PHOTOCATALYTIC SOLAR ENERGY CONVERSION ON METAL-FREE SEMICONDUCTORS

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A thesis submitted for the degree of Doctor of Philosophy

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# Table of Contents

Declaration...........................................................................................................................................i
Acknowledgements ............................................................................................................................ii
Abstract................................................................................................................................................iii
Publications during PhD Study ............................................................................................................vi
Chapter 1 ..............................................................................................................................................1
  1.1 Scope and Significance of the Project..........................................................................................1
  1.2 Objective of the Thesis..................................................................................................................1
  1.3 Outline of the Thesis ....................................................................................................................2
  1.4 References ..................................................................................................................................3
Chapter 2 ............................................................................................................................................4
  Literature Review ...............................................................................................................................4
    2.1 Introduction ...............................................................................................................................4
    2.2 2D Phosphorene as a Water-Splitting Photocatalyst: Fundamentals to Applications ..........4
    2.3 Carbon, Nitrogen, and Phosphorous Containing Metal-free Photocatalysts for Hydrogen Production: Progress and Challenges ..............................................................27
    2.4 Advent of 2D Rhenium Disulfide (ReS$_2$): Fundamentals to Applications ..................47
Chapter 3 ............................................................................................................................................71
  Surface Activated Carbon Nitride Nanosheets with Optimized Electro-Optical Properties for Highly Efficient Photocatalytic Hydrogen Production .....................................................71
    3.1 Introduction and Significance ..................................................................................................71
    3.2 Surface Activated Carbon Nitride Nanosheets with Optimized Electro-Optical Properties for Highly Efficient Photocatalytic Hydrogen Production ........................................72
Chapter 4 ............................................................................................................................................97
  A Benchmark Quantum Yield for Water Photoreduction on Amorphous Carbon Nitride ..........97
4.1 Introduction and Significance .............................................................. 97

4.2 A Benchmark Quantum Yield for Water Photoreduction on Amorphous Carbon Nitride ............................................................... 98

Chapter 5 ..................................................................................................... 131
Recombination and Separation of Charge Carrier in Binary and Ternary Metal-Free Homo-Heterojunction Photocatalysts ................................................................. 131

5.1 Introduction and Significance .............................................................. 131

5.2 Natively Grown Metal-Free Hybrid Photocatalyst: An Efficient Way of Reduced Recombination and Low-Resistive Transport of Electrons for Photo-Redox Reactions ........................................................................... 132

5.3 Graphene Oxide Coupled Carbon Nitride Homo-Heterojunction Photocatalyst for Enhanced Hydrogen Production ................................................................. 145

Chapter 6 ..................................................................................................... 176
Counteracting Blueshift Optical Absorption and Maximizing Photon Harvest in Carbon Nitride Nanosheets Photocatalyst ................................................................. 176

6.1 Introduction and Significance .............................................................. 176

6.2 Counteracting Blueshift Optical Absorption and Maximizing Photon Harvest in Carbon Nitride Nanosheets Photocatalyst ................................................................. 177

Chapter 7 ..................................................................................................... 207
Phosphorene Photo-Redox Catalyst-Cocatalyst for Solar Hydrogen Production .......... 207

7.1 Introduction and Significance .............................................................. 207

7.2 Phosphorene Photo-Redox Catalyst-Cocatalyst for Solar Hydrogen Production ......................................................................................... 207

Chapter 8 ..................................................................................................... 227
Conclusions and Recommendations for Future Works ........................................ 227

8.1 Conclusions ......................................................................................... 227

8.2 Recommendations for Future Works .................................................. 229
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All praises to Allah, the Almighty and the most merciful. I firmly believe nothing happens in my life without His will and wish. Salam and salutation to Prophet Muhammad (peace be upon him) whose ways give me solace, tranquillity and guidance in my day-to-day life.

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In this occasion, I would like remember all those friends, relatives and colleagues anywhere in this universe who actively and passively inspired me and had believe on me.

I didn’t take care of my wife and my son as much as they deserved because of being super-busy during this PhD time. I don’t know how to payback their sacrifices. Hopefully, they will find it is as their achievement, and perhaps be proud of me now.
ABSTRACT

Photocatalytic conversion of solar energy into hydrogen fuel via water-splitting in the presence of suitable semiconductor(s) photocatalysts is considered a ‘green and renewable energy’ solution for the era post-fossil-fuels. The development of semiconductors from earth abundant materials is therefore crucial for an economic and sustainable hydrogen production. Metal-free carbon nitrides show practical promise over metal-based semiconductors for stable and economic hydrogen production. However, the photocatalytic efficiency of carbon nitrides is poor. The optimization of the physical and chemical properties of pristine carbon nitrides is therefore very important. This thesis focuses on the photo-physicochemical modulation of intrinsic and extrinsic properties of carbon nitrides for enhanced quantum yield for solar hydrogen production, and the development of phosphorous-based new metal-free photocatalysts.

The first part of this thesis focuses on the identification and remediation of problems with polymeric and amorphous carbon nitride. It is found that incomplete polycondensation of precursor and structural destruction of 2D nanosheets of polymeric carbon nitride (CN) are serious problems. Moreover, polymeric carbon nitride is highly dependent on a precious Pt metal-cocatalyst. Therefore, optimization of its structural and electro-optical properties is urgent necessity for economic hydrogen production from water. To address this issue, here sub-nanometre thin carbon nitride nanosheets are fabricated by combined three-step methods including co-polymerization, surface activation and exfoliation. The resultant nanosheets are structurally very robust and catalytically highly efficient as evidenced by 38 time enhancement in hydrogen production as compared to the pristine carbon nitride, with 100 times smaller loading of Pt as the co-catalyst. These nanosheets show suppressed charge carriers recombination, enhanced charge separation, low over-potential and high surface area that positively impact an improved hydrogen production.

Amorphous carbon nitride (a-CN) is a less-explored but a promising photocatalyst for hydrogen production. Despite its extended visible light absorption (EVLA), a long standing problem is its very low apparent quantum efficiency (AQE) for water photoreduction to produce hydrogen. This implies that EVLA is not proportionally translated into collection of large-amount photogenerated electrons. Here, a sponge-like hierarchical structure of a-CN that addresses this apparent mismatch is developed and reported. Combined experimental and finite difference time domain (FDTD) simulations demonstrate the capability of the a-CN sponge to
induce scattering for total internal light reflection which promotes localized charge carrier generation. Diffused reflectance and transient fluorescence decay studies show good agreement with simulations with a 40% enhanced light-trapping and a ~23 times longer electron lifetime in spongy a-CN compared with that of the bulk material. This finding is a new, high benchmark for hydrogen production of 203.5 µmol h⁻¹ with an AQE of 6.1% at 420 nm in a reaction system of 10 vol. % triethanolamine and 1 wt. % Pt cocatalyst. The enhanced water photoreduction is a result of amenable photophysical and electrochemical attributes existing within the a-CN sponge.

The second part of this thesis focus on suppressing the charge carrier recombination and improving the charge separation in carbon nitrides photocatalysts. It is because photoinduced charge separation against their faster recombination is a rate determinant for photocatalytic proton reduction to hydrogen. Dissociation of electron-hole pairs into free electrons and holes in carbon nitrides greatly suffered from inherent high recombination rate. To overcome this, it is shown here that coupling two energetically optimized but different phase carbon nitrides (CN) in the form of hybrid significantly inhibits the charge carrier recombination and facilitates the overall charge transfer processes. It is found also that the potential gradient in this homojunction delocalized electrons and holes increases the spatial charge separation. This leads therefore to an enhanced photocatalytic hydrogen production from water under visible light irradiation.

Following the formation of binary heterojunction, the research further extends to the synthesis, characterization and application of a new, ternary homo-heterojunction photocatalyst. This heterostructure is constructed by soft-grafting of graphitic carbon nitride and graphene oxide into amorphous carbon nitride substrate. In this ternary hybrid, a cascaded redox-junction is formed that significantly facilitates separation of photogenerated electron-hole pairs (EHP), retards EHP recombination and shuttles electrons to photocatalyst/liquid interface for proton reduction reactions. When deposited with 3 wt. % Pt as a cocatalyst, this new photocatalyst exhibited a hydrogen production of 251 µmol h⁻¹ from 10 vol. % aqueous triethanolamine solution under visible light (420 nm) irradiation with an apparent quantum efficiency of 6.3%. This ternary photocatalyst therefore outperformed stand-alone/binary photocatalysts. Notably, it promises therefore to be a viable alternative to metal-based photocatalysts.

The third part of this thesis focus on solving fundamental problems with polymeric carbon nitride nanosheets. For example, blue-shift of optical absorption and corresponding widening of the bandgap is a fundamental problem with 2D carbon nitride nanosheets (CNNS). An additional problem is low AQE (< 9%) due to higher-loss of absorbed photons. These problems
impose a significant restriction to photocatalytic performance of CNNS. Therefore, the synthesis of narrow bandgap CNNS with high quantum efficiency was seen as of a pressing research importance. This thesis reports melem-derived narrow bandgap CNNS with a record-low bandgap of 2.45 eV. The narrowing in bandgap comes with improved optical absorption and use of visible-light photons, together with excellent charge transport dynamics. This is demonstrated by a record high hydrogen evolution rate of 863 µmol h⁻¹ with apparent quantum efficiency of 16 % at 420 nm.

The fourth and final part of this thesis focuses on phosphorene, a 2D counterpart of black phosphorous. Due to faster degradation under the influence of light, water and air; phosphorene is believed to be a material that exists only theoretically for photocatalytic applications. Here however the first practical demonstration of photocatalytic hydrogen production on phosphorene under visible light irradiation (420 nm) is shown. It is found that a microwave-assisted synthesis of few layers of phosphorene is active in unassisted proton reduction from pure water without addition of any sacrificial agents and a support from a noble metal co-catalyst. These results therefore are a first step toward water photolysis where phosphorene can potentially be used for solar fuel production. The understanding of photo-physicochemical reasons behind this success are discussed.

