 °C for 1 h. Even before annealing, the mechanochemical formation of the g-PCN network shows an energy draw value 10 times lower than that of the g-C<sub>3</sub>N<sub>4</sub>.

Method	Milling and Aging Time / h	Annealing / Temp, Time	Energy draw / kWhg <sup>-1</sup>
Furnace	-	550 °C, 4 h	1.87
Ball milling	0.5, 24	-	0.19
Ball milling	0.5, 24	200 °C, 1 h	0.75
Ball milling	0.5, 24	300 °C, 1 h	1.07
Ball milling Ball milling	0.5, 24 0.5, 24 0.5, 24	- 200 °C, 1 h 300 °C, 1 h	0.75 1.07

**Table 5.1.** Comparison of energy usage metrics for traditionally used annealing method, to the hybrid milling-aging-annealing method.

The catalytic behaviour towards the hydrogen evolution reaction was optimized for a variety of reaction times, platinum cocatalyst loadings and total composite catalyst used. Initial

studies showed an increase in catalytic activity of g-PCN compared to g-C<sub>3</sub>N<sub>4</sub>. However, despite the increase in exciton lifetime and improved photocurrent upon annealing to obtain g-PCN200 and g-PCN300, catalytic activity was shown to decrease (Figure 5.6a).



**Figure 5.6.** a) Catalytic activity of varied photocatlyst, b) varied mass loading of g-PCN, c) reaction time and d) loading of Pt cocatlyst.

Increasing the composite catalyst loading in the reaction also led to a decrease in catalytic activity, producing 68 µmol H<sub>2</sub> h<sup>-1</sup> g<sup>-1</sup> when using 10 mg and 47 µmol H<sub>2</sub> h<sup>-1</sup> g<sup>-1</sup> when using a total of 20 mg of composite catalyst (Figure 5.6b). This effect could be related to the haze created by the high amount (oversaturated) of dispersed photocatalyst blocking the light in the reaction medium. In parallel, it was also shown that 4 h reaction times were the most efficient (Figure 5.6c) and that a cocatalyst loading of 4 wt. % Pt produced rates upwards of ca. 122 µmol H<sub>2</sub> h<sup>-1</sup> g<sup>-1</sup> (Figure 5.6d). The loss in catalytic activity with increasing annealing temperature led to investigating the effect of milling times, annealing temperature and further milling treatment following isolation, on material surface area. g-C<sub>3</sub>N<sub>4</sub> made through a conventional tube furnace method showed a surface area of ~19 m<sup>2</sup> g<sup>-1</sup>. Comparing this initial data with g-PCN, shows a similar surface area of ~11 m<sup>2</sup> g<sup>-1</sup> (Table 10.2, Entry 2). Extending the milling time to 90 min shows an increase to ~57 m<sup>2</sup> g<sup>-1</sup> (Table 10.2, Entry 3). For the g-PCN300 material, the surface area remains unchanged at 13 m<sup>2</sup> g<sup>-1</sup>

<sup>1</sup> (Table 10.2, Entry 4) or a posttreatment milling of g-PCN300 with ten 1 mm zirconia balls at ~8  $m^2 g^{-1}$  (Table 10.2, Entry 5). The understanding of the mechanism for P- and N-doped and bridged carbons is still under considerable investigation and debate.<sup>103, 104</sup> However, based on the presented data, two factors seem to be the driving force for the improved reactivity of g-PCN. Firstly, the overall addition of strongly electron donating phosphorus-linkages in place of carbon or nitrogen allows for improved charged separation with the phosphorus-linked series as opposed to g-C<sub>3</sub>N<sub>4</sub>, as demonstrated by a reduced PL signal and extended lifetime for the g-PCN series (Figure 4b and 4c).<sup>104,105</sup> Additionally, the amorphous g-PCN showed improved catalytic activity over samples showing improved crystallinity after annealing. Therefore, it can be hypothesized that defects present in g-PCN following milling and aging allow for the trapping of photoexcited charges, previously demonstrated to improve the evolution of hydrogen.<sup>105,106</sup>

### **5.4 Conclusion**

In conclusion, we have presented the first mechanochemistry-based approach to phosphorusbridged triazine-based carbon nitride photocatalysts. A combination of experimental and theoretical analysis confirms the successful, mild, and simple, synthesis of several layered phosphorus-linked carbon nitride structures, without resorting to complex phosphorus sources or high temperatures. Importantly, periodic DFT calculations provided a unique example of a structurally-characterized phosphorus-bridged triazine-based carbon nitride, whose structure was validated by an excellent match of calculated and measured <sup>31</sup>P NMR and PXRD data, the closest correlation for phosphorus-linked carbon nitrides, to date. The photocatalytic behaviour of these triazine-based materials was evaluated towards the hydrogen evolution reaction and shown to feature improvement over traditional graphitic carbon nitride producing 122  $\mu$ mol H<sub>2</sub> h<sup>-1</sup> g<sup>-1</sup>. The simplicity of the synthetic procedure and starting materials, combined with access to a clear

structural understanding of the resulting material, presents mechanochemistry as a valuable and powerful new route for the synthesis and development of phosphorus-bridged carbon nitride network photocatalysts.

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### 6. Discussion and Conclusions

#### **6.1 Conclusions**

The application of mechanochemistry for the development of various phosphorus-containing materials has led to new discoveries in materials design and synthesis, while simultaneously demonstrating the improved sustainability of mechanochemical techniques for making these classes of materials. Additionally, the field of mechanochemical phosphorus chemistry is still in its infancy, particularly in the application of feedstocks and reagents which, by the nature of their poor solubility or resemblance to PR feedstocks, are amenable to investigation using mechanochemistry. The projects in this Thesis have demonstrated initial proof-of-concept applications of solid-state phosphorus reagents towards a variety of materials and applications, including polymer functionalization for flame-retardants (Chapter 3), the development of heterogeneous metal phosphide- (Chapter 4) or phosphorus-bridged (Chapter 5) carbon nitride-based heterogenous photocatalysts for hydrogen evolution.

For the development of phosphorylated nanocellulose, lignin and several synthetic polymers, the application of  $P_4O_{10}$ , as a polyphosphate analogue which closely resembles PR feedstocks proved to be effective for direct functionalization and resulted in loadings over twice that of previously employed solution-based methods. The developed method involved the combination of  $P_4O_{10}$  with equimolar amounts of the desired substrate, as well as urea to act as a buffer during phosphorylation. Such mechanochemical phosphorylation showed broad applicability to both bio-based substrates, such as lignin and nanocellulose, as well as to synthetic polymers such as PVA, PVC, and PEG. Unique to this mechanochemical method, compared to solution methods, was the additional discovery of direct polyphosphorylation using  $P_4O_{10}$ . The resulting phosphorylated materials were characterized in-depth using a novel, quantitative MAS
NMR technique, which allowed for not only quantification but also the speciation of the available phosphate half-ester groups. The phosphorylated nanocellulose proved to act as an effective flame retardant coating when applied to poly laminate spruce panelling, similar to what would be found in traditional wooden structure.

We then expanded on the application of underutilized phosphorus sources by mechanochemistry, by employing sodium phosphide for the bottom-up synthesis of nickel phosphide nanoparticles and phosphorus-bridged carbon nitride as heterogeneous photocatalysts for photocatalytic water splitting. The direct synthesis of nickel phosphide nanoparticles was achieved through the milling of sodium phosphide with anhydrous nickel chloride in the presence of an alkyl amine capping ligand. These binary nanoparticles not only showed diameters averaging 2 nm, a size typically unattainable using solution methods, but additionally could be made with almost 20-fold reduction in energy input and a 3-fold reduction in overall solvent usage, while still providing a viable photocatalytic cocatalyst for hydrogen evolution. Finally, the use of sodium phosphide proved equally versatile for the formation of P-C bonds toward the formation of extended triazine networks with bridging phosphorus atoms. These networks, in turn, were fully characterized using a combination of <sup>31</sup>P MAS NMR, XPS, PXRD FTIR-ATR and TEM as well as computational methods using CASTEP to validate the expected NMR shifts, as well as the expected X-ray reflections seen in PXRD. To the best of my knowledge, this is the closest correlation yet presented in the literature for these types of materials. The networks were then applied as photocatalytic supports, showing a marked improvement over carbon nitride for the hydrogen evolution reaction. Carbon nitride material with no phosphorus present showed no measurable activity towards HER, while the phosphorus-bridged triazine networks showed moderate effectiveness, generating 122  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> under broad spectrum visible light.

