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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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.

PUBLICATIONS DURING PHD STUDY

Referred Journal Articles:

[1] 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.

[IF = 29.5]

[2] Mohammad Rahman, Patrick Tapping, Tak Kee, Ronald Smernik, Nigel Spooner, Jillian Moffatt, Youhong Tang, Kenneth Davey and Shizhang Qiao, A benchmark quantum yield of water photoreduction in amorphous carbon nitride, ***Advanced Functional Materials***, 2017, 27, 1702384.

[IF = 12.2]

[3] Mohammad Rahman, Kenneth Davey and Shizhang Qiao, Advent of 2D rhenium disulfide (ReS_2): fundamentals to applications, ***Advanced Functional Materials***, 2017, 27, 1606129.

[IF = 12.2]

[4] Mohammad Rahman, Kenneth Davey and Shizhang Qiao, Counteracting blue-shift light absorption and maximizing photon harvest in carbon nitride nanosheet photocatalysts, ***Small***, 2017, 13, 1700376.

[IF = 8.6]

[5] Mohammad 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 article in 2016**].

[IF = 8.86]

[6] Mohammad 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 [**Hot article in 2017**].

[IF = pending]

[7] **Mohammad Rahman**, Kenneth Davey, and Shizhang Qiao, Carbon, nitrogen, and phosphorous containing metal-free photocatalysts for hydrogen production: Progress and challenged, electro-optical properties for highly efficient photocatalytic hydrogen production, ***Journal of Materials Chemistry A***, 2018, 6, 1305. [**Hot article in 2018**] [IF = 8.86]

[8] **Mohammad 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, ***Chemical Science*** (to be ***submitted***), 2018. [IF = 8.66]

[9] **Mohammad Ziaur Rahman**, Munkhbayer Batmunkh, , Sherif Abdulkader Tawfik, Joe Shapter and Shizhang Qiao, Phosphorene photo-redox catalyst-cocatalyst for hydrogen production, ***Journal of American Chemical Society*** (to be ***submitted***), 2018. [IF = 13.85].

Conference Proceedings

[1] **Mohammad Rahman** and Shizhang Qiao, Increasing visible light photocatalysis on melem, International Symposium on Energy Conversion and Storage Materials, Brisbane, Australia, 2017.

[2] **Mohammad Rahman** and Shizhang Qiao, Thermally exfoliated 2D nanosheets of amorphous carbon nitride (ACN), International Conference on Green and Sustainable Chemistry, Melbourne, Australia, 2017.

[3] **Mohammad Rahman**, Kenneth Davey and Shizhang Qiao, Recombination suppressed amorphous carbon nitride (ACN) nanosheet photocatalyst for Co-catalyst-free solar hydrogen production, 9th International Conference on Materials for Advanced Technologies, Singapore, 2017.

[4] **Mohammad Rahman**, Kenneth Davey and Shizhang Qiao, Caramelin as an infra-red-light absorber and charge-separation enhancer for photocatalytic hydrogen production, 9th International Conference on Materials for Advanced Technologies, Singapore, 2017.