This research will aid understanding of factors that contribute to conversion of solar energy into hydrogen fuel from water in the presence of suitable photocatalysts.

Findings will be of immediate interest in the development of semiconductors from earth abundant materials to be applied to economic and sustainable hydrogen production for the era post-fossil-fuels.
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Conference Proceedings


Chapter 1

Introduction

1.1 Scope and Significance of the Project

Energy is one of the basic requirements for the development and sustainability of the modern world.¹ Fossil-fuels are the primary sources of production of this energy. However, the reserves of fossil-fuels is finite, and the burning of fossil-fuels causes imperious and undesired anthropogenic and climate problems.² Therefore, the world is facing a growing anxiety with security of energy supply and climate change. Solar energy assisted splitting of water to produce hydrogen, in this regard, is a remarkable strategy to provide a green and renewable energy solution.³,⁴ It is because, hydrogen can be generated from inexhaustible sources (i.e. sun and water), stored directly to supply in demands (in the dark particularly), and burned without emission of toxic effluents (such as, CO, NOₓ gases).⁵ Photocatalysis is one of the effective way to solar-driven hydrogen production via water-splitting.⁶ As the sun and water are the constant raw materials, the success of the photocatalysis process solely depends on the light absorbing semiconductor material(s) which is known as photocatalyst. The past four decades of research developed hundreds of photocatalysts, and can be categorized broadly into metal-based and metal-free photocatalysts.⁷ Metal-free photocatalysts are more promising than metal-based systems for low-cost and sustainable hydrogen production.⁸ However, metal-free photocatalysts are less effective than metal-based systems in terms of quantum yield of hydrogen production.⁹ Therefore, optimization of physical and chemical properties of promising metal-free photocatalysts, and quest for new metal-free photocatalyst materials are necessary to augment the performance of hydrogen production.

1.2 Objective of the Thesis

This project aims to develop a series of metal free photocatalyst consists of carbon, nitrogen and phosphorous for efficient, stable and low-cost production of hydrogen from water under visible light irradiation. Specifically,
• Adopt a design strategy to lower the dependence on precious metal-cocatalyst (i.e. Pt) through functional nanostructuring of polymeric carbon nitride for low-cost hydrogen production.

• Enhance the quantum yield of hydrogen production on amorphous carbon nitride through modulation of photophysical and physicochemical properties.

• Construct binary and ternary metal-free heterostructures to deal with the complex charge-transfer kinetics and explain the synergistic actions toward increased hydrogen production.

• Overcome the fundamental challenges in optical absorption and excitons dissociation, and maximize the photon harvest in carbon nitride nanosheets.

• Realize the practical demonstration of photocatalytic hydrogen production on phosphorene, and elucidate the underlying photo-redox mechanism.

1.3 Outline of the Thesis

This thesis is composed of the journal publications that have been produced out of my PhD research. There are 8 (eight) chapters in this thesis. The sequence and a brief overview of each chapter are described below:

Chapter 1 includes the scopes and significances, and aims and objectives of the proposed research, and outlines of the structure of this thesis.

Chapter 2 provides a critical review of the recent progress and challenges in metal-free photocatalysts containing carbon, nitrogen and phosphorous for hydrogen production via water-splitting. A review of the fundamentals properties of ReS$_2$ is presented as guideline for its future application as a photocatalyst.

Chapter 3 describes the synthesis of surface activated carbon nitride with optimized optoelectronic properties to reduce the dependence on Pt for low-cost hydrogen production.

Chapter 4 elucidates the fundamental mechanisms of enhancing the quantum yield of water-photoreduction on amorphous carbon nitride.

Chapter 5 presents the development of binary and ternary metal-free heterostructures with a purpose to increase the overlap in solar spectrum, and to delocalize the photogenerated charge carrier for suppression of recombination.
Chapter 6 investigate the fundamental challenges in optical absorption and photon loss in carbon nitride nanosheets, and provide an effective strategy to overcome these.

Chapter 7 presents the practical demonstration of photocatalytic hydrogen production on phosphorene and explain the underlying mechanisms.

Chapter 8 concludes the outcome of the entire research presented in the preceding chapters, and recommends new directions for future research to enhance the hydrogen production on metal-free photocatalysts via overall water-splitting.

1.4 References

Chapter 2

Literature Review

2.1 Introduction

A comprehensive review of the fundamental properties of phosphorene to assess its feasibility as a water-splitting photocatalyst has been provided here. This chapter also includes the significant progress and the challenges of carbon, nitrogen, and phosphorous containing metal-free photocatalysts for hydrogen evolution. Additionally, a review on the fundamental properties of rhenium disulfide (ReS$_2$) has been appended here as a guide to the future research on this exception dichalcogenide material.

2.2 2D Phosphorene as a Water-Splitting Photocatalyst: Fundamentals to Applications

This section includes as it appears as a journal article published by Mohammad Rahman, Chi Wai Kwong, Kenneth Davey and Shizhang Qiao. 2D phosphorene as a water splitting photocatalyst: fundamentals to applications, *Energy and Environmental Science*, 2016, 9, 709–728.
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2.3 Carbon, Nitrogen, and Phosphorous Containing Metal-free Photocatalysts for Hydrogen Production: Progress and Challenges

This section includes as it appears as a journal article published by Mohammad Rahman, Kenneth Davey and Shizhang Qiao, Carbon, Nitrogen, and Phosphorous Containing Metal-free Photocatalysts for Hydrogen Evolution: Progress and Challenges, *Journals of Materials Chemistry A*, 2018, 6, 1305.
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2.4 Advent of 2D Rhenium Disulfide (ReS$_2$): Fundamentals to Applications

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Chapter 3

Surface Activated Carbon Nitride Nanosheets with Optimized Electro-Optical Properties for Highly Efficient Photocatalytic Hydrogen Production

3.1 Introduction and Significance

Photocatalysis is a green and pollutant-free way to produce hydrogen from water under solar irradiation. Photocatalyst is the cornerstone of this process. Graphitic carbon nitride (GCN) as a photocatalysts has recently attracted significant attention. Because it consists of earth abundant carbon and nitrogen, can be synthesized from inexpensive raw materials, and shows reasonable stability during catalytic reactions. But its photocatalytic performance is far from satisfactory. Therefore, an optimization of electro-optical properties of carbon nitride is necessary for enhancing the hydrogen production. In this study, we report the synthesis of carbon nitride nanosheets by a three-step preparation method (multi-precursor copolymerization, surface activation and liquid exfoliation). In comparison with traditional single precursor synthesis route, new catalysts exhibits superior performance toward hydrogen production from water splitting under visible light irradiation.

The highlights of this work include:

New preparation method of GCN. The traditional single precursor route for the preparation of GCN suffers from incomplete polymerization or condensation, and is considered as a great reason for its under-performed photocatalytic activity. This problem has been overcome by multi-precursor copolymerization.

Enhanced structural and electro-optical properties. Along with structural disconformity, faster recombination of charge carrier and inefficient charge separation are the two main reasons for the limited photocatalytic activity of bulk GCN. New nanosheets can extend photon absorption window, suppress carrier recombination, enhance charge separation-transfer
efficiency and provide higher surface area which lead to significant improvement in photocatalysis efficiency.

**Superior photocatalytic hydrogen production performance.** The as-prepared nanosheets show 38 times higher hydrogen production rate than pristine GCN, and outperforms the contemporary carbon nitride base photocatalysts. In addition, such a high performance was achieved with 100 times less loading of precious Pt as a co-catalyst.

Apart from photocatalytic hydrogen production, a broad spectrum of energy-related uses of carbon nitride could be envisaged, such as electrocatalytic carbon dioxide reduction, oxygen evolution and hydrogen evolution etc. Its publication will attract a broad readership, especially researchers working on materials science, catalysis, electrochemistry and renewable energy areas.

### 3.2 Surface Activated Carbon Nitride Nanosheets with Optimized Electro-Optical Properties for Highly Efficient Photocatalytic Hydrogen Production

This section includes as it appears as a journal article published by Mohammad Ziaur Rahman, Jingrun Ran, Youhong Tang, Mietek Jeroniece, and Shizhang Qiao, Surface activated carbon nitride nanosheets with optimized electro-optical properties for highly efficient photocatalytic hydrogen production. *Journal of Materials Chemistry A* 2016, 4, 2445-2452. [Hot paper in 2016]
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Chapter 4

A Benchmark Quantum Yield for Water Photoreduction on Amorphous Carbon Nitride

4.1 Introduction and Significance

Due to distinguished electro-optical and physicochemical properties, crystalline carbon nitride (c-CN) and amorphous carbon nitride (a-CN) are promising for photocatalytic hydrogen production via water-splitting. The c-CN is widely known as graphitic carbon nitride (GCN), and has been studied extensively (more than hundreds of publications), whilst research on a-CN as photocatalyst remains relatively less (< 5 publications). A remarkable advantage of a-CN over c-CN is its inherent ability of extended visible light absorption (EVLA).

Despite its ability of EVLA, the extremely low quantum efficiency (QE) of water photoreduction to produce hydrogen is a long standing problem. It infers that the EVLA is not proportionally translated into collection of large-amount photogenerated electrons. Therefore, minimizing the mismatch between light-absorption and charge-collection remains a great scientific challenge.

Here we report for the first time a new sponge-like hierarchical structure of a-CN that addresses this apparent mismatch. Combined experimental and finite difference time domain (FDTD) simulations demonstrate the ability of the newly synthesised a-CN sponge to induce scattering for total internal light reflection that promotes localized charge carrier generation.

Diffused reflectance and transient fluorescence decay studies show good agreement with simulations with a 40 % enhanced light-trapping and ~ 23 longer electron lifetime in spongy a-CN compared with that of the bulk (pristine) material. The result is a new high benchmark for hydrogen production of 203.5 µmol h⁻¹ with a QE of 6.1 % at 420 nm in a reaction system of 10 vol. % triethanolamine and 1 wt. % Pt cocatalyst.

We conclude the enhanced water photoreduction is a result of amenable photophysical and electrochemical attributes existing within the a-CN sponge.