## **6.2 Suggested directions for future work**

Considering how essential phosphorus is to humanity, sustainable applications of PR and waste phosphorus feedstocks will be an area of continual growth in the coming years. The direct mechanochemical activation of PR towards the incorporation of phosphorus into a variety of reactions, particularly in the context of phosphorus-containing pharmaceuticals, will greatly reduce the energy and solvent waste associated with the industry. Additionally, the ability for mechanochemistry to impart novel reactivity, not seen in the presence of bulk solvent or through conventional heating, lends itself to both the development of new phosphorus-containing reagents as well as novel reaction development. With the recent explosion of interest into phosphorus centered catalysis, as well as continually growing ligand development, the application of mechanochemistry for novel molecular and material design of phosphorus-based materials will be paramount in these areas of discovery.

Regarding the specific works presented throughout this Thesis, I can suggest several areas of future research and development. Firstly, for the mechanochemical phosphorylation of cellulosic materials and synthetic polymers (Chapter 3), investigation of different phosphate sources, particularly polyphosphates such as those presented by Cummins and Jessen, would more accurately mimic biological phosphorylation pathways, while limiting chain hydrolysis, typically seen under strongly acidic conditions, such as the hydrolysis of  $P_4O_{10}$  to phosphoric acid. Additionally, more in-depth analysis of the phosphorylation of synthetic polymers, including changes in their molecular weight, or what degree of mono- or polyphosphorylation was achieved, should be investigated in more detail. Towards the mechanochemical synthesis of metal phosphide nanoparticles for catalysis (Chapter 4), other metals beyond nickel should also be investigated, such as cobalt or rhodium, as well as the possibility to employ NaPH<sub>2</sub> as a reagent in place of

#### Chapter 6 – Discussion and Conclusions

sodium phosphide. The benefit in using NaPH<sub>2</sub> would be the increased stability against selfreduction, the opportunity to form the generally poorly soluble and non-reactive red phosphorus as a byproduct, as well as improved purification by crystallization to afford a clean starting material. Finally, on improving the application of sodium phosphide towards the bottom-up synthesis of phosphorus-bridged carbon nitrides (Chapter 5), a similar improvement could be made by employing NaPH<sub>2</sub> as an alternative solid-state phosphorus source, as well as by expanding beyond the presented 1,3,5-substituted triazine linker, to investigate the effect of pore size and linker type on the morphology, photochemical behaviour, and ultimately photochemical activity of the P-bridged carbon nitride material. Additionally, for both the bottom-up mechanochemical synthesis of metal phosphide nanoparticles (Chapter 4) or the development of phosphorus-bridged carbon nitride supports (Chapter 5), both systems would benefit from further investigation into their application towards total water splitting (*i.e.* effectiveness for both half reactions) or carbon dioxide reduction. The removal of sacrificial agents in both cases would be a marked improvement, as the oxidative by products of these reagents can often hinder or play secondary roles in the catalytic performance.

## 7. Appendix A: Additional published works

- 1. **Fiss, B. G.**; Douglas, G.; Ferguson, M.; Becerra, J.; Valdez, J.; Do, T.-O.; Friščić, T.; Moores, A. Mechanochemical bottom-up synthesis of phosphorus-linked, heptazine-based carbon nitrides using sodium phosphide, *Beilstein Arch.*, **2022**, DOI: 10.3762/bxiv.2022.45.v1
- 2. Richard, A. J.; Ferguson, M.; **Fiss, B. G.**; Titi, H. M.; Valdez, J.; Provatas, N.; Friščić, T.; Moores, A. *In situ* study of Au nanoparticle growth in a mechanochemical-aging-based synthesis, *ChemRxiv*, **2022**, DOI: 10.26434/chemrxiv-2022-r3w01
- 3. **Fiss, B. G.**; Douglas, G.; Ferguson, M.; Becerra, J.; Valdez, J.; Do, T.-O.; Friščić, T.; Moores, A. Mechanosynthesis of a well-defined graphitic phosphorus-linked carbon nitride (g-PCN) with water splitting activity, *ChemRxiv*, **2022**, DOI: 10.26434/chemrxiv-2022-15cwv-v2
- 4. Titi, H. M.; Marrett, J. M.; Jobin, O.; Mottillo, C.; **Fiss, B. G.**; Moores, A. H.; Robert, É.; Rogers, R. D.; Friščić, T., Metal-organic frameworks induce hypergolic ignition of bulk metals, *ChemRxiv*, **2021**, DOI: 10.33774/chemrxiv-2021-f4dh4
- 5. Fiss, B. G.; Richard, A. J.; Friščić, T.; Moores, A., Mechanochemistry for sustainable, efficient dehydrogenation/hydrogenation, *Can. J. Chem.*, **2020**, *99*, 93-112. DOI: 10.1139/cjc-2020-0

# 8. Appendix B: Supplementary Information for "Mechanochemical Phosphorylation of Polymers and Synthesis of Flame-Retardant Cellulose Nanocrystals"

## **8.1 General Experimental**

## 8.1.1 Materials

All materials were used without further purification unless otherwise specified. HPLC grade phosphoric acid solution (85 %) was purchased from Fischer Scientific<sup>®</sup>. Reagent grade urea was purchased from BioShop Canada Inc<sup>®</sup>. Reagent grade phosphorus pentoxide was purchased from Sigma-Aldrich<sup>®</sup> and stored in a vacuum desiccator until required. All synthetic polymers were purchased from Sigma-Aldrich<sup>®</sup>. Freeze-dried softwood Kraft cellulose nanocrystals were graciously obtained from FPInnovations<sup>®</sup>.

## 8.1.2 Solid/liquid solution-based phosphorylation of cellulose nanocrystals

The reaction was first conducted in a solution state, using deionized water as a solvent. To create the 3 wt. % stock solution, freeze dried CNC (9 g) was suspended in deionized water (291 mL) and stirred vigorously for 24 hrs to ensure good dispersion. 3 wt. % solution (58 g) and 85 % phosphoric acid solution (5.5 g) were combined in a 250 mL three necked flask equipped with a thermometer, and a water condenser. The phosphoric acid was added dropwise to the solution under stirring while it was cooled in an ice bath. The mixture was then stirred while heating at 150 °C for 30 mins, after which the flask was cooled back down to room temperature.<sup>1</sup> Work up of the produced suspensions involved centrifugation 3 times at 9000 RPM for 15 mins, washing with 50 mL deionized water in between to remove any residual acid. The washed samples were then placed

in 14 kDa dialysis membranes (Spectra/Por<sup>®</sup>) and underwent dialysis for 5 days, exchanging the deionized water daily.

#### 8.1.3 Solution based phosphorylation of cellulose nanocrystals

Urea (11 g, 183 mmol) was first melted at 140 °C with stirring in a round bottom flask, the reaction was stirred at 600 RPM while the 3 wt. % cellulose suspension (58 g, 9.66 mmol of glucose monomer) and 85 % phosphoric acid solution (12 g, 104 mmol) were added sequentially dropwise using syringes. Upon complete addition, the reaction flask was reheated to 150 °C and left to stir for 30 mins. 1M sodium hydroxide solution (100 mL) was added to quench the reaction before precipitating the final product in approximately 300 mL of methanol. The resulting product was then washed using centrifugation and dialyzed for 5 days in 14 kDa dialysis membranes (Spectra/Por<sup>®</sup>), exchanging the deionized water daily.

## 8.1.4 Mechanochemical phosphorylation of cellulose nanocrystals in a shaker mill

Freeze dried cellulose nanocrystals (50 mg, 0.28 mmol based on glucose monomers) were combined with urea (168 mg 2.8 mmol) and phosphorus pentoxide (39 mg, 0.28 mmol) in a 10 mL zirconia milling jar with a single 10 mm zirconia milling ball. The reactions were carried out at room temperature for 90 mins at a vibration frequency of 29.5 Hz in a Retsch<sup>®</sup> MM400 shaker mill. Upon completion, the jars were filled with deionized water and hand shaken 3 times for 20 seconds each before transferring the suspension to centrifuge tubes, filling with deionized water to a total volume of 50 mL centrifuging at 9000 RPM for 20 mins and replacing with fresh deionized water in between for a total of 3 cycles before samples were then freeze dried for 48 hrs prior to storage and analysis.

