Rational design of highly efficient visible light driven photocatalyst for enhanced H₂ evolution

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**Rational Design of Highly Efficient Visible Light Driven
Photocatalyst for Enhanced H₂ Evolution**

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Publications

† denotes equal authorship

- 1 **C.K. Ngaw**†, V.B. Wang†, Z. Liu, Y. Zhou, S. Kjelleberg, Q. Zhang*, T.T.Y*. Tan, S.C.J. Loo*, Enhancement in hydrogen evolution using Au-TiO₂ hollow spheres with microbial devices modified with conjugated oligoelectrolytes, **Npj Biofilms And Microbiomes**, 2015, 1, 15020.
- 2 **C.K. Ngaw**, Q. Xu, T.T.Y. Tan,* P. Hu, S. Cao, J.S.C. Loo*, A strategy for in-situ synthesis of well-defined core-shell Au@TiO₂ hollow spheres for enhanced photocatalytic hydrogen evolution, **Chemical Engineering Journal**, 2014, 257, 112-121.
- 3 P. Hu, **C.K. Ngaw**, Y.Y. Tay, S. Cao, J. Barber, T.T.Y. Tan*, S.C.J. Loo*, A "uniform" heterogeneous photocatalyst: integrated p-n type CuInS₂/NaInS₂ nanosheets by partial ion exchange reaction for efficient H₂ evolution, **Chemical Communications**, 2015, 51, 9381-9384.
- 4 J. Lin, P. Hu, Y. Zhang, M. Fan, Z. He, **C.K. Ngaw**, J.S.C. Loo*, D. Liao, T.T.Y. Tan*, Understanding the photoelectrochemical properties of a reduced graphene oxide-WO₃ heterojunction photoanode for efficient solar-light-driven overall water splitting, **RSC Advances**, 2013, 3, 9330-9336.
- 5 P. Hu, S.S. Pramana, S. Cao, **C.K. Ngaw**, J. Lin, S.C.J. Loo*, T.T.Y. Tan*, Ion-Induced Synthesis of Uniform Single-Crystalline Sulphide-Based Quaternary-Alloy Hexagonal Nanorings for Highly Efficient Photocatalytic Hydrogen Evolution, **Advanced Materials**, 2013, 25, 2567-2572.
- 6 **C.K. Ngaw**, J.J. Varghese, P.J.S. Buenconsejo, Y.Y. Tay, Q. Gu, J. Liu, Z. Liu, P. Hu, S.H. Mushrif, J.S.C. Loo*. T.T.Y. Tan*, Surface and site-dependent Visible-light Photocatalytic H₂ Evolution of Octahedral NaInS₂ Nanocrystals: Experimental and Theoretical Studies, **Nano Energy**, under review.

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List of abbreviations

Chemical Names

Bi ³⁺	Bismuth ions
CdS	Cadmium sulphide
Ca ²⁺	Calcium ions
CNTs	Carbon nanotubes
C ₃ N ₄	Carbon nitride
Co	Cobalt
DSSN+	4,4' -bis(4' -(N,N-bis(6" -(N,N,N-trimethylammonium)hexyl)amino)- styryl)stilbene tetraiodide
DSTN+	4,4'-thiophene-2,5-diylbis(ethene-2,1-diyl))bis(N,N-bis(6-iodohexyl)aniline)
EtOH	Ethanol
Fe	Iron
MeOH	Methanol
MoS ₂	Molybdenum di-sulphide
NiS	Nickel sulphide
Pt	Platinum
NaInS ₂	Sodium indium sulphide
TiO ₂	Titanium dioxide
TIPP	Titanium isopropoxide
V	Vanadium
Zn ²⁺	Zinc ions

Physical Variable

P	Pressure
V	Voltage
Z	Impedance
λ	Wavelength

Abbreviations

AM	Air mass
CB	Conduction band
COEs	Conjugated oligoelectrolytes
EIS	Electrochemical impedance spectra
FESEM	Field transmission scanning electron microscopy
FTO	Fluorine-doped Tin-oxide
HRTEM	High resolution transmission electron microscopy
MFC	Microbial fuel cell
NHE	Normal hydrogen electrode
PEC	Photoelectrochemical
STH	Solar to hydrogen efficiency
SMC	Solar microbial cell
UV-vis	Ultra-violet visible
VB	Valance band
XRD	X-ray diffraction

Abstract

This thesis focuses on the development of highly active nanomaterials for H₂ evolution based on the rationale design of semiconducting materials. Core shell Au@TiO₂ nanocomposite was designed by incorporating the Au (nanoparticles) NPs into the TiO₂ hollow cavity, and their H₂ activity was further compared with conventional Au-P25. Higher H₂ rates generated by the Au@TiO₂ can be attributed to its larger surface area and the encapsulation of Au NPs inside the hollow nanocomposites. The encapsulated Au NPs were developed to increase the degree of light absorption through multiple light scattering and induced a stronger localized SPR effect for higher H₂ generation. Based on the excellent H₂ photocatalytic activity exhibited by the Au@TiO₂ hollow spheres, these photocatalysts were fabricated into a photoelectrode, and further employed in a solar assisted microbial hybrid device (Au-TiO₂-hybrid device) for H₂ generation. This hybrid device, which was driven by solar energy (from PECs) and the metabolism of microorganisms (in MFCs), exhibited higher photocurrent output than conventional standalone PEC devices. The hybrid system employing Au-TiO₂ hollow spheres and DSSN⁺ generated a photocurrent of $\sim 0.35 \text{ mA/cm}^2$ at zero bias (0 V vs. Pt), while the conventional stand-alone PEC cell employing only Au-TiO₂ hollow spheres was $\sim 0.04 \text{ mA/cm}^2$. The enhancement was attributed to the additional electrons originated from the MFC in the hybrid system. Results also show that when these hybrid devices were chemically modified with conjugated oligoelectrolytes (COEs), their photocurrent output and H₂ evolution were further enhanced due to better charge collection of the MFCs in the modified hybrid system.