Because of its excellent optical and electronic properties, a-CN sponge could readily be applied to photovoltaics, optoelectronics, energy storage and other catalytic processes including
electro-catalytic hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and carbon dioxide reduction. Findings will be of immediate interest to a broad readership, especially those in materials science, catalysis and renewable energies.

4.2 A Benchmark Quantum Yield for Water Photoreduction on Amorphous Carbon Nitride

This section includes as it appears as a journal article published by Mohammad Ziaur Rahman, Patrick Charles Tapping, Tak Wee Kee, Ronald Smernik, Nigel Spooner, Jillian Moffatt, Kenneth Davey, and Shizhang Qiao, A Benchmark Quantum Yield for Water Photoreduction on Amorphous Carbon Nitride. *Advanced Functional Materials* 2017, 27, 1702384.
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Chapter 5

Recombination and Separation of Charge Carrier in Binary and Ternary Homo-Heterojunction Photocatalysts

5.1 Introduction and Significance

Photoinduced charge carrier separation against their faster recombination is a rate determinant for photocatalytic proton reduction to hydrogen. Dissociation of electron-hole pairs into free electrons and holes in carbon nitrides greatly suffered from inherent high recombination rate. This study has shown that coupling two energetically optimized but different phases carbon nitrides in the form of hybrid could significantly inhibit the charge carrier recombination and facilitate the overall charge transfer processes. It is also found that the potential gradient in this homojunction delocalize electrons and holes increase the spatial charge separation. This therefore leads to an enhanced photocatalytic H₂ production from water under visible light irradiation.

In this regard, here, we report that in-situ coupling of both polymeric carbon nitride (PCN) and amorphous carbon nitride (ACN) is an effective solution to suppress the charge carrier recombination. The coupling was done by thermal polycondensation of melamine onto thiourea derived ACN. This coupling creates a homojunction between PCN and ACN (we named it as PACN for convenience) which facilitates accumulation of opposite polarities charge carriers in two different sides of the junction, thus inhibit them to meet one-another. As a result, PACN exhibited significantly high hydrogen evolution compared to pristine ACN.

We also report a metal-free ternary heterostructure as hydrogen evolution photocatalyst for the first time. This new ternary hybrid is made of graphene oxide, ACN and graphitic carbon nitride. We have implemented the concept of dual homo-heterojunction for the first time to address the inherent problems of restricted visible light absorption, and recombination, separation and utilization of charge carriers for improved hydrogen production via water
splitting. With a hydrogen production rate of 251 µmol h⁻¹ and 6.3% quantum efficiency at 420 nm, this ternary hybrid outperforms the previously reported metal-free photocatalysts. We have shown that coupling different carbon nitrides in a hybrid form is an effective way to suppress recombination, reduce the charge transfer resistance, and accelerate the transfer of photogenerated charge carriers. An additive photon absorption effect has also been realized to get an overlap in solar spectrum without extending photon absorption edge to longer wavelength. These findings are new and have high research value for the design of semiconductor photocatalysts. Due to excellent charge separation and transport abilities, these hybrids are equally potential for electrocatalysis, solar cells and many other applications. It is believed that this work will inspire to develop more advanced metal-free hybrid photocatalysts for hydrogen production from water.

5.2 Natively Grown Metal-Free Hybrid Photocatalyst: An Efficient Way of Reduced Recombination and Low-Resistive Transport of Electrons for Photo-Redox Reactions

This section includes as it appears as a research article to be submitted for publication by Mohammad Ziaur Rahman, Youhong Tang, Chi Wai Kwong, and Shizhang Qiao, Natively Grown Metal-Free Hybrid Photocatalyst: An Efficient Way of Reduced Recombination and Low-Resistive Transport of Electrons for Photo-Redox Reactions (to be Submitted).
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The future energy problems under the threat of depleting fossil fuels could possibly be solved by collecting and storing solar energy directly into simplest chemical bonds, for example, H₂.¹ In this regard, the photocatalytic water splitting into usable hydrogen might provide an promising route to clean fuel generation.² Efficient and stable photocatalyst is the core of this process. Photon assisted hydrogen production via a photoelectrochemical cell was first demonstrated in 1972.³ Since then hundreds of photocatalyst have been developed. Most of the research endeavours in this direction were brought into design, synthesis and fabrication of metal based photocatalyst.⁴,⁵ Metal based photocatalysts suffered from narrower absorption range in solar spectrum, inefficient charge transfer kinetics, recombination of photogenerated carriers and instability in acidic/alkaline medium.⁶⁻⁷ This is therefore directed to explore alternative photocatalyst materials beyond metal.

When stability and inexpensive raw materials is a concern, metal-free photocatalyst were shown to be a viable alternative to metal-based photocatalysts.⁸,⁹ Indeed, it has been recently demonstrated that polymeric carbon nitride with different crystalline phases is a pH independent stable photocatalysts.¹⁰ A polycrystalline polymeric carbon nitride (PCN) is the intensely studied metal-free photocatalyst since 2009.¹¹ PCN is extensively but erroneously reported as graphitic carbon nitride, g-C₃N₄ in the literature. Because a perfect structure of g-C₃N₄ is yet to define, and varied significantly with synthesis conditions.¹² Recently, an amorphous carbon nitride (ACN) was also reported as hydrogen evolution photocatalyst.¹³ However, the photocatalytic performance of pristine PCN and ACN is not satisfactory.

The low-performance has ascribed to higher recombination rate and higher charge transport resistance which greatly reduces the probability of available photogenerated charge carriers for redox reactions. In the past, research efforts were carried out to augment the performance of both PCN and ACN photocatalysts by modifying morphological features, doping and breaking of terminal hydrogen bonds.¹⁴⁻¹⁶ However, only marginal success was achieved in the improvement of overall efficiency. The fundamental limitations in suppressing the charge carrier recombination and manipulation of interfacial charge transfer remain a challenge to date.

While assessing the previous efforts, we have come across that each individual technique has its own demerits. For example, morphological tuning could provide larger reaction sites, increase light absorption but also a greater source of recombination sites due to aggregated lateral edges, grain and grain boundaries, and also widen the bandgap in some instances. Hence, having larger reaction sites is turned out as little beneficial as not much of charge carriers are available to reaction sites. Another widely used technique is doping heteroatoms. Doping, as usual, can increase the overall conductivity and light absorption, but in most of the cases, doping of heteroatoms creates shallow or deep level energy states in the bandgap which greatly inhibit the charge carrier recombination.¹⁷ However, the ultimate results were the marginal improvement in photocatalytic performance. This situation suggests that a singlet carbon nitride is not sufficient...
to deal with the charge carrier recombination problems to achieve high production rate.

To devise out a feasible solution, here, we report that in-situ coupling of both PCN and ACN is an effective solution to suppress the charge carrier recombination. The coupling was done by thermal polycrystallization of melamine onto thiourea derived ACN. This coupling creates a homojunction between PCN and ACN (we named it as PACN for convenience) which facilitates accumulation of opposite polarities charge carriers in two different sides of the junction, thus inhibit them to meet one-another.

The photocatalyst generates charge carriers when absorb photons of a definite wavelength. It is therefore advantageous to have a wide photon absorption window that span from UV to visible spectra of solar energy.\textsuperscript{19, 20} The pristine PCN has a restricted absorption edge between 410-450 nm. Research efforts were made to increase the visible light absorption of pristine PCN.\textsuperscript{21} Recently ACN was reported with an absorption edge beyond 650+ nm.\textsuperscript{14} This was actually derived from PCN through heating at elevated temperature (620 °C). Despite a ~200 nm increase in photon absorption edge, the increment in photocatalytic performance of ACN is negligible in compared with PCN. It is because in amorphous phase, atoms are randomly oriented and forms numerous dangling bonds which increase recombination of charge carriers. It implies that recombination is ruled over absorption. In this regard, the grafting of melamine monomer on pre-synthesized ACN (to create PACN) provides a trade-off between recombination and absorption.

The absorption edge of hybrid PACN is ~500 nm (see Fig. 1a). This is clearly lower than absorption edge of ACN, indicating a structural change after grafting melamine monomer on ACN. We have investigated this structural change using XRD, TEM and SAED. It can be seen that hybrid PACN is polycrystalline. For example, in the XRD patterns (Fig. S1), the characteristic peaks at (100) plane and (002) plane of PACN hybrid are noticeably sharper than that of ACN. This is also supported by TEM images and XPS spectra (Fig. S2 and Fig. S3). This structural and optical information justify that the polycondensation of melamine increase the bandgap of ACN but repair the crystallinity of amorphous phase.

The improved crystallinity has positive impact on the reduction of the recombination of charge carrier.\textsuperscript{22} We have investigated the extent of reduction of charge carrier recombination by measuring respective photoluminescence (PL) spectra of ACN and PACN. Compare to ACN, PL intensity of PACN is greatly reduced (see Fig. 2a), meaning that radiative recombination of electron-hole pairs (EHP) is significantly suppressed in PACN.\textsuperscript{23} It is believed that a potential-barrier is formed in PACN homojunction due to respective band alignment PCN and ACN. With the change of this potential gradient, only electrons accumulates in one side of the junction while the holes presents in the other side. This prevents the electrons and holes from meeting each other and consequently reduce the efficiency in charge carrier’s recombination.\textsuperscript{24, 25} The mechanisms of this process is investigated further below.

We have calculated the bandgap and conduction band (CB) positions of PCN and ACN to understand the band bending in PACN by dint of Kubelka-Munk (K-M) and Mott-Schottky (M-S) plots, respectively (Fig. S4-S8). Positive slope of M-S plot confirms that both PCN and ACN are n-type semiconductors but with different Fermi levels. When PCN and ACN are combined in a form of PACN hybrid, Fermi levels are aligned which results in band bending between corresponding CBs and VBs of PCN and ACN. Through band bending, a barrier potential creates that hinders back traversing of electrons from CB of ACN to CB of PCN other, and holes from VB of PCN to VB of ACN. Thus, electrons and holes are delocalized which obstructs their recombination.