## **8.1.5** Mechanochemical phosphorylation of synthetic polymers in a shaker mill (Table 8.2, Entry 3)

Polyvinyl(alcohol) (180 mg, 0.5 mmol based on the monomer) was combined with phosphorus pentoxide (80 mg, 0.5 mmol) and urea (339 mg, 5 mmol) in a 10 mL zirconia milling jar with one 10 mm zirconia ball and milled for 90 mins at 29.5 Hz at room temperature. The jars were then washed three times with methanol, hand shaking the jars for 20 s each time. The solid was then filtered and dried *in vacuo*.

## 8.1.6 <sup>31</sup>P Magic Angle Spinning (MAS) NMR

Direct polarization <sup>31</sup>P solid-state NMR was performed using a Varian 400 MHz VNMRS widebore spectrometer operating at a <sup>1</sup>H frequency of 399.76 MHz with a 4 mm double-resonance probe spinning at 13 kHz. The <sup>31</sup>P excitation pulse was 2.2  $\mu$ s long and <sup>1</sup>H decoupling was performed using SPINAL-64 decoupling at 110 kHz. In order to acquire quantitative spectra, a recycle delay of 150 s was used. 128 transients were acquired of each sample, for a total experiment time of just under 5.5 hours. Sample integration was compared to an external ammonium dihydrogen phosphate standard. Mnova NMR software (Mestrelab Research) was then used to process spectra and determine phosphorus content. A spectrum for a sample of a known mass of ammonium dihydrogen phosphate was collected and its absolute integration value measured (I<sub>ref</sub>). This integration was then related to the number of moles of phosphate in the reference and used as a point of comparison for the integral of each sample (I<sub>sample</sub>). The calculated mmol of phosphate for each sample was then divided by the mass of the sample in the rotor to give the phosphate loading in mmol kg<sup>-1</sup> of sample:

(I<sub>sample</sub>/I<sub>ref</sub>)(mmoles of reference) = mmoles of phosphate in sample

Phosphate loading = mmoles of phosphate in sample/sample mass loaded into rotor

## 8.1.7 Calculation of polyphosphate loading using <sup>31</sup>P MAS NMR

The integral of all signals in the solid-state NMR <sup>31</sup>P spectrum between +10 and -20 ppm was assigned to polyphosphate and was integrated using a straight summation in MestReNova 12.0.4 (MestreLab, Santiago de Compostela, Spain, 2018). Using the quantitation module provided in MestReNova, which takes into account the number of scans of the spectrum when scaling the integral, these integrals were compared to the integral of the reference ammonium dihydrogen phosphate sample spectrum. The reference spectrum integral was scaled to the total number of millimoles of phosphorus present in the sample, so the quantitation module allowed us to calculate the number of millimoles of phosphorus present in our modified polymers. Loadings were then calculated using the known mass of sample in the NMR rotor.

## 8.1.8 Determination of Degree of Substitution (D<sub>s</sub>)

$$\boldsymbol{D}_{\boldsymbol{S}} = \frac{1.5N_{mod}}{X_{cel}N_{OH}} \tag{1}$$

Where  $N_{mod}$  is the number of modified hydroxyls in mol/g,  $X_{cel}$  is the mass fraction of cellulose in the sample and  $N_{OH}$  is the total number of available hydroxyl groups on the surface in mol g<sup>-1</sup>. 1.5 is a coefficient relating to the free number of hydroxyl groups from anhydroglucose units on the crystals surface.<sup>2</sup> For acid hydrolysis methods, it was calculated that there were an average of 1.7 mmol g<sup>-1</sup> of hydroxyl groups available. With phosphorylated CNCs, the moles of phosphate bonded to the material was determined by <sup>31</sup>P MAS NMR. The phosphate loading was converted to mol/g of the original sample and the fraction of cellulose was also calculated from the original sample mass. This value was then converted to a percentage of substitution by multiplying the

resulting number by 100. All resulting errors were calculated as the standard deviation of samples run in triplicate.

## 8.1.9 X-Ray Photoelectron Spectroscopy (XPS)

Samples were analysed on a Fischer Scientific K $\alpha$  spectrometer using a spot size of 200  $\mu$ m, running 5 survey scans at 200 mV for 50 ms residence times, and 10 scans for specific elements, also at residence times of 50 ms. Desummation and peak position were determined using Avantage processing software.

## 8.1.10 Fourier Transform Infrared Spectroscopy (FTIR)

To further validate that the phosphate ester groups were covalently bound to polymer substrates, both synthetic and biological, samples were analysed *via* FTIR using a Fourier Diagform-Infrared Attenuated Total Reflection PerkinElmer UATR Two Spectrometer through a range of 400 to 4000 cm<sup>-1</sup>, with a resolution of 1 cm<sup>-1</sup>. OPUS 7.5 was used to process and analyse the resulting data.

## 8.1.11 Powder X-Ray Diffraction (PXRD)

Powder sample crystallinity was tested from a 2 $\theta$  range from 4° to 65° on a zerobackground plate using a Bruker D8 Advantage X-Ray Diffractometer equipped with a Cu-Ka ( $\lambda = 1.5418$  Å) source, LinxEye detector, and a Ni filter.

## 8.1.12 Determination of Crystallinity Index (CrI)

The crystallinity index of phosphorylated CNCs, both made in solution and *via* mechanochemistry was conducted using the DiffractSuite Software by Bruker after removing the low-angle signal produced from the zero-background sample holder. Measurements were taken from a  $2\theta$  range of  $10^{\circ}$  to  $65^{\circ}$  to account for small angle scattering.

## 8.1.13 Thermogravimetric Analysis (TGA)

The thermal stability of the samples was subsequently tested using a Mettler-Toledo STARe DSC/TGA. Approximately 5 mg of each sample was analysed in air through a temperature range of 30 to 500°C at a ramp rate of 10°C/min using alumina crucibles. The difference in mass was then calculated using STARe Evaluation software to determine the total mass loss during the temperature ramp, as well as the inflection temperature of the sample.

## 8.1.14 Transmission Electron Microscopy (TEM)

Samples were prepared by first placing a drop of the nanocellulose suspension (0.1 wt. % onto a Cu grid with a carbon backing, followed by staining with a 2 % solution of uranyl acetate. The images were taken on a Technai GF-20 with an accelerating voltage of 200 kV. Particle sizes were measured using ImageJ software over a sample size of 20 particles.

#### 8.1.15 Coating Preparation for Flame-Retardant Testing

1 wt. % suspensions of milled CNC were prepared by suspending 100 mg of modified CNC into 9.9 mL of deionized water. Laminated spruce plywood was cut into 4 cm x 4 cm squares before being hand coated (with two coats in total) and dried in an oven at 85 °C for 5 mins before curing at 150 °C for 5 mins.

## 8.1.16 Qualitative Flame-Retardance Testing

A qualitative test was also conducted to see how 1 wt. % coatings on 4 cm x 4 cm spruce substrates responded to a flame from a butane torch. Samples we exposed to the hottest part of the flame for 10 seconds. Recorded video was analysed frame by frame to determine the point at which ignition of the substrate occurred. The point of ignition was the point at which the generation of a second flame, produced from the burning of the substrate underneath, was detected in the video.

## **8.2 Results and Discussion**

## 8.2.1 Reaction Optimization

Along with choosing alternate additives, the effect of varying the equivalency of the phosphorylating agent as well as the overall milling time was also investigated. Varying the ratio of phosphorylating agent revealed that loadings of 0.1 and 0.2 equivalents did not impart enough phosphorylation, with D<sub>s</sub> values of 0.17 % and 0.28 % respectively. This in turn afforded poorer thermal stability having mass losses of 91 and 80 %, with inflection temperatures of 251 and roughly 202 °C. (Table 8.1, Entries 1-2). Loadings greater that 1 equivalent did not fare any better, showing a D<sub>s</sub> of 1.4 % with 2 equivalents and an undetectable amount of phosphate detected when milling with 5 equivalents. Surprisingly, both samples still show mass loss percentages around 72 and 73 % respectively, with lower inflection temperatures compared to samples which used sub stoichiometric amounts of phosphorus pentoxide. This could support the idea that a secondary reaction is occurring, producing a species which can still aid in flame-retardancy of the material, with a lower phosphate loading. One hypothesis is that higher loadings are favouring the formation of ammonium dihydrogen phosphate, the product of phosphoric acid and ammonia, both degradation products of the starting materials.<sup>3</sup> A second possible reason would be that at higher phosphorus pentoxide loading begin to favour the direct dehydration of the CNC as opposed to favouring only phosphorylation.