The suppression of recombination leads efficient separation and transfer of charge carrier to the surface of the photocatalyst to initiate redox reactions. We have measured the charge transfer resistance and the extent of separation of charge carriers by adopting the widely accepted Nyquist plot and transient photocurrent measurement techniques, respectively. It can be seen in Fig. 2b that the radius of Nyquist semi-circle is the smallest between ACN and PACN, which confirmed the reduction of charge transfer resistance of PACN.\textsuperscript{23} This low
resistivity enhance faster interfacial charge transfer. Because charge carriers in their way of motion always try to follow the low resistive path so that they are less scattered and gets high mobility. The suppressed recombination and lower charge transfer resistance significantly improve the transient photocurrent (Fig. 2c), which is usually used as a proof of efficient separation of recombination. 

The hydrogen production rate is important to get the impression of how efficient the photocatalyst actually is. There are two units are frequently used to report the hydrogen production rate. One is µmol h\(^{-1}\) and other is µmol h\(^{-1}\) g\(^{-1}\). As the increment of production rate is not proportional to the increasing amount of photocatalyst, the unit ‘µmol h\(^{-1}\) g\(^{-1}\)’ is considered apparently wrong.\(^{26, 27}\) In fact, there are several reports where we can see that the hydrogen production rate of > thousands µmol h\(^{-1}\) g\(^{-1}\) turns upon conversion into < 100 µmol h\(^{-1}\).\(^{28, 29}\) Comparing to those recently reported CN-based photocatalysts, indeed PACN is a truly efficient photocatalyst.

![Fig. 2](image)

**Fig. 2** (a) Room temperature PL spectra, (b) Nyquist plot and (c) Transient photocurrent responses of ACN and PACN.

We have evaluated the photocatalytic activities of ACN and PACN, respectively by suspending 100 mg of photocatalyst in 10 vol. % triethanolamine (TEOA) and using 1 wt. % Pt as a cocatalyst under 420 nm irradiation of monochromatic light. The hydrogen production rates (Fig. 3a) on ACN and PACN were 11.2 and 87 µmol h\(^{-1}\), respectively. The time course of hydrogen production over 12 h with intermittent evacuation in each 4 h shows the consistent hydrogen generation in PACN (Fig. 3b). Before each evacuation, the reaction system was stored in room temperature for an interim period of 7 days.

A point to be noted that the correct unit for hydrogen production rate is important to get the impression of how efficient the photocatalyst actually is. There are two units are frequently used to report the hydrogen production rate. One is µmol h\(^{-1}\) and other is µmol h\(^{-1}\) g\(^{-1}\). As the increment of production rate is not proportional to the increasing amount of photocatalyst, the unit ‘µmol h\(^{-1}\) g\(^{-1}\)’ is considered apparently wrong.\(^{26, 27}\) In fact, there are several reports where we can see that the hydrogen production rate of > thousands µmol h\(^{-1}\) g\(^{-1}\) turns upon conversion into < 100 µmol h\(^{-1}\).\(^{28, 29}\) Comparing to those recently reported CN-based photocatalysts, indeed PACN is a truly efficient photocatalyst.

![Fig. 3](image)

**Fig. 3** (a) Hydrogen production rate and (b) hydrogen production stability under visible light irradiation (420 nm) in presence of 10 vol. % TEOA and 1 wt. % Pt.

The photocatalytic mechanisms of the PACN is explained here with the help of Fig. 4. In PACN, a CB barrier potential (denoted as ΔE\(_{CB}\)) and VB barrier potential (denoted as ΔE\(_{VB}\)) created due to alignment of positions of respective CBs and VBs of PCN and ACN. The PCN and ACN both can capture visible light photons which allow to have an additive photon absorption effect in PACN without an extension of absorption edge to longer wavelength of solar spectrum. As CB position of PCN lies above the ACN’s CB positions, electrons from PCN will migrate to ACN, and due to CB barrier potential electron can’t travel back to PCN. Similarly, holes created in VB of ACN will migrate to VB of PCN as VB of ACN lies below than that of PCN. The VB barrier potential will also obstruct the backward traveling of
holes from PCN to ACN. This way holes accumulates in VB of PCN where electrons accumulates in CB of ACN. As a result, electrons and hole become decentralized and survive recombination. The electrons in CB of ACN then initiate proton reduction reaction to generate hydrogen molecules, and the holes in PCN consumed by TEOA and oxidized.

![Fig. 4 Hypothetical sketch of photocatalytic mechanisms.](Image)

Conclusions
In this contribution, a natively grown PACN hybrid was synthesized by polycondensation of melamine onto urea derived ACN, and demonstrated for photocatalytic hydrogen production. We have shown that coupling PCN with ACN in a hybrid form is an effective way to suppress recombination, reduce the charge transfer resistance, and accelerate the transfer of photogenerated charge carriers. An additive photon absorption effect has also been realized to get an overlap in solar spectrum without extending photon absorption edge to longer wavelength. These findings are new and have high research value for the design of semiconductor photocatalysts. As a result, PACN exhibited significantly high hydrogen evolution compared to pristine ACN. Due to excellent charge separation and transport abilities, PACN is equally potential for electrocatalysis, solar cells and many other applications. It is believed that this work will inspire to develop more advanced metal-free hybrid photocatalysts for hydrogen production from water.

Acknowledgements
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References
Supporting Information

Natively Grown Metal-Free Hybrid Photocatalyst: An Efficient Way of Reduced recombination and Low-Resistive Transport of Electrons for Photo-Redox Reactions

M. Z. Rahman\textsuperscript{a}, Y. Tang\textsuperscript{b}, C.W. Kwong\textsuperscript{a}, and S. Z. Qiao\textsuperscript{*a}

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\textsuperscript{b}School of Computer Science, Engineering and Mathematics, Flinders University, SA 5001, Australia.
I. Experimental Section

a. Synthesis

*Synthesis of ACN:* 15 g of thiourea was heated in a tube furnace under N₂ flow at 620 °C with a heat ramp rate of 2.0 °C min⁻¹ following a subsequent heating for 5 h. The furnace was let to cool down to room temperature (RT) and brownish ACN powder was collected.

*Synthesis of PACN:* 3.5 g of as-prepared ACN was mixed with 6 g of melamine in 25 mL of deionized water (DI) water and magnetically stirred rigorously for an hour. The suspension was then dried in an oven overnight, and the solids were heated in a tube furnace under N₂ flow at 550 °C with a heat ramp rate of 2.3 °C min⁻¹ following a subsequent heating for 4.5 h. After reaching the furnace to room temperature (RT), natively grown bright yellowish PACN powder was collected.

*Synthesis of PCN:* 6 g of melamine was heated in a tube furnace under N₂ flow at 550 °C with a heat ramp rate of 2.3 °C min⁻¹ following a subsequent heating for 4.5 h. After reaching the furnace to room temperature (RT), natively grown yellowish GCN powder was collected.

b. Characterization

Optical properties were analyzed from UV-Vis diffuse reflectance spectra (DRS) using UV-Vis spectrophotometer (UV2600, Shimadzu, Japan) in the wavelength of 200 to 800 nm at RT. The crystal structure was characterized by X-ray diffraction (XRD) using a powder X-ray diffractometer (Miniflex, Rigaku) at 40 kV and 15 mA with Cu Kα radiation (λ = 0.154178 nm). Transmission electron microscope (TEM) images were obtained with Tecnai G² spirit. An AXIS ultra-spectrometer (Kratos Analytical Ltd., GB) was employed to obtain XPS spectra. The Fourier transform infrared (FTIR) spectrum was recorded on FTIR spectrometer (Nicolet 6700). Photoluminescence (PL) spectra were measured at RT using a fluorescence spectrometer (RF-5301PC, Shimadzu, Japan).

c. Photocatalytic H₂ production test

100 mg of photocatalyst was dispersed in 80 mL 10 vol% triethanolamine (TEOA) and Pt was loaded onto the surface of the catalyst by an *in-situ* photodeposition method using H₂PtCl₆ as a precursor. To maintain anaerobic conditions, the openings of the flask were sealed with silicone rubber-septa and the suspension was thoroughly degassed with Ar for 30 min. A Xenon arc lamp (300 W) with a cut-off filter (λ > 420 nm) was used to achieve visible-light
irradiation. Rate of H₂ evolution was evaluated by sampling 0.4 mL of gas intermittently each hour through the septum of an online gas chromatograph (GC) (Clarus 480, PerkinElmer, USA). The GC was equipped with a thermal conductive detector (TCD) with a 5 Å molecular sieve column and Ar as carrier gas. The reactor was evacuated each 4 h of a 12 h recycling period and kept under continuous stirring to prevent sedimentation of the photocatalyst during H₂ production. Before each evacuation, the reaction system was stored in RT for 7 days. Deionized water was used to rinse glassware prior to experiments. Experiments were carried out at ambient temperature and pressure.

d. Photo-electrochemical measurement

The working electrode was prepared by grinding 0.1 g of photocatalyst with 0.03 g of polyethylene glycol (PEG) in 0.5 mL of ethanol to make a slurry. Using a doctor-blade method, the slurry was then coated on the fluorine-doped tin oxide (FTO) glass electrode (3 cm²) and dried in an oven at 350 °C for 30 min under N₂ gas flow. Electrodes coated with slurry had a measured film thickness around 10 to 11 μm. The active area of the electrode was about 1.35 cm². The photocurrent and electro-impedance spectroscopy (EIS) measurements experiments were performed in a three-electrode electrochemical system (CHI 650D instruments) where the sample coated FTO was used as a working-electrode whilst Pt and Ag/AgCl were used as a counter- and a reference-electrode, respectively. During photocurrent measurements, light was produced by a 300 W Xe arc lamp and 0.2M Na₂S + 0.05 M Na₂SO₃ aqueous solution was used as the electrolyte. EIS was recorded over a 0.005 – 10^5 Hz frequency with ac amplitude of 10 mV at 0.5 V bias. Mott-Schottky plot has also been recorded in same electrochemical system using 0.5 M Na₂SO₄ as electrolyte.
II. Supplementary Results

The vibrational and stretching bands in FTIR spectra (Fig. S5) for PACN are noticeably pronounced than that of ACN which suggest the repairing of crystallization after polycondensation of melamine onto ACN. This also supports XRD results.
Fig. S3 XPS survey of ACN.

C = 61.4 at.%
N = 37.9 at.%
O = 0.7 at.%

Fig. S4 XPS survey of PACN.

C = 54.1 at. %
N = 43.3 at. %
O = 2.7 at. %

Fig. S5 Kubelka-Munk Plot ACN.
Fig. S6 Kubelka-Munk Plot of PCN.

Fig. S7 Mott-Schottky plot of ACN.

Fig. S8 Mott-Schottky plot of PCN.
5.3 Graphene Oxide Coupled Carbon Nitride Homo-Heterojunction Photocatalyst for Enhanced Hydrogen Production

This section includes as it appears as a research article published by Mohammad Ziaur Rahman, Jun Zhang, Youhong Tang, Kenneth Davey, and Shizhang Qiao, Graphene oxide coupled carbon nitride homo-heterojunction photocatalyst for enhanced hydrogen production, *Materials Chemistry Frontiers* 2017, 1, 562-571.
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<td>Youhong Tang</td>
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Chapter 6

Counteracting Blueshift Optical Absorption and Maximizing Photon Harvest in Carbon Nitride Nanosheets Photocatalyst

6.1 Introduction and Significance

Interest in 2D carbon nitride nanosheets is a result of their unique physicochemical properties. However, when thinned-down from bulk, problems emerge that set a limit to performance. For example, these 2D nanosheets exhibit a blue-shift in optical absorption and widening of the bandgap. This is detrimental to application as a photocatalyst for visible-light hydrogen evolution via water-splitting. Photocatalytic performance of 2D carbon nitride nanosheets is presently limited to quantum efficiency of $< 9\%$. For greater efficiencies it is necessary to increase visible-light absorption of nanosheets. A practical demonstration to overcome these problems remains relatively unexplored.

In this contribution, we report blue-shift counteracted narrow-bandgap CN nanosheets (NB-CNNS). The NB-CNNS showed a record high-hydrogen evolution of 863 $\mu$mol h$^{-1}$ with an apparent quantum efficiency of 16 % at 420 nm. To date both of this production rate and AQE are greatest among standalone CN photocatalysts. The photocatalyst has three rate determining properties: 1) extended visible light absorption and abundant photogeneration of electron-hole pairs, 2) suppressed charge carrier recombination and efficient separation, and; 3) high surface area and utilization of charge carrier for redox reactions.

We explain physicochemical phenomena and reasons for the record hydrogen evolution on the NB-CNNS. These new insights will aid design of future 2D photocatalysts.

Because of its excellent optical and electronic properties, NB-CNNS could readily be applied to photovoltaics, optoelectronics, energy storage and other catalysis processes including electro-catalytic hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and carbon dioxide reduction. Findings will be of immediate interest to a broad readership, especially those in materials science, catalysis and renewable energies.
6.2 Counteracting Blueshift Optical Absorption and Maximizing Photon Harvest in Carbon Nitride Nanosheets Photocatalyst

This section includes as it appears as a research article published by Mohammad Ziaur Rahman, Kenneth Davey, and Shizhang Qiao, Counteracting Blueshift Optical Absorption and Maximizing Photon Harvest in Carbon Nitride Nanosheets Photocatalyst, *Small* 2017, 13, 1700376.
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Chapter 7

Phosphorene Photo-Redox Catalyst-Cocatalyst for Solar Hydrogen Production

7.1 Introduction and Significance

Phosphorene is a 2D counterpart of black phosphorous. It shows unusual electrical, optical and chemical properties. The theoretical studies predicted feasibility of phosphorene as a water-splitting photocatalyst. However, a practical demonstration of standalone phosphorene is not yet explored.

In this thesis, we report that phosphorene can be used as a hydrogen evolution photocatalysts without any help of precious metal cocatalyst. The nanosheets of phosphorene has synthesized using a microwave-exfoliation techniques. The microwave-exfoliated phosphorene shows excellent stability against ambient degradation which is a serious problem for phosphorene.

With a combined study of experiment and Density Functional Theory (DFT) calculation, we explain photo-physicochemical phenomena for hydrogen evolution on phosphorene. This is a highly significant results to advance the phosphorene based photocatalysts research. This findings will therefore be of immediate interest to a broad readership, especially those in materials science, catalysis and renewable energies.

7.2 Phosphorene Photo-Redox Catalyst-Cocatalyst for Solar Hydrogen Production

This section includes as it appears as a research article to be submitted for publication by Mohammad Ziaur Rahman, Munkhbayer Batmunkh, Sherif Abdulkader Tawfik, Joe Shapter and Shizhang Qiao, Phosphorene Photo-Redox Catalyst-Cocatalyst for Solar Hydrogen Production (to be submitted).
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ABSTRACT: Due to faster degradation under the influence of light, water and air; phosphorene is believed to be a material that exists only theoretically for photocatalytic applications. Here we show the practical demonstration of photocatalytic hydrogen production on phosphorene under visible light irradiation (420 nm). We have found that a microwave assisted synthesis of few layer phosphorene is active in proton reduction from pure water without addition of any sacrificial agents and supporting noble metal co-catalyst. This represents a first step toward water photolysis where phosphorene only can potentially be used for solar fuel production. Additionally, we also have extended our research to assess the suitability of phosphorene as a cocatalyst for a number of metal-free photocatalysts including carbon nitride, red-phosphorous, and carbon dots. These materials showed an enhanced hydrogen production in presence of phosphorene; indicating phosphorene can be used as a noble-metal (i.e. Pt) substituted metal-free cocatalyst. Understanding of photo-physicochemical reasons behind this success is elucidated with the results obtained from physical characterization, density functional theory calculations, and finite difference time domain simulations.

Introduction

The energy that is being produced from the combustion of fossil fuels is the primary cause of global warming, causing pervasive and lasting damage to the earth’s climate and ecosystems.\(^1\) Additionally, the fast depletion of fossil fuel sources creates a daunting threat for the scarcity and reliability of energy supply in foreseeable future.\(^2\) To ensure sustainability in energy supply and to mitigate the potentially catastrophic effects of climate change, an immediate and extensive reduction in CO\(_2\) emission must occur.

Sunlight is mankind’s largest energy source, which must be exploited to reduce CO\(_2\) emissions and minimize global warming.\(^3\) Natural photosynthesis is the perfect example how sunlight can be used to produce renewable fuel. Bio-inspired approaches – artificial photosynthesis – have shown great promise.\(^4\) One particularly promising approach is the solar driven photolysis of water – water splitting – which produces hydrogen fuel; a fuel that burns cleanly back to water without any CO\(_2\) release.\(^5\)\(^a\)(a)\(^5\)

During the past four decades, hundreds of photocatalyst materials (mainly transition metal-based oxides, sulfides, oxynitrides semiconductors) have been catalogued.\(^5\) The materials synthesized as photocatalysts in the intervening four decades can be conveniently categorized into three generational types. The first and second generations of photocatalysts were based on oxides, sulfides and nitrides of titanium, cadmium, tungsten and transition-metals-dichalcogenides (TMD). A serious drawback is that metal-based photocatalysts are toxic to humans, and corrosive.\(^6\)\(^\text{-}^7\) Sometimes these materials can work only in the presence of cocatalysts of precious metals (Pt, Au, Ag etc.).\(^8\)\(^\text{-}^9\)

Alternatives to metal-based systems, metal-free photocatalysts have recently been developed. A key breakthrough was metal-free graphitic carbon nitride. This is non-toxic, highly stable in both acidic and alkaline solution, and is independent of noble metal co-catalysts for hydrogen evolution.\(^10\) The other metal-free photocatalysts are elemental red-phosphorous (red-P, alpha-Sulfur (\(\alpha-S\)), and boron.\(^10\) However, the bulk elemental photocatalysts exhibited low photocatalytic activities. A change in research direction was therefore directed to quest for a few atomic layers thick but which were highly functional when compared with bulkier counterparts.

Discovery of graphene started revolution in 2D materials research.\(^11\) Unfortunately, lack of a suitable bandgap makes graphene undesirable as core photocatalyst. This shortcoming has encouraged material scientists to search for other 2D sheet-like materials but with properties that graphene lacks. Hexagonal boron nitride (h-BN), silicene, germanene, stanene etc. are a few notable 2D materials with non-zero bandgap.\(^12\) However, the bandgap these 2D materials are also not suitable for photocatalytic hydrogen production.

In 2014, a monolayer of black phosphorous (BP) was synthesized using the same sticky-tape technique as used for graphene; the material was titled ‘phosphorene’.\(^13\) Phosphorene has shown a tunable band gap and anisotropic properties. It is now being used in transistors, optoelectronics, batteries, gas storage and solar cell.\(^14\)

Phosphorene has exhibited some properties that are highly desirable in photocatalysis applications. These include (i) quantum confinement in the direction perpendicular to the 2D plane, which results in noble electronic and optical properties; (ii) natural surface passivation without any dangling bond (a suppressed carrier recombination is expected); (iii) no lattice mismatch issues for constructing vertical heterostructure with other 2D materials; (iv) large lateral size with ultra-high specific surface area and high ratios of exposed surface atoms; and, (v) strong interaction with light.\(^12\)\(^\text{-}^15\) However, successful application of standalone phosphorene as a photocatalyst is yet to be convincingly demonstrated.
Sa et al. and Hu et al. theoretically predicted that phosphorene could be used as a photocatalyst. We have reviewed the fundamental properties to assess its suitability as a water-splitting photocatalyst. Zhu et al. demonstrated lithium intercalated BP-nanosheets for photocatalytic hydrogen evolution with an apparent quantum efficiency (AQE) of 0.47% at 420 nm in presence of sacrificial electron donors (SED). However, hydrogen production in absence of SED (i.e. from pure water which is the ultimate purpose of solar fuel production via water-splitting) has not yet been practically demonstrated using phosphorene.