**Table 8.1.** Effect of phosphorylating agent loading on the thermal stability of phosphorylated CNC.

CNC $P_2O_5$ (X equiv.), Urea (10 equiv.)							
90 mins, 30 Hz, ZrO <sub>2</sub> jar							
10 mm ZrO <sub>2</sub> ball							
Entry	P-Agent Equiv.	P loading / mmol kg <sup>-</sup>	<sup>.1</sup> Ds/%	Mass Loss / %	Inflection Temp. / °C		
1	0.1	21 ± 2	0.17 ± 0.02	91 ± 4	251 ± 3		
2	0.2	$34 \pm 4$	0.28 ± 0.03	80.4 ± 0.1	201.8 ± 0.1		
3	1	3300 ± 160	26 ± 1	70 ± 1	172.0 ± 0.1		
4	2	172 ± 4	1.40 ± 0.03	71.7 ± 0.1	182 ± 2		
5	5	-	-	72.7 ± 0.1	179 ± 5		

The showings of these initial results confirmed that in terms of reagent loadings, that for CNC phosphorylation, the optimum loading was 1:10:1 of CNC to urea, to phosphorus pentoxide.

While the majority of testing at this stage had focused on 90 min reactions, the influence of milling time was also investigated on the phosphate loading,  $D_s$  as well as the thermal behaviour of the final product. Milling for 180 mins total showed a 2 % substitution, while maintaining a mass loss of 73 % at an inflection temperature of 212 °C (Table 8.2, Entry 1). This further supports the hypothesis of a competing reaction in which the dehydration of the CNC is favoured at longer milling times. Samples run for 60 mins showed a lower  $D_s$  than samples run for 90 mins at 11 %, retaining 79 % of their mass with a far later inflection point of 435 °C (Table 8.2, Entry 3). When milled for only 30 mins showed very little variation in terms of thermal stability compared to samples run for 15 mins, but a decrease in  $D_s$  to 1.6 %. After only 15 mins, a  $D_s$  of only 0.5 was achieved, with a higher mass loss of 83 % at a later inflection point of 218 °C (Table 8.2, Entries 4 & 5) compared to samples run for 90 mins. This implies that milling times of 90 mins give the highest degree of functionalization, without favouring the formation of undesirable by-products after longer runtimes.

X mins, 30 Hz, ZrO <sub>2</sub> jar 10 mm ZrO <sub>2</sub> ball								
Entry	Milling Time / min	P loading / mmol kg <sup>-1</sup>	D <sub>s</sub> / %	Mass Loss / %	Inflection Temp. / °C			
1	180	269 ± 207	2 ± 2	73 ± 6	212 ± 23			
2	90	3300 ± 160	26 ± 1	70 ± 1	172.0 ± 0.1			
3	60	1400 ± 70	11 ± 1	79 ± 3	439 ± 5			
4	30	200 ± 97	$1.6 \pm 0.8$	82 ± 1	292 ± 5			
5	15	62 ± 14	$0.5 \pm 0.1$	83 ± 1	218 ± 3			

CNC  $P_2O_5$  (1 equiv.), Urea (10 equiv.)  $\rightarrow$  Phosphorylated CNC

**Table 8.2.** Optimization of milling time at 29.5 Hz for CNC phosphorylation.

As a final test to see if the reaction was impact-dependant, meaning that the reaction didn't proceed simply by mixing the reagents, but rather that the impact force of milling was required, a control was conducted in which the powdered reagents were mixed together, as powders in the absence of solvents. This control was mixed without solvent in a beaker for 90 mins at 650 RPM and showed a mass loss of 71 % with a later inflection temperature of 277 °C in air. While the mass loss is consistent with samples prepared by milling, the later inflection temperature may imply that some dehydration of the CNC may be occurring *in situ* upon reacting with  $H_3PO_4$  during mixing.

## 8.2.2 <sup>31</sup>P Magic Angle Spinning NMR of CNC samples



**Figure 8.1.** <sup>31</sup>P MAS NMR of solution phosphorylated cellulose nanocrystals without urea. Asterisks denote spinning sidebands.



**Figure 8.2.** <sup>31</sup>P MAS NMR of solution phosphorylated cellulose nanocrystals with urea. Asterisks denote spinning sidebands.



**Figure 8.3.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated cellulose nanocrystals without the assistance of urea. Asterisks denote spinning sidebands.



**Figure 8.4.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated cellulose nanocrystals with the assistance of urea. Asterisks denote spinning sidebands.





**Figure 8.5.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated poly(vinyl alcohol) (P-PVA). Asterisks denote spinning sidebands.



**Figure 8.6.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated poly(vinyl chloride) (P-PVC). Asterisks denote spinning sidebands.



**Figure 8.7.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated poly(ethylene glycol) (P-PEG). Asterisks denote spinning sidebands.



**Figure 8.8.** <sup>31</sup>P MAS NMR of mechanochemically phosphorylated poly(ethylene glycol) methyl ester (P-mPEG). Asterisks denote spinning sidebands.



Figure 8.9. <sup>31</sup>P MAS NMR of mechanochemically phosphorylated Kraft lignin. Asterisks denote spinning sidebands.

8.2.4 X-Ray Photoelectron Spectroscopy (XPS)



Figure 8.10. Survey scan of heterogeneously phosphorylated CNC from solution.



Figure 8.11. Phosphorus focused scan of heterogeneously phosphorylated CNC from solution.



Figure 8.12. Carbon focused scan of heterogeneously phosphorylated CNC from solution.



Figure 8.13. Survey scan of homogeneously phosphorylated CNC from solution.

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Figure 8.14. Phosphorus focused scan of homogeneously phosphorylated CNC from solution.



Figure 8.15. Carbon focused scan of homogeneously phosphorylated CNC from solution.



Figure 8.16. Survey scan of CNC mechanochemically phosphorylated in a MM 400 mill.



Figure 8.17. Phosphorus focused scan of CNC mechanochemically phosphorylated in a MM 400 mill.

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Figure 8.18. Carbon focused scan of CNC mechanochemically phosphorylated in a MM 400 mill.



Figure 8.19. Oxygen focused scan of CNC mechanochemically phosphorylated in a MM 400 mill.

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Figure 8.20. Nitrogen focused scan of CNC mechanochemically phosphorylated in a MM 400 mill.

8.2.5 Fourier Transform Infrared Spectroscopy (FTIR)



**Figure 8.21.** FTIR of CNC phosphorylated in solution with the assistance of molten urea (red) compared to untreated CNC (blue).

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Figure 8.22. FTIR of CNC phosphorylated in solution without urea (red) compared to untreated CNC (blue).



Figure 8.23. FTIR of CNC phosphorylated in Retsch MM400 mill with urea (red) compared to untreated CNC (blue).





Figure 8.24. Comparative PXRD patterns of untreated and phosphorylated cellulose nanocrystals.



## 8.2.7 Transmission Electron Microscopy of Modified CNC

Figure 8.25. TEM image of untreated CNC stained with uranyl acetate.



Figure 8.26. TEM image of CNC following phosphorylation in solution, assisted by urea.



Figure 8.27. TEM image of CNC following phosphorylation by ball-milling, assisted by urea.

## 8.2.8 Thermogravimetric Analysis (TGA)

When investigating the type of jar material used for milling, it was noted that samples milled in Teflon had minimal mass loss and a much higher inflection temperature (Table 8.3). It was thus hypothesized that the strong acidic conditions along with the milling of cellulose nanocrystals caused excessive abrasion on the jars interior, resulting in Teflon leaching into the final product.

Table 8.3. Comparative TGA data of	phosphorylated CNC in Teflon <sup>™</sup>	and zirconia jars to untreated CNC

Entry	Jar Material	Average Mass Loss / %	Avg. Inflect Temp. / °C
1	Teflon™	$7.8 \pm 0.3$	496 ± 1
2	Zirconia	70 ± 1	172.0 ± 0.1

Chapter 8 – Appendix B: Supplementary Information for "Mechanochemical Phosphorylation of Polymers and Synthesis of Flame-Retardant Cellulose Nanocrystals"



Figure 8.28. TGA of CNC phosphorylated only with phosphorus pentoxide (red) compared to untreated CNC (blue).



Figure 8.29. TGA of CNC milled only with urea (red) compared to untreated CNC (blue).

Chapter 8 – Appendix B: Supplementary Information for "Mechanochemical Phosphorylation of Polymers and Synthesis of Flame-Retardant Cellulose Nanocrystals"



**Figure 8.30.** TGA of CNC phosphorylated with the assistance of urea in solution (red) compared to untreated CNC (blue).



**Figure 8.31.** TGA of CNC phosphorylated with the assistance of urea in MM 400 mill (red) compared to untreated CNC (blue).

## 8.3 References

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- 2. Eyley, S.; Thielemans, W. Surface Modification of Cellulose Nanocrystals. *Nanoscale* **2014**, *6* (14), 7764–7779.
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9. Appendix C: Supplementary Information for "Solvent-free mechanochemical synthesis of ultrasmall nickel phosphide nanoparticles and their application as a catalyst for the hydrogen evolution reaction (HER)"

## **9.1 General Experimental Procedures**

## 9.1.1 Materials

Unless otherwise stated, all manipulations were done under the rigorous exclusion of air and moisture in an argon-filled glovebox or standard Schlenk line techniques. NiCl<sub>2</sub> (Strem Chemicals Inc. 99.999 % trace metal basis) was used as received. Oleylamine (Sigma Aldrich, tech. grade 70 %) was and degassed prior to use by heating under vacuum at 100 °C for 4 hours and stored in an argon-filled glovebox with O<sub>2</sub> and H<sub>2</sub>O levels both at and below 0.5 ppm. Pentadecylamine (Sigma Aldrich, 96 %), hexadecylamine (Sigma Aldrich, 98 %), Trioctylphosphine (Sigma Aldrich, 97 %) and 1-aminoheptadecane (TCI Chemicals, >95 %) and tetraethylammonium hydroxide solution (Sigma Aldrich, 40 % in water) were used as received. Sodium phosphide was made based on a previous procedure published by Heift *et al.*, using standard Schlenk line techniques and an argon-filled glovebox.<sup>1</sup>

#### 9.1.2 Mechanochemical synthesis of nickel phosphide nanoparticles

To a 10 mL zirconia jar was added anhydrous nickel (II) chloride (0.38 mmol, 0.05 g), sodium phosphide (0.26 mmol, 0.026 g) and oleylamine (1.3 mmol, 0.345 g) along with one 10 mm zirconia ball. The jar was then sealed under argon and sealed with electrical tape before milling at 30 Hz for 90 mins and aging at room temperature for 18 hours. Upon opening the jar, a black paste

was noted. The particles were then washed first by centrifugation in a 3:1 v/v EtOH/hexanes mixture all at 12 000 rpm for 20 minutes, this washing cycle was repeated a total of 3 times before being dried *in vacuo* and resuspended in hexanes.

## 9.1.3 Varying the washing solvent

It was consistently noted, that simply by washing the particles by centrifugation with a 3:1 ethanol/hexane mixture would often leave residual ligand or NaCl in the samples, noted by their reflections in diffractograms (Figure 9.18). The washing procedure was thus improved by centrifuging the particles first in a 3:1 mixture of ethanol/hexane at 12 000 rpm for 20 minutes followed by 2 washes in 2:2 methanol/hexanes, to remove any excess ligand, or halide salt precursors or by-products.

## 9.1.4 Synthesis of bulk g-C<sub>3</sub>N<sub>4</sub>

Bulk g-C<sub>3</sub>N<sub>4</sub> (denoted as CN) was prepared from dicyandiamide using the method reported previously.<sup>2,3</sup> Briefly, dicyandiamide powder was calcined under air at 550 °C for 2h (2 °C min<sup>-1</sup>). The obtained bulk was rinsed with water before filtering and drying at 70 °C.

## 9.1.5 Synthesis of g-C<sub>3</sub>N<sub>4</sub> supported Ni<sub>x</sub>P<sub>y</sub> photocatalysts

## Approach 1

Bulk g-C<sub>3</sub>N<sub>4</sub> was synthesized from dicyandiamide following the method reported in our previous publication.<sup>4</sup> Subsequently, 1.00 g of the bulk g-C<sub>3</sub>N<sub>4</sub> powder and 0.03 g of Ni<sub>x</sub>P<sub>y</sub> powder were dispersed in 400 mL of anhydrous ethanol under the sonication for 30 minutes. The solution was kept stirring for 1h before drying thoroughly at 60°C. The dried powder was heated to 300-400 °C (heating rate of 3 °C min<sup>-1</sup>) for 4 h under Ar flow (100 mL min<sup>-1</sup>) (denoted as CN-NiP) (Figure 9.1).



Figure 9.1. Preparation of CN-Ni<sub>x</sub>P<sub>y</sub> sample.

## Approach 2

#### Step 1: Protonation of carbon nitride material

1.00 g of the bulk g-C<sub>3</sub>N<sub>4</sub> powder was dispersed in distilled water (V=200 mL) under the sonication for 30 minutes, followed by the addition of the HCl solution (200 mL, 1M). After stirring for 24 hours, the solution was centrifuged to obtain protonated g-C<sub>3</sub>N<sub>4</sub>. The protonated g-C<sub>3</sub>N<sub>4</sub> was washing several times with distilled water to remove excess HCl before re-dispersing in 200 mL water (sol A) (Figure 9.2).



Figure 9.2. Schematic preparation of protonated g-C<sub>3</sub>N<sub>4</sub>.

#### **Step 2: Cation exchanging**

The cation exchange followed the method reported in our previous publication.<sup>5</sup> Ni<sub>x</sub>P<sub>y</sub> powder (0.3 g) was dispersed in the mixture of ethanol (30 mL), water (30 mL), and 1 g of tetraethylammonium hydroxide (TEAOH) under the sonication for 30 minutes. The mixture was stirred for 24 hours for the cation exchange. Acetone (200 mL) was then added to the obtained cloudy solution to precipitate nanoparticles (TEA-Ni<sub>x</sub>P<sub>y</sub>). The precipitate was centrifuged and washed several times with acetone before re-dissolving in 50 mL water (sol B) (Figure 9.3).



Figure 9.3. Schematic illustration of the cation exchange of Ni<sub>x</sub>P<sub>y</sub> nanoparticles.

#### Step 3: Deposition on the g-C<sub>3</sub>N<sub>4</sub> surface

Firstly, 9.25 mL sol B was added to 200 mL sol A (the content of  $Ni_xP_y$  was 3 wt. %). The mixture was stirred for 12 hours followed by centrifugation. The obtained solid was dried at 70 °C overnight before heating to 300-400 °C for 4 hours under argon flow (100 mL min<sup>-1</sup>) (denoted as CNH-Ex-300) (Figure 9.4). On the other hand, after stirring for 12 hours, the mixture was dried

thoroughly at 60 °C. The obtained powder was similarly heated to 300-400 °C for 4 hours under argon flow (100 mL min<sup>-1</sup>) (denoted as CNH-Im-300) (Figure 9.4).



Figure 9.4. Schematic preparation of CNH-Ex-300 and CNH-Im-300 samples.

#### **9.1.6 Photocatalytic test**

To investigate the viability of these mechanochemically synthesized nickel phosphide nanoparticles as catalysts for hydrogen production, we paired them with a graphitic carbon nitride support. The photocatalytic reaction was carried out in an oxygen-free closed reactor at the ambient temperature and atmospheric pressure (Figure 10.5), similarly to our previous work.<sup>2</sup> First, 50 mg of the prepared-photocatalyst was added to reaction cells containing 100 mL of pure water and 5g of triethanolamine (TEOA). This solution is thoroughly stirred, followed by purging with N<sub>2</sub> for 30 minutes to remove oxygen. The reaction was initiated by irradiating with the simulated sunlight of 100 mW.cm<sup>-2</sup> (150 W xenon lamp,  $259 < \lambda < 1904$  nm). The evolved H<sub>2</sub> was analyzed after 1, 2, 3 and 4h of reaction using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and using N<sub>2</sub> as the carrier gas.

The photocatalytic stability of as-prepared photocatalyst was tested for 3 cycles of 4 hours. The second and third cycles were carried out without repeating the photo-deposition step.


**Figure 9.5.** Schematic illustration of the photocatalytic test. Reactions were conducted using 50 mg of photocatalyst, in 100 mL of  $H_2O$  under simulated sunlight conditions of 100 mW cm<sup>-2</sup> for 3 hours.

#### 9.1.7 Photoelectrochemical characterization

Similarly to our previous work, working electrodes were fabricated by spraying the photocatalyst slurry (5 mg in ethanol) onto the FTO glass slides (S = 1 cm<sup>2</sup>) followed by calcination under air at 250 °C for 4 h.<sup>6</sup> Photoelectrochemical characterizations were determined by an electrochemical Autolab PGSTAT-204 workstation with the prepared electrode, Pt wire and Ag/AgCl electrode as the working, counter and reference electrodes, respectively. The electrodes were all immersed in Na<sub>2</sub>SO<sub>4</sub> solution (0.5 M). The transient photocurrent was collected by irradiating the working electrode under the solar simulator light (150 W xenon lamp, 259 <  $\lambda$  < 1904 nm). The electrochemical impedance spectroscopy (EIS) Nyquist plots were recorded with an amplitude of 10 mV and frequencies from 100 kHz to 0.1 Hz.