In photocatalytic hydrogen production, the cocatalyst also plays crucial role to enhance the activity of a photocatalyst. Incorporation of a suitable cocatalyst brings three advantageous attributes that favor the overall redox reactions. These attributes include (i) lowering the activation energy for redox reactions, (ii) assisting in separation of electron-hole at the interface, and (ii) suppressing photo-corrosion that increases the stability of the photocatalyst. Therefore over the years many cocatalysts have been developed. Transition metals (Pt, Cu, Ni, Co etc.), and their oxides, hydroxides, and sulfides are more commonly used cocatalysts. Pt dominates among all cocatalysts because of its low activation energy and faster charge transport abilities. These metal based cocatalysts are sometimes not cost-effective for hydrogen production. This led to development of metal-free cocatalyst from earth-abundant raw materials. There are few metal-free cocatalyst, such as, carbon nanotubes, graphene, and hydrogenase which have been tried for hydrogen production. However, the quest for new metal-free cocatalyst beyond those is highly desirable.

Here we report phosphorene as both a visible light hydrogen production photocatalyst and a cocatalyst. To understand the catalyst-cocatalyst activities of phosphorene, we have also unveiled the photo-physical attributes through physical characterization, density functional theory (DFT) calculations and finite difference time domain (FDTD) simulations.

Synthesis and Photo-Physical Characterization

The synthesis process significantly influences the stability of phosphorene at ambient conditions. The synthesis of phosphorene using commonly techniques, such as, mechanical cleavage and liquid-exfoliations, has generated material which has proven to be unstable. BP-nanosheets synthesized by Ball-milling with LiOH were shown to be stable, however, it could create violent sparking, and unless removed completely, the presence of Li could induce undesired charging effects. Contrarily, the phosphorene in our experiments was produced using a microwave assisted exfoliation technique (Figure 1a, see Supporting Information for detailed synthesis procedure). This phosphorene is solution processable and showed low oxidation levels in ambient conditions. Moreover, the microwave assisted exfoliation technique could produce high quality phosphorene nanosheets in less than 12 min.

We have investigated the morphology of the phosphorene using Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). The AFM image (Figure 1b) shows a mix of large and small area nanoflakes. The height profile measurements shows that the thickness of these flakes could vary up to 15 nm (Figure S1) with a lateral size up to 5 µm indicating dispersed phosphorene nanoflakes of single to multilayers. AFM results are supported by the TEM image (Figure 1c) which clearly shows dispersed nanosheets of phosphorene of various sizes. A high resolution TEM image (Figure S2) shows that these nanosheets are crystalline with defined atomic fringes. Therefore, it produces an ordered diffraction spots in selected area diffraction (SAED) pattern as is shown in the inset of Figure 1c. The Raman spectrum exhibited characteristic A₁g, B₁g, and A₂g phonon modes at ~362, ~440, and ~467 cm⁻¹, respectively. These are the signature phonons modes that can be usually observed in phosphorene nanosheets. The absence of broad features in this Raman spectrum indicate the structural robustness against ambient oxidation. We have studied the optical absorption properties of phosphorene using diffuse reflectance spectroscopy. Figure 2 shows the UV-Vis spectra and corresponding K-M plot. A bandgap of ~2.0 eV has been extrapolated from K-M plot. This experimental bandgap has shown good agreement with theoretical absorption spectra as is shown in Figure S3. Phosphorene therefore meets the bandgap requirements for thermodynamics of water-splitting.

**Figure 1.** a) Synthesis of phosphorene. b) AFM image showing the nanoflakes of phosphorene. c) TEM image of phosphorene, scale bar 100 nm. Inset is the SAED pattern. d) Raman spectra of phosphorene.
Assessment of Suitability of Phosphorene as a Photocatalyst through DFT Calculations

In principle, the splitting of water into its constituents (i.e. hydrogen and oxygen) required a bandgap of the photocatalyst material to be higher than 1.23 eV. Moreover, the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) potentials should lie between the valence band maximum (VBM) and the conduction minimum (CBM) of the surface. The potential of phosphorene for the photocatalysis of the water splitting reactions was assessed by performing first principle density-functional theory (DFT) calculations (details in the Supplementary Information). The electronic structure of phosphorene was explored to compare the position of its band edges with respect to the redox potential of the OER and HER (Figure 3 a–c).

![Image](https://example.com/image.jpg)

**Figure 2.** a) UV-Vis spectra of phosphorene, and corresponding b) K-M plot for bandgap calculation using the formula (hνa). Phosphorene is considered as a direct bandgap semiconductor, and therefore n = 0.5.

The equilibrium atomic structure of the phosphorene monolayer unit cell was calculated using the generalized gradient approximations (GGA) as parametrized by Perdew, Burke and Ernzerhof (PBE) and gives a bandgap of 0.92 eV. This bandgap, however, would not be suitable for catalyzing the water splitting reactions. However, by applying the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional, we obtain the bandgap value of 1.57 eV which compares well with the experimental value of 1.45 eV. The bandgap obtained by HSE06 is indeed higher than the redox potential of the water splitting reaction. We calculate the band edge alignment with the redox potentials by applying the following equation,

\[ E_{OER} = -5.67 + pH \times 0.059 \]  
where \( E_{OER} \) is the pH-shifted OER redox potential. We display the density of states and band edge alignment in Figure 3a, which shows that a pH = 7 would shift the redox potentials in such a way that they will lie within the band edges of phosphorene, thus indicating the suitability of phosphorene for catalyzing the water splitting reactions.

Phosphorene as a Photocatalyst

The as-prepared phosphorene was subjected to the photocatalytic hydrogen production test. As is shown in Figure 4, phosphorene can produce hydrogen at a rate of 9.5 µmol h⁻¹ g⁻¹ under visible light irradiation (420 nm) in absence of any sacrificial agents and noble metal co-catalyst. To the best of our knowledge, this is a first practical demonstration of hydrogen production from pure water on a phosphorene photocatalyst. An enhanced production rate (17.92 µmol h⁻¹ g⁻¹) was observed in triethanolamine-water solution. This enhancement in presence of triethanolamine indicates that phosphorene suffered from a high recombination rate in pure water, while in contrast, a 10 vol. % of triethanolamine abates the recombination by scavenging holes. These results confirm that phosphorene can be used a metal-free hydrogen evolution photocatalyst without incorporation of undesired noble metal co-catalyst, for example, Pt.

![Image](https://example.com/image.jpg)

**Figure 3.** a) The density of states of phosphorene, shifted with respect to the vacuum level \( E_0 \). The vertical dashed line indicate the position of the Fermi level, the vertical purple lines indicate the positions of the CBM and VBM, the vertical blue line displays the redox potentials of OER and HER reactions with the pH correction in Equation 1, while the vertical red lines indicate the positions of the redox potentials without the pH correction. b) The band structure of phosphorene, and c) molecular structure of 2D phosphorene.

Understanding Distribution of Charge Carriers in Phosphorene

Despite a prevailing broad absorption spectrum spanning to the near infrared (NIR), the low hydrogen production rates in phosphorene might be correlated to asymmetric/non-homogeneous charge carrier generation of the material, and the corresponding availability of active electrons for proton reduction reaction. To probe this possibility, the identification of the catalytic active sites taking the photogeneration into consideration is therefore necessary. However, there are no such prior studies for phosphorene. To assess this, we have carried out FDTD simulations. When few layer phosphorene is subjected to irradiation from the UV-VIS to NIR,
the probabilistic distribution pattern of the generation of charge carriers within a given area of the nanosheets will give an idea of the active sites for catalytic reactions.

In FTDT simulation, a phosphorene nanosheet was subjected to illumination from a continuum electro-magnetic light source to get the absorption spectra that matches the experimental data (Figure S4). The lateral sizes of the modelled nanosheets was set to 1 – 1.4 nm. The simulated distribution of photogenerated charge carriers is shown in Figure 5.

From the simulation results (Figure 5), the rate of generation is found to be inversely proportional to the distant from surface to bulk. We have noticed a strong absorption of photon energy on the surface, and therefore generation of charge carriers is significantly profound at a distance up to 0.4 nm from the surface. Above 0.4 nm, this generation rate gradually decreased and eventually reached zero at the same points. This indicates that the photogeneration of charge carriers in phosphorene is inhomogeneous, and the probability of accommodating catalytic active sites with electrons therefore is high within a distance of 0 – 0.4 nm from the surface. It also means that vectorial transfer of electrons requires travel of a distance of about 0.4 nm to reach surface which seems very promising for enhanced proton reduction.

Despite the short migration distance of electrons, a low rate of hydrogen evolution could preassembly be due to high surface and bulk recombination of electron-hole pairs, and high resistive pathways of transferring electrons to surface.27

Although the FDTD results give an idea of generation of charge carriers, it doesn’t give any information about how the charge carriers are separated and transported to catalytic active sites to take part in redox reactions. Therefore further studies are needed to understand the percolation of charge carriers, and complex interaction of recombination, trapping and transport of charge carrier from point of generation to the surface.

### Phosphorene as a Cocatalyst

Co-catalysts play important role in enhancing the catalytic activities of a photocatalyst. Unfortunately, the widely used co-catalysts are precious metals (i.e. Pt), and also not abundant in the earth’s crust. Therefore, earth abundant metal-free cocatalysts are as important as metal-free photocatalysts for low-cost and sustainable hydrogen production. Here, research to assess the efficiency of standalone phosphorene as both a catalyst and co-catalyst for solar hydrogen production has been examined. We already have demonstrated the activity of phosphorene solely as a photocatalyst.

Recently, Ran et al. has demonstrated that phosphorene could lead to an increased reduction/oxidation activity for CB electrons and VB holes, a decrease in electron-hole recombination probability, and production of much more exposed sites with strong electron coupling. These properties are favorable for used as a co-catalysts for hydrogen production. Indeed, when phosphorene was incorporated in zinc-cadmium-sulfide (ZCS), it significantly augmented hydrogen quantum yield in ZCS system.