#### 9.1.8 X-Ray Photoelectron Spectroscopy (XPS)

Samples were analysed on a Fischer Scientific K $\alpha$  spectrometer using a spot size of 200  $\mu$ m, running 5 survey scans at 200 mV for 50 ms residence times, and 10 scans for specific elements, also at residence times of 50 ms. Desummation and peak position were determined using Avantage processing software.

#### 9.1.9 Fourier Transform Infrared Spectroscopy (FTIR)

Samples were analysed via FTIR using a Fourier Diagform-Infrared Attenuated Total Reflection PerkinElmer UATR Two Spectrometer through a range of 400 to 4000 cm<sup>-1</sup>, with a resolution of 1 cm<sup>-1</sup>. OPUS 7.5 was used to process and analyse the resulting data.

#### 9.1.10 Powder X-Ray Diffraction (PXRD)

Powder sample crystallinity was tested from a  $2\theta$  range from 8° to 80° on a zero-background plate using a Bruker D8 Advantage X-Ray Diffractometer equipped with a Cu-Ka ( $\lambda = 1.5418$  Å) source, LinxEye detector, and a Ni filter.

#### 9.1.11 Thermogravimetric Analysis (TGA)

The thermal stability of the samples was subsequently tested using a TA instruments Discovery TGA 5500. Approximately 5 mg of each sample was analysed in nitrogen through a temperature range of 30 to 700°C at a ramp rate of 20°C/min using alumina crucibles. The difference in mass was then calculated using TRIOS Evaluation software to analyze the residues upon thermal removal of the surface ligands.

#### 9.1.12 Transmission Electron Microscopy (TEM)

Samples were prepared by first placing a drop of the nanoparticle suspension in hexanes onto a Cu grid with a carbon backing, allowing to dry overnight in a vacuum oven prior to imaging. The images were taken on a Technai GF-20 with an accelerating voltage of 200 kV. All HAADF measurements were conducted on a Technai TALOS using an accelerating voltage of 200 kV.

#### 9.1.13 Mass Intensity (MI) and Energy Measurements

All literature procedures were followed as they are presented in their respective references. Energy draw of each reaction was measured using a Kill-A-Watt P3 P4600 Power meter, recording the

energy demand in kWH and diving this by the mass of dry product obtained to give the energy

usage in kWHg<sup>-1</sup>.

# 9.2 Results and Discussion



#### 9.2.1 Transmission Electron Microscopy (TEM) Images

**Figure 9.6.** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of  $NiCl_2$ , 2 molar equivalents of  $Na_3P$  and 2 equivalents of pentadecylamine ligand ( $Ni_xP_y$ -2-C15).



**Figure 9.7.** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of  $NiCl_2$ , 2 molar equivalents of  $Na_3P$  and 5 equivalents of pentadecylamine ligand ( $Ni_xP_y$ -5-C15).



**Figure 9.8.** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of  $NiCl_2$ , 2 molar equivalents of  $Na_3P$  and 2 equivalents of hexadecylamine ligand ( $Ni_xP_y$ -2-C16).



**Figure 9.9.** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of  $NiCl_2$ , 2 molar equivalents of  $Na_3P$  and 5 equivalents of hexadecylamine ligand ( $Ni_xP_y$ -5-C16).



**Figure 9.10.** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 2 equivalents of heptadecylamine ligand ( $Ni_xP_y$ -2-Cl7).



**Figure 9.11.** TEM images of NixPy nanoparticles made mechanochemically using 3 molar equivalents of NiCl2, 2 molar equivalents of Na3P and 10 equivalents of oleylamine ligand (NixPy-10-OAm).



**Figure 9.12** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 2 equivalents of TOP ligand ( $Ni_xP_y$ -2-TOP).



**Figure 9.13** TEM images of  $Ni_xP_y$  nanoparticles made mechanochemically using 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 5 equivalents of TOP ligand ( $Ni_xP_y$ -5-TOP).

#### 9.2.2 Energy-Dispersive X-Ray (EDX) Spectroscopy



Figure 9.14 EDX Analysis of Ni<sub>3</sub>P<sub>2</sub> nanoparticles prepared with 10 equivalents of oleylamine ligand (Ni<sub>x</sub>P<sub>y</sub>-10-OAm).

#### 9.2.3 X-Ray Photoelectron Spectroscopy (XPS)



**Figure 9.15** XPS spectra for the a) phosphorus 2p orbital focused scan and b) Ni 2p orbital scans for freshly made of nickel phosphide nanoparticles made using 5 equivalents of tris-*n*-octylphosphine ligand (Ni<sub>x</sub> $P_y$ -5-TOP).



**Figure 9.16** XPS Survey scan of as-made  $Ni_xP_y$  nanoparticles made with 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 5 molar equivalents of heptadecylamine ( $Ni_xP_y$ -5-C17).



**Figure 9.17** XPS Survey scan of as-made  $Ni_xP_y$  nanoparticles made with 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 5 molar equivalents of heptadecylamine on a 2.5 gram scale in a planetary mill (Ni<sub>x</sub>P<sub>y</sub>-5-C17).



**Figure 9.18** XPS spectra for the a) phosphorus 2p orbital focused scan and b) Ni 2p orbital scans for as-made Ni<sub>x</sub>P<sub>y</sub> nanoparticles made with 3 molar equivalents of NiCl<sub>2</sub>, 2 molar equivalents of Na<sub>3</sub>P and 5 molar equivalents of heptadecylamine on a 2.5 gram scale in a planetary mill (Ni<sub>x</sub>P<sub>y</sub>-5-C17).

Table 9.1 Calculation of stoichiometr	y based on XPS	survey scan data.
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Entry	Sample	Ni atomic %	P atomic %	O atomic %	Final stoichiometry
1	Ni <sub>x</sub> P <sub>y</sub> -5-C17 Retsch MM400 shaker mill	12.8	6.7	44.8	Ni <sub>2.3</sub> PO <sub>6.3</sub>
2	Ni <sub>x</sub> P <sub>y</sub> -5-C17 planetary mill	9.1	4.7	38.0	Ni <sub>1.9</sub> PO <sub>8</sub>

#### 9.2.4 Powder X-Ray Diffractograms (PXRD)



Figure 9.19. PXRD diffractograms of  $Ni_3P_2$  nanoparticles prepared with 5 equivalents of heptadecylamine ligand using mechanochemical methods, compared to simulated patterns for various phosphide phases, as well as reactants and by-products.



Figure 9.20. PXRD diffractograms of  $Ni_2P$ ,  $Ni_5P_4$  and  $NiP_3$  nanoparticles as well as the effect of washing procedure on ligand removal.

9.2.5 Fourier Transform Infrared Resonance Spectroscopy (FTIR)



**Figure 9.21.** FTIR of freshly made  $Ni_xP_y$  nanocatalyst made with 3 equivalents of NiCl<sub>2</sub>, 2 equivalents of Na<sub>3</sub>P and 5 equivalents of heptadecylamine ligand ( $Ni_xP_y$ -5-Cl7).

Chapter 9 – Appendix C: Supplementary Information for "Solvent-free mechanochemical synthesis of ultrasmall nickel phosphide nanoparticles and their application as a catalyst for the hydrogen evolution reaction (HER)"



**Figure 9.22.** FTIR of freshly made  $Ni_xP_y$  nanocatalyst made with 3 equivalents of  $NiCl_2$ , 2 equivalents of  $Na_3P$  following ligand exchange with tetraethylammonium ligand and mounting onto g-C<sub>3</sub>N<sub>4</sub> support (CNH-Im-300).

9.2.6 Thermogravimetric Analysis (TGA)



**Figure 9.23.** TGA of freshly made  $Ni_xP_y$  nanocatalyst made with 3 equivalents of  $NiCl_2$ , 2 equivalents of  $Na_3P$  and 5 equivalents of heptadecylamine ligand ( $Ni_xP_y$ -5-C17).