We have extended the use of phosphorene as a cocatalyst for a number of photocatalysts, such as, polymeric carbon nitride (CN), red-P, and carbon dots (CD). Carbon nitride and carbon dots are synthesized following the procedures describe elsewhere, while red-P was purchased and used without any modification (see the corresponding XRD spectra as is shown in Figure S5).27 The phosphorene is incorporated in these materials by freeze-drying followed by a Ball-milling.

The influence of phosphorene as a cocatalyst in photocatalytic hydrogen production is shown in Figure 6. Noticeably, the phosphorene enhanced the hydrogen production on these materials. For example, carbon nitride showed a ~ 4.5 times greater, and red-P showed 6 times greater hydrogen production when phosphorene was added with these materials. Standalone carbon dots showed no activity but hydrogen production was observed when incorporated with phosphorene. These results manifest the effectiveness of phosphorene as a suitable cocatalyst.

The enhancement in hydrogen production on CN, red-P and CDs with phosphorene is due to the merits of heterojunction formed between them. This heterojunction led to delocalization of electrons, and therefore inhibited the recombination of electrons with holes. It consequently increased the availability of electrons for proton’s reduction reaction to evolve hydrogen.29

We also compared the efficiency of phosphorene with the widely used Pt cocatalyst. Although, red-P and carbon-dots showed greater hydrogen production with Pt than phosphorene, carbon nitride showed almost comparable performances (see Figure S6 - S8). It is a promising result to use phosphorene as a noble-metal substituted co-catalyst for photocatalytic hydrogen production.

More importantly, while pristine phosphorene showed a stable hydrogen production for < 4 h, phosphorene as co-catalyst showed a stable hydrogen production for many hours (~72 h) when incorporated with carbon nitride, red-P, and carbon dots, respectively (see...
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REFERENCES

Supporting Information

Phosphorene Photo-Redox Catalyst-Cocatalyst for Solar Hydrogen Production

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Table of Contents

Synthesis ...........................................................................................................................................S2
Characterization ...............................................................................................................................S2
Photocatalytic test ............................................................................................................................S3
DFT calculation .................................................................................................................................S4
FDTD simulation ..............................................................................................................................S4
Supplementary Figures ....................................................................................................................S5
References ..........................................................................................................................................S11
Synthesis

Synthesis of phosphorene: The phosphorene was synthesized using a microwave-exfoliation technique. Briefly, 25 mg of bulk BP was dispersed in 5 mL of N-Methyl-2-pyrrolidone (NMP), and exfoliated using two microwaves (MW) of different power ratings. In the first microwave exfoliation, the mixture was heated in a microwave (StartSYNTH Microwave Synthesis Labsta- tion, Milestone s.r.l) operating at 50 °C with 600 W for 8 min. This step was used to weaken the van der Waals interaction between BP layers. The second microwave step was carried out using CEM Discover SP – MW operating at 70 °C with 220 W for 3 min. This step further exfoliates and separates the BP to provide a yellow dispersion. The supernatant (4 mL) was centrifuged at 6000 rpm for 30 min. Top 70 % of the centrifuged solution was then collected for further analysis and application.

Synthesis of carbon nitride: 5 g of dicyandiamide was placed in a crucible and heated in a muffle furnace up to 550 °C at a rate of 2.3 °C min⁻¹ for 4.5 h. After cooling down the furnace at a rate of 10 °C min⁻¹, yellow agglomerate was collected.

Synthesis of carbon dots: 5 g of citric acid was placed in a crucible and heated in a muffle furnace up to 180 °C at a rate of 5 °C for 40 h followed by subsequent heating up to 320 °C at a rate of 5 °C min⁻¹ for 100 h. After cooling down the furnace at a rate of 10 °C min⁻¹, dark brown carbon dots were collected. These carbon dots were stirred with DI water (300 mL) and NaOH (5 M, 10 mL). The solution then filtered to remove the insoluble particles. The filtered solution was freeze-dried to obtain carbon dots.

Synthesis of phosphorene/(carbon nitride, carbon dots, and red-P): 1 g of carbon nitride, carbon dots, and red-P were separately dispersed in 25 mL of DI water and stirred to make a suspension. 50 µL of phosphorene dispersion was then added to each 25 mL solution and vigorously stirred. The mixtures were freeze-dried and ball-milled. Red-P was purchased and used without any further modification.

Characterization

Atomic force microscopy (AFM) was performed in air using a Bruker Dimension FastScan AFM with Nanoscope V controller while operating in Peak Force Tapping mode or standard tapping mode. Peakforce tapping mode images were acquired using Bruker ScanAsyst-air probes (nominal tip diameter and spring constant is 4 nm and 0.4 N/m respectively) and for tapping mode the probes used were silicon HQNSC15/AlBS Mikromasch probes (nominal tip diameter and spring constant is 16 nm and 40 N/m respectively). The AFM topography images
have been flattened, and thickness measurements were made using the section analysis tool of Nanoscope Analysis 1.4. For AFM analysis, the samples were prepared by spin coating the as-prepared solutions onto cleaned silicon substrates at 3000 rpm for 20 s.

Bright-field transmission electron microscopy (TEM) images were acquired using a FEI Titan Themis at 80 kV accelerating voltage. Samples were dispersed by drop-casting onto quantifoil SQR12-200CU grids at 80 °C in air for ~2 mins until dry, and then immediately transferred to high vacuum storage prior to analysis.

Raman spectra were acquired using a LabRAM HR Evolution spectrometer (Horiba Jobin Yvon, Japan) at an excitation laser wavelength of 532 nm with a 40x objective (numerical aperture 0.60).

The optical absorption of the as-prepared dispersions of phosphorene was analyzed using a UV-vis-NIR spectroscopy (Perkin Elmer Lambda 950) at wavelengths ranging from 200 nm to 2200 nm. The XRD pattern was recorded using X-ray diffractometer (Miniflex, Rigaku) at 40 kV and 15 mA with Cu Kα radiation (λ = 0.154178 nm).

Photocatalytic test
Two reactor systems were prepared using three-neck Pyrex flasks to test photocatalytic activities of phosphorene. For the first one, 5 mg of phosphorene photocatalyst was dispersed in 50 mL of DI water, while for the second one, 5 mg of photocatalyst was dispersed in 50 mL of 10 vol. % triethanolamine.

To test the cocatalyst activities of phosphorene, 100 mg of each phosphorene/carbon nitride, phosphorene/carbon dots, and phosphorene/red-P was dispersed in 80 mL of 10 vol. % triethanolamine. For comparison purposes, 100 mg of carbon nitride, carbon dots and red-P only were dispersed in 80 mL of 10 vol. % triethanolamine. Afterwards, 3 wt. % H2PtCl6 was added as a source of Pt.

In all cases, the openings of the flask were sealed with silicone rubber septa. Following degassing in argon flow for 30 min, the reactor was irradiated by a light source (300 W Xenon arc lamp) mounted with a 420 nm cut-off filter. The evolved gas was sampled through an online gas chromatograph (Clarus 480, Perkin-Elmer) every hour and the rate of hydrogen production was quantified. The gas chromatograph (GC) consisted of 5 Å molecular sieve column and a built-in thermal conductivity detector. For GC, Ar was used as a carrier gas. The experiment was carried out at RT and atmospheric pressure.
**DFT calculation**
Density functional-theory (DFT) calculations were performed using VASP \(^1\) and SIESTA \(^2\). VASP and SIESTA calculations were performed using the generalized gradient approximation by Perdew, Burke and Ernzerhof (PBE)\(^3\) and, in addition, the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional\(^4\) implementation in VASP was applied.

For the VASP calculations, geometry relaxation was carried out to obtain the equilibrium atomic structure and lattice geometry for the phosphorene monolayer unit cell, with a \(k\)-space of 8 x 8 x 1, an energy cut-off for the plane wave basis of 400 eV, and the energy tolerance of \(10^{-7}\) eV. In the structural energy minimization, the force tolerance is set to 0.01 eV/ Å. A vacuum region of 18 Å is added between the periodic images. The lattice constant obtained using the PBE approximation are \(a = 3.305\) Å and \(b = 4.572\) Å. For the SIESTA calculations for zero-dimensional structures, the calculations were performed at the \(\Gamma\) point, and an energy cutoff of 300 Ry applied, and the basis functions are radially confined using an energy shift of 0.005 Ry. The double-\(\zeta\) with polarization (DZP) basis set was used. In the structural energy minimization, the force tolerance is set to 0.01 eV/ Å. A vacuum region of 18 Å is added between the periodic images.

**FDTD simulation**
Lumerical FDTD solutions has been employed to carry out the electromagnetic simulations. Perfectly matched layer (PML) boundary conditions in the x-axis and y-axis was used to set the unit cell of the structure as the simulation region. A plane-wave light source irradiated normally to the device was set to be transverse magnetic (TM) polarized. One monitor was placed between the source plane and device surface in order to detect the device absorption. The current density vectors are collocated at the positions of the electric field vectors.
Supplementary Figures

Figure S1. Height profile measurements using atomic force microscopy.
Figure S2. a) TEM image of phosphorene nanosheets, scale bar 200 nm. b) High resolution TEM images, and corresponding c) SAED pattern.

Supplementary DFT results
The impact of the flake size on the bandgap of phosphorene was investigated. PBE was applied for the calculation of the electronic structure of phosphorene islands because, for zero-dimensional structures with large supercells, the application of the HSE method would be prohibitively difficult. For two monolayer phosphorene fragments, $P_{77}H_{25}$ and $P_{252}H_{46}$, the bandgaps, are 1.74 eV and 1.27 eV, respectively. That is, the bandgap of the phosphorene fragment increases as the phosphorene cluster size decreases, which indicates that those fragments might improve the photocatalytic performance because they have optical absorption spectra that span the visible light spectrum.

The atomic structure of the two H-passivated monolayer phosphorene clusters, $P_{77}H_{25}$ and $P_{252}H_{46}$, are displayed in Figure S3 a, b. These structures were obtained by performing density functional-theory (DFT) calculations within the generalized gradient approximation by Perdew, Burke and Ernzerhof \(^3\) using the SIESTA code.\(^2\) Geometry relaxation was done to obtain the ground state atomic structure at the $\Gamma$ point, where the simulation box is 40 Å x 40 Å x 20 Å. SIESTA represents the basis sets in terms of numerical atomic orbitals, and approximates the ionic potential in terms of Troullier-Martins norm-conserving pseudopotentials.\(^5\) The auxiliary basis uses a real-space mesh with a kinetic energy cutoff of
300 Ry, and the basis functions are radially confined using an energy shift of 0.005 Ry. In the structural energy minimization, the internal coordinates are allowed to relax until all of the forces are less than 0.01 eV Å.

The UV-visible optical absorbance spectra of these structures, in comparison with that of the two-dimensional phosphorene monolayer, are displayed in Figure S3 d. The optical absorption, $I(\omega)$ is computed as the imaginary part of the dielectric function in the linear response approximation, and the optical absorbance is proportional to $\omega I(\omega)$. These optical calculations are performed with an incident polarization along the zigzag direction (the average optical spectrum for the armchair and zigzag polarizations is qualitatively similar to the zigzag polarization, therefore we only adopt the zigzag polarization in the present results).

**Figure S3.** The atomic structure of (a) the H-passivated monolayer phosphorene clusters, (b) $P_{77}H_{25}$, and (c) $P_{252}H_{46}$. (d) The optical absorbance of the two phosphorene clusters, compared to that of the two-dimensional phosphorene monolayer. The results presented in this figure are reproduced with slight modification from our previously published paper.
Figure S4. Absorption spectrum of phosphorene when subjected to illumination from continuous electro-magnetic light source in FDTD simulations.

Figure S5. XRD spectra of carbon nitride, carbon dots and red-P.
**Figure S6.** Comparison of hydrogen production rate using carbon nitride alone, with phosphorene and with Pt cocatalyst.

**Figure S7.** Comparison of hydrogen production rate using carbon dot alone, with phosphorene and with Pt cocatalyst.

**Figure S8.** Comparison of hydrogen production rate with red-p alone, with phosphorene and with Pt cocatalyst.
**Figure S9.** Time course of hydrogen production using CN, CDs and red-P in presence of phosphorene under visible light irradiation. The production rate of evolved gas was measured with GC after each hour of irradiation. After 4 h, the reaction system was evacuated under Ar gas flow for 45 min to remove the evolved gas inside the flask for next time course of hydrogen production.

**Figure S10.** The 18th time course of hydrogen production in CN, CDs and red-P in presence of phosphorene. Before re-irradiation under visible light, the evolved gas was evacuated under the Ar flow for 45 min after 17th time course of hydrogen production.
References

Chapter 8

Conclusions and Recommendations for Future Works

8.1 Conclusions

The research that presented in this thesis was carried out to optimize photophysical and physicochemical properties of carbon nitride and phosphorene photocatalysts for enhanced hydrogen production. Following conclusions have been made in this regard:

- Instead of a single precursor route, copolymerization of dual precursors combined with surface activation and liquid exfoliation is proposed to synthesize carbon nitride-based nanosheets photocatalysts with beneficial properties that are required for a highly effective photocatalyst. These properties include wider photon absorption window in the visible range, greatly suppressed charge carrier recombination, higher charge transfer efficiency, abundant amount of reactive sites, and lower HER over-potential. It is concluded that this combined three-step synthesis route (co-polymerization, surface activation and liquid exfoliation) likely to open up new avenues for the development of highly functional carbon nitride and its composites.

- An apparent mismatch between optical absorption and charge collection in bulk a-CN can be addressed by developing a morphological tuning. In this regard, a hierarchical sponge-like a-CN has been reported for the first time as a hydrogen evolution photocatalyst having a new high bench-mark hydrogen production of 203.5 μmol h⁻¹ with an apparent quantum efficiency of 6.1% at λ = 420 nm. The new morphology has optimized structural, electrochemical, and optical properties. It can be synthesized using easily available and cheap raw materials. Due to its extended visible light absorption edge and excellent charge separation and transport ability, sponge-like a-CN appears a promising material for optoelectronics and photovoltaic applications. Because of its lower barrier potential it may promote the faradic reaction rate and should therefore be exploitable for electrocatalysis and applications in fuel cells. Additional carbon-based photocatalysts could be synthesized combining both metal and metal-free elements.

- Coupling PCN with ACN in a hybrid (known as PACN) form can be synthesized by polycondensation of melamine onto urea-derived CAN. This PACN was shown as an
effective way to suppress recombination, reduce the charge transfer resistance, and accelerate the transfer of photogenerated charge carriers. An additive photon absorption effect has also been realized to get an overlap in solar spectrum without extending photon absorption edge to longer wavelength. These findings are new and have high research value for the design of semiconductor photocatalysts. As a result, PACN exhibited significantly high hydrogen evolution compared to pristine ACN. Due to excellent charge separation and transport abilities, PACN is equally potential for electrocatalysis, solar cells and many other applications. It is believed that this work will inspire to develop more advanced metal-free hybrid photocatalysts for hydrogen production from water.

- A new ternary homo-heterojunction can be developed by grafting graphene oxide and graphitic carbon nitride into amorphous carbon nitride (which was named as GCN/ACN/GO). Such a new ternary hybrid has been demonstrated for photocatalytic hydrogen evolution for the first time. This ternary composite exhibited an exceptional rate (251 mmol h\(^{-1}\)) of H\(_2\) production from water with an AQE of 6.3% under visible light irradiation when 10 vol. % triethanolamine was used as a hole scavenger and 3 wt. % Pt as a co-catalyst. This hydrogen evolution rate outperformed that of metal-free compound semiconductors or binary composite photocatalysts irrespective of the inclusion of Pt as a co-catalyst. Experimental results confirmed that this new ternary heterostructure enhanced the performance for photocatalytic hydrogen production, because of: (i) participating semiconductors of different bandgaps that absorb multiple wave-length photons of visible light that increase photogeneration of EHPs; (ii) a built-in potential as a means to separate photogenerated EHPs effectively, which in turn, prevent electron–hole annihilation; and (iii) inclusion of GO to promote the collection and migration of photogenerated electrons that expand the reduction reaction surface through apparent synergistic effects of GO. It is concluded that these new findings will promote future synthesis of feasible metal-free composites combining elemental photocatalysts (i.e. P and S) to the CN framework for enhanced hydrogen production via water splitting. Due to its optimized electro-optical-chemical properties, this ternary hybrid is also promising for CO2 reduction, electrocatalysis, energy storage, photovoltaics and many more applications.

- A blue-shift in optical absorption is inevitable in traditionally fabricated carbon nitride nanosheets. A fabrication method has been demonstrated to counteract this blue-shift. This is a breakthrough in carbon nitride nanosheets fabrication. It has shown that melem (an intermediate of carbon nitrides) is an effective starting material to produce NB-CNNS. The
fabricated NB-CNNS exhibited an experimentally tested photocatalytic hydrogen production of an unprecedented 863 µmol h\(^{-1}\) with an AQE of 16%. These are record high rates among standalone carbon nitride photocatalysts. This unprecedented photocatalytic performance has been concluded as a result of a redshift in visible-light absorption, efficient separation and transport of charge carriers, together with a high specific surface area for utilization of recombination suppressed electrons for reduction reactions. In addition to a highly efficient photocatalyst, it is believed NB-CNNS will have potential for practical application in electrocatalysis, photovoltaics, and energy storage. Results should therefore encourage exploration of narrow bandgap 2D nanosheets of alternative layered materials, including CdS and transition metal dichalcogenides such as MoS\(_2\), MoSe\(_2\), WS\(_2\), and WSe\(_2\).

- Standalone phosphorene can be practically used as a hydrogen evolution photocatalyst. It has shown that phosphorene is active in hydrogen production from pure water while other metal-free photocatalysts are highly dependent on sacrificial agents and noble-metal cocatalyst. It is therefore a breakthrough result.

### 8.2 Recommendations for Future Works

Despite a significant improvement in the performance of photocatalytic hydrogen production, metal-free photocatalysts are yet not ready to be used in industrial scale. Here are some recommendations to enhance the hydrogen evolution performance to be viable for largescale and economic hydrogen production.

- Development of metal-free heterojunction from earth-abundant raw materials using the economically viable and industrially upscalable process. The chemical vapor deposition (CVD) process in this regard can be modified to facilitate the generation of this heterojunction.

- Investigating how these junctions works, what limits their efficiency, and develop design strategies to further improve them. A laser spectroscopy study would be able to give unique insights into how these junctions work.

- Investigating noble-metals substituted co-catalysts for enhancing the performance of metal-free photocatalysts.

- Improving the fundamental understanding of the processes taking place in metal nanoparticle-catalyzed chemical reactions. Transient absorption spectroscopy can be used to monitor the reaction kinetics.

- In-depth understanding of the complex surface chemistry of these heterogeneous catalysts on the atomic level. A combined density functional theory (DFT) calculation and
experiment are needed thereof.

- Understanding of photochemical processes comprise of reactive species like radicals, molecular switching, charge- and energy-transfer processes, photoinduced structural changes and rearrangements, photolysis, and photoluminescence after an ultrafast intersystem crossing. Transient absorption spectroscopy can be used in this purpose.

Pristine phosphorene is not efficient in hydrogen production from pure water. A further increase in hydrogen production required efficient reduction of photogenerated charge carrier recombination. A great deal of research therefore will be needed to optimize its photophysical properties.

Due to time constraint, this thesis didn’t investigate the photocatalytic properties of ReS$_2$. However, a concise review on the fundamental properties of ReS$_2$ has been made. ReS$_2$ has the favorable electronic, optical and chemical properties to be a next generation photocatalyst, and therefore, highly recommended to invest time on this new materials.