Chapter 9 – Appendix C: Supplementary Information for "Solvent-free mechanochemical synthesis of ultrasmall nickel phosphide nanoparticles and their application as a catalyst for the hydrogen evolution reaction (HER)"



**Figure 9.24.** TGA of  $Ni_xP_y$  nanocatalyst made with 3 equivalents of  $NiCl_2$ , 2 equivalents of  $Na_3P$  following ligand exchange with tetraethylammonium ligand and mounting onto  $g-C_3N_4$  support (CNH-Im-300).

Entry	Catalyst	H₂ Production / µmol g <sup>-1</sup> h <sup>-1</sup>	Key Parameter	Reference
1	3 wt. % Ni <sub>x</sub> P <sub>y</sub> @g- C <sub>3</sub> N <sub>4</sub>	233.90	Uses no solvent or high temperature for ultrasmall Ni <sub>x</sub> P <sub>y</sub> synthesis	This work
2	0.45 wt. % CoP	1074	Use of ultrasmall CoP cocatalyst at very low loading	Luo <i>et al.</i> 7
3	8 wt. % Fe <sub>x</sub> P@g- C₃N₄	~90.00ª	Uses least toxic Fe <sub>x</sub> P cocatalyst	Zhao et al.8
4	10 wt. % Cu <sub>3</sub> P@g- C <sub>3</sub> N <sub>4</sub>	159.41	Low toxicity Cu <sub>3</sub> P, in-house made C <sub>3</sub> N <sub>4</sub>	Shen <i>et al.</i> 9
5	2 wt. % Ni <sub>2</sub> P@sg- C <sub>3</sub> N <sub>4</sub>	644.00	In-house made sol-gel $C_3N_4$	Indra <i>et al.</i> <sup>10</sup>
6	5 wt. % Ni₂P@g- C₃N₄	162.00		Sun <i>et al.</i> <sup>11</sup>
7	5 wt. % Ni <sub>12</sub> P <sub>5</sub> @g- C <sub>3</sub> N <sub>4</sub>	120.00 <sup>b</sup>	Comparison of active phase for Ni <sub>x</sub> P <sub>y</sub> cocatalyst	Sun <i>et al.</i> <sup>11</sup>
8	5 wt. % Ni₃P@g- C₃N₄	110.00 <sup>b</sup>		Sun <i>et al.</i> <sup>11</sup>
9	2 wt. % Co <sub>2</sub> P@g- C <sub>3</sub> N <sub>4</sub> +1 mM K <sub>2</sub> HPO <sub>4</sub>	556°	Low loading and high turnover with Co <sub>2</sub> P; additive role of external phosphate also boosted activity	Shen <i>et al.</i> <sup>12</sup>
10	$Co_2PO_4OH@g-C_3N_4$	254	Shows synergistic role of metal phosphate hydroxide for HER; direct sunlight	Lakhera et al.13

**Table 9.2.** Comparison of selected key works using earth-abundant metal phosphide cocatalysts on a g-C<sub>3</sub>N<sub>4</sub> support to this presented work.

<sup>a</sup> Based on a best approximation from Figure 5c after 1 hour

<sup>b</sup> Based on a best approximation from data from Figure 6

<sup>c</sup> Best approximation to give comparable hydrogen production in µmol g<sup>-1</sup> h<sup>-1</sup>

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# **10.** Appendix D: Supplementary Information for "Mechanosynthesis of a well-defined graphitic phosphorus-linked carbon nitride (g-PCN) with water splitting activity"

# **10.1 Materials and Methods**

Caution: Sodium phosphide readily decomposes in the presence of moist air, and protic organic solvents to produce toxic and pyrophoric phosphane gas, all workups should be conducted in a glovebox or well ventilated fumehood.

All manipulations were conducted in an argon-filled glovebox with O<sub>2</sub> and H<sub>2</sub>O levels both  $\leq 0.5$  ppm. Dimethoxyethane (DME) was dried and distilled under argon over sodium metal with a benzophenone radical indicator. All other solvents were used as received. Cyanuric chloride (Sigma Aldrich, 99 %) was recrystallized from toluene and stored in the glovebox prior to use. Urea was purchased from VWR and ground into a fine powder with an agate mortar and pestle prior to use. Sodium phosphide was made using a previously reported method from red phosphorous, sodium metal and naphthalene using standard Schlenk techniques and an argon-filled glovebox.<sup>1</sup> All nanomaterial workups were conducted at room temperature (20 °C) and atmospheric pressure, unless otherwise stated.

#### 10.1.1 Furnace synthesis of g-C<sub>3</sub>N<sub>4</sub>

To an alumina crucible was added melamine (5 g) before loosely capping. The crucible was then heated in a box furnace at 550 °C for 4 hours with a ramp rate of 5 °C min<sup>-1</sup>.<sup>2</sup> The resultant pale-yellow powder (1.4 g) was collected and pulverized in a mortar and pestle prior to storage.

#### 10.1.2 Furnace synthesis of P@CN

The solid-state synthesis of phosphorus-doped graphitic carbon nitride was adapted from literature.<sup>3</sup> To a 250 mL beaker, melamine (5.0 g) was suspended in 100 mL of DI water. After 30 minutes of stirring at room temperature, 85 % phosphoric acid solution (2.8 mL) was added using a micropipette. The suspension was then heated to 80 °C to dryness (approximately 6 hours) and the resulting colourless solid (8.0 g) was collected and added to an alumina crucible. The crucible was then loosely capped and heated in a box furnace at 560 °C for 4 hours with a ramp rate of 5 °C min<sup>-1</sup>. The resulting pale-yellow powder (3.0 g) was pulverized in a mortar and pestle before storage.

#### 10.1.3 Mechanochemical Synthesis of phosphorus-linked graphitic carbon nitride (g-PCN)

To a 10 mL FormTech Scientific zirconia milling jar cyanuric chloride (0.360 g, 1 mmol) and sodium phosphide (0.195 g, 1 mmol) were added with two 7 mm zirconia balls. The jars were then sealed with electrical tape, both over the seam and along the length of the jar before taking them out of the glovebox and milling on a Retsch MM400 mixer mill for 30 minutes at 29.5 Hz. The powder was then washed in 3:1 95 % ethanol/water mixture (v/v) by centrifuging at 10 000 rpm for 15 minutes. The supernatant was decanted and replaced with 10 mL of water and 30 mL of ethanol, for a total of 3 washings before suspending the g-PCN in ethanol and drying *in vacuo* at 50 °C for 8 hours.

#### 10.1.4 XPS analysis of pristine and phosphorus-linked carbon nitrides

Samples were analysed on a Fischer Scientific K $\alpha$  X-Ray spectrometer with an excitation source of Al K $\alpha$  = 1486.6 eV. The binding energies were corrected by referencing the C 1s line to 284.80 eV. A spot size of 400 µm was used, running 5 survey scans at 200 mV for 50 ms residence times, and 10 scans for specific elements, also at residence times of 50 ms. Charge shifting and peak

desummation were performed using Avantage processing software. Peak binding energies of g-PCN200 and g-PCN300 were positionally referenced to g-PCN to compare ratios of similar surface species following annealing.

#### 10.1.5 <sup>31</sup>P MAS NMR analysis of g-PCN series

Direct polarization <sup>31</sup>P solid-state NMR was performed using a Varian 400 MHz VNMRS widebore spectrometer operating at a <sup>1</sup>H frequency of 399.76 MHz with a 4 mm double-resonance probe spinning at 13 kHz. The <sup>31</sup>P excitation pulse was 2.2 µs long and <sup>1</sup>H decoupling was performed using SPINAL-64 decoupling at 110 kHz. For all phosphorylated materials, a recycle delay of 150 s was used and 128 transients were acquired of each sample, for a total experiment time of just under 5.5 hours. Sample integration was compared to an external ammonium dihydrogen phosphate standard acquired in one single scan after 2.5 min in the magnet (to ensure full polarization).

#### 10.1.6 Powder X-Ray Diffraction (PXRD) analysis of g-PCN series

Powder X-ray diffraction patterns were acquired over a range of 8° to 80°  $2\theta$  with a step size of 0.02° 2 $\theta$  and an integration time of 0.5 s using a Bruker D8 Advantage X-Ray Diffractometer equipped with a Cu-Ka ( $\lambda = 1.5418$  Å) source, LinxEye detector, and a Ni filter. Measurements were performed using a Si zero background holder. PXRD patterns were analysed using X'Pert HighScore Plus.

#### **10.1.7 Determination of Crystallinity Index (CrI)**

The crystallinity index was measured using the DiffractSuite Software by Bruker after removing the low-angle signal produced from the zero-background sample holder. Measurements were taken over a range of 8° to 80°  $2\theta$  to account for small angle scattering.

# **10.1.8** Scanning tunneling electron microscopy- electron energy loss spectroscopy (STEM-EELS)

STEM-EELS measurements were performed using a ThermoFisher Talos F200X transmission electron microscope operated at 200 keV, equipped with a high brightness XFEG Schottky source and a Gatan Enfinium ER 970 EELS spectrometer. The core-loss spectra were corrected using the zero-loss peak (ZLP) shift correction from a Dual-EELS measurement. The dwell time for EELS acquisition on every spectrum image was 0.5 sec, with a drift correction at every row. Relative thickness was measured from an area of 100 nm  $\times$  100 nm.

#### 10.1.9 Prediction of NMR spectra through Gaussian and CASTEP calculations

Structures of the suspected by-products of the reaction between C<sub>3</sub>Cl<sub>3</sub>N<sub>3</sub> and Na<sub>3</sub>P (Chart S1) were optimized using the Gaussian 16<sup>4</sup> code using through its density functional theory (DFT) modules. All input files including the original generation of atomic coordinates were prepared using the GaussView 6.1 package.<sup>5</sup> Species were treated as isolated molecules and thus described by an atom-centered basis set, 6-311+G(d,p)<sup>6,7</sup> using the B3LYP functional.<sup>8,9</sup> Basis sets used in this study were obtained from https://www.basissetexchange.org/.<sup>10-12</sup> Predicted <sup>31</sup>P NMR shielding tensors for the optimized structures were obtained using the gauge independent atomic orbital (GIAO) method<sup>13-17</sup> in Gaussian 16. GaussView 6.1 was used to analyze the predicted magnetic shielding tensors and obtain the isotropic chemical shifts,  $\delta_{iso}$ , of the isolated molecules using,  $\delta_{iso} = \sigma_{ref} - \sigma_{iso}(1)$  Where  $\sigma_{iso}$  is the isotropic magnetic shielding of the molecule studied and  $\sigma_{ref}$  is the shielding of a given reference species. The chemical shifts of the isolated molecules in this study were referenced to triphenylphosphine oxide (TPPO) with its experimental peak known to be at 26.63 ppm.

Bulk g-PCN was studied using periodic DFT calculations employing the CASTEP<sup>18</sup> plane wave code (v20.11) with input files generated using the cif2cell program.<sup>19</sup> Structural optimizations were performed using the PBE<sup>20</sup> functional with the Grimme-D3<sup>21</sup> correction. The planewave energy cut off was converged at 900 eV and the core regions of electron density were described by On-The-Fly ultrasoft pseudopotentials from the CASTEP library. The Brillouin zone was sampled using a Monkhorst-Pack<sup>22</sup> grid with a k-point spacing of 0.08  $2\pi$  Å<sup>-1</sup>. The initial structure for g-PCN was generated by modifying the experimentally resolved structure of g-C<sub>3</sub>N<sub>4</sub> obtained by Cooper, Bojdys and coworkers<sup>23</sup> with the bridging nitrogen atoms replaced by phosphorus. Predictions of the <sup>31</sup>P MAS NMR shielding tensors were calculated using the gaugeinducing projector augmented waves (GIPAW) method<sup>24,25</sup> available in CASTEP, where the core regions were, again, described by pseudopotentials from the CASTEP library. The online tool MagresView v1.6.2<sup>26</sup> was used to analysis the magnetic shielding data. The isotropic chemical shifts,  $\delta_{iso}$ , were obtained using Eqn. (1) where the chosen reference species was ammonium dihydrogen phosphate (ADHP) with its experimental peak known to be 0.9 ppm. The magnetic shielding of ADHP was calculated using the outlined calculation strategy with the same plane wave energy cutoff and k-point spacing. The initial structure of ADHP was obtained from the Cambridge Structural Database, reference code VITPIA.<sup>27</sup>

#### **10.1.10** Photoluminescence measurements

The photoluminescence (PL) emission spectra and time-resolved PL (TRPL) spectra were recorded in a PTI QuantaMaster 500 spectrofluorometer and TimeMaster Lifetime fluorometer (Horiba, France). PL excitation wavelength was fixed at 350 nm with a slit overture of 2.0 nm and the decay was obtained with a LED with a fixed excitation wavelength of 369 nm and an overture of 0.3 nm for 30 s.

#### **10.1.11 Photoelectrochemical measurements**

A standard three-electrode system was used to determine the photo-electrochemical properties and band structure, using Pt wire and Ag/AgCl as counter and reference electrodes, respectively. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass (2.5 x 2.5 cm), which was cleaned by sonication in acetone for 3 h and then dried. The FTO slide was spin-coated with 5 ml of slurry, which was obtained by the sonication of 20 mg of photocatalyst in ethanol for 3h. The transient photocurrent response was performed on an Autolab PGSTAT204 electrochemical workstation with a 0.5 M aqueous solution of Na<sub>2</sub>SO<sub>4</sub> as the electrolyte. The photocurrent was measured at a bias voltage of 0.8 V under solar light irradiation (150 W xenon lamp) with a 10 s light on-off cycle.

#### 10.1.12 Fourier Transform Infrared Spectroscopy (FTIR)

Samples were analysed via FTIR using a Fourier Diagform-Infrared Attenuated Total Reflection PerkinElmer UATR Two Spectrometer through a range of 400 to 4000 cm<sup>-1</sup>, with a resolution of 1 cm<sup>-1</sup>. OPUS 7.5 was used to process and analyse the resulting data.

#### 10.1.13 Thermogravimetric analysis (TGA)

The thermal stability of the samples was subsequently evaluated using a TA instruments Discovery TGA 5500. Approximately 5 mg of each sample was analyzed in nitrogen through a temperature range of 30 to 700°C at a ramp rate of 20°C/min using alumina crucibles. The difference in mass was then calculated using TRIOS Evaluation software.

#### **10.1.14 BET Measurements**

The nitrogen adsorption and desorption isotherm measurements were performed on a Quantachrome instrument at a temperature of 77 K. Samples were activated at 120 °C for 12 h prior to each measurement.

# **10.2 Results and Discussion**



**10.2.1** Fourier transform infrared attenuated total reflectance (FTIR-ATR)

**Figure 10.1.** FTIR-ATR of furnace synthesized P@CN reference material (green), g-PCN (teal) g-PCN200 (blue) and g-PCN300 (purple).





Figure 10.2. TGA of g-PCN under N<sub>2</sub> from 30 to 800 °C.

10.2.3 X-ray Photoelectron Spectroscopy (XPS)



Figure 10.3. XPS scan of a) C 1s b) N 1s and c) P 2p for furnace made P@CN.



Figure 10.4. XPS scan of a) C 1s b) N 1s and c) P 2p for g-PCN200.



#### **10.2.4 Photoelectrochemical Analysis**

Figure 10.5. Mott-Schottky plots of a) g-C<sub>3</sub>N<sub>4</sub> b) g-PCN c) g-PCN200 and d) g-PCN300.

# **10.2.5** Computational Analysis



Chart 10.1. Structure scope of GIAO analysis using Gaussian 16.

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Table 10.1. Chemical shielding of structure sco	be and chemical shifts compa	ared to a triphenyl	phosphine reference.
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Molecule	Chemical shielding / ppm	Chemical shift / ppm
1 <sup>a</sup>	301.34	8
2	299.39	6.05
3	103.76	-189.58
4	239.02	-54.32
5	296.83	3.49
6	192.49	-100.85
7	302.23	8.89
8	305.05	11.71
9	300.98	7.64
10	267.23	-26.11
11	294.42	1.08
12	265.24	-28.1
13	307.49	14.15

#### 10.2.6 <sup>31</sup>P MAS NMR



Figure 10.6. <sup>31</sup>P MAS NMR of a) g-PCN and b) g-PCN200. Asterisks denote spinning sidebands.

#### **10.2.7 BET Measurements**

Table 10.2. Measured BET values for phosphorus-linked triazine networks compared to traditionally made g-C<sub>3</sub>N<sub>4</sub>.

Entry	Material	MBET measured surface area / m <sup>2</sup> g <sup>-1</sup>
1	g-C <sub>3</sub> N <sub>4</sub>	18.77
2	g-PCN (milled 30 min, aged 1 d)	10.68
3	g-PCN (milled 90 min, aged 1 d)	56.38
4	g-PCN (milled 30 min, aged 7 d)	49.61
5	g-PCN300	13.00
6	g-PCN300 (milled 1 h at 30 Hz after isolation)	7.84

# **10.3 References**

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