The H₂ performance of a photocatalyst can also be enhanced by morphological control because the catalytic properties of nanocrystals depend strongly on the enclosed facets derived from a particular morphology. NaInS₂ nanostructures with different morphologies, including octahedral nanocrystals (NCs), nanosheets and microspheres were prepared, and the effect of morphologies on the performance for H₂ evolution was investigated. The octahedral NaInS₂ NCs exhibited the highest H₂ evolution and the superior performance can be attributed to the active facets enclosed on these NCs, which provided more active sites to accelerate the water splitting process for H₂ generation. To further improve the performance of the octahedral NaInS₂ NCs, a quaternary sulphide (Ca-ZnIn₂S₄) NCs was synthesized via a cation-exchange template strategy. As the morphology and the crystallinity of the NCs were well preserved during the cation-exchange reaction, these obtained quaternary Ca-ZnIn₂S₄ NCs were able to produce new enhanced properties, while inheriting properties from its parent ternary NaInS₂ structure. Higher H₂ rates were observed for the Ca-ZnIn₂S₄ NCs and the enhancement can be attributed to the incorporation of the Ca²⁺ and Zn²⁺ cations in the NaInS₂ structure, which results in a significant improvement to its light absorption, charge separation and stability of the material.

In summary, high performance novel photocatalyst were developed by encapsulating Au NPs in hollow nanocomposites, morphological control and through the formation of quaternary-based nanocomposites.

1 Chapter 1 Introduction

1.1 Background and significance

The global energy crisis and related environmental issues are two major problems confronted by scientists and technologists in the 21st century. [1, 2] In 2008, studies have shown that the worldwide energy consumption rate has reached 15 TW and is expected to be double by 2050 due to the growing human population and rise in living standards. At present, fossil fuels remains the most important source of energy contributing about 86% of the world energy consumption with 36%, 27% and 23% of energy coming from petroleum oil, coal and natural gases respectively. With the high dependency of combustion fossil fuels for power generation, it is likely that these fuels will be fully depleted within the next few decades. [3-5] In addition, combustion of fossil fuels have also caused a series of environmental problems, ranging from air pollution, adverse weather patterns to global warming, posing a threat to our future generations. Therefore, searching for new renewable energy solutions with minimal environmental impact is urgently needed to reduce the world's dependency on fossil fuels and to keep up with the projected increase in energy demand. [6]

Over the last decade, alternative clean energy sources have been proposed to alleviate the dependency of burning fossil fuels for energy production. For example, renewable energies such as wind energy, geothermal energy, biomass and solar energy have attracted consideration attention to mitigate the current energy crisis problem. [7-10] Among all these renewable energies, solar energy remains as the most attractive solution owing to its free, abundant

and inexhaustible primary energy source. Studies have reported that the solar flux striking the earth surface is estimated to be $\sim 3.8 \times 10^{24}$ W per year. [11] With the current annual world energy consumption only constituting $\sim 0.012\%$ of the earth's energy from the sun, solar energy has the potential to meet future increase in energy demand and also to completely replace fossil fuels. [12, 13]

One of the ways to produce useable energy from solar energy is via the photocatalytic method. This approach relies on direct transformation of solar energy into hydrogen energy (H_2) by using a semiconductor photocatalyst via the water splitting process. Photocatalytic water splitting principally encompasses two processes, (1) sunlight absorbed by the photocatalysts suspended in water will produce electron-hole charge carriers and (2) these excited electrons and holes will trigger reduction and oxidation reactions for the generation of H_2 and O_2 gases. The photocatalytic generation of H_2 from water has become the most attractive strategy for harnessing solar energy because of the following advantages:

- Simple setup
- Low cost
- H_2 generation can occur at ambient conditions using sunlight and a semiconductor photocatalyst
- Water is abundant

1.2 Motivation

Inspired by the pioneering work of Honda and Fujishima on water splitting using titania (TiO_2) in 1972, photocatalysis has since attracted tremendous attention for H_2 generation. Over the years, various semiconducting materials (ca. 130 types) ranging from metal oxides, sulphide and nitrides have been extensively studied, leading to the development of many interesting photocatalysts for H_2 evolution. Although many semiconducting materials have been shown to exhibit good H_2 activity, defects within the crystalline matrix resulted in rapid recombination rate of the photo-induced electrons (e^-) and holes (h^+), greatly reducing the efficiency of the photocatalyst. In order to suppress charge recombination rate, noble metals such as platinum (Pt) have been deposited onto the photocatalyst surface, which act as electron traps to increase the lifetime of the charge carriers. However, the presence of excess Pt on the surfaces could reduce the photocatalyst exposure to light, greatly decreasing the amount of charge carriers generated, thus affecting its photocatalytic activity. [14]

Other than its rapid charge recombination rate, the poor light absorption of large band gap semiconductors is another problem directly affecting its photocatalytic H_2 performance. The light absorption of large band gap nanomaterials is limited only to the ultraviolet (UV) region, which corresponds to a small fraction of the entire sun's spectrum ($\sim 4\%$). Since most of the light energy falls within the visible region ($\sim 50\%$), it is necessary to red shift its light absorption into the visible range ($>420\text{ nm}$) so as to enhance the efficiency of the photocatalyst. Improving the light absorption of a large band gap semiconductor can be achieved by elemental doping. The incorporation of foreign element into the

crystal lattice matrix of the host material induces an intermediate band energy level within the band gap, extending its light absorption into the visible region. However, heavy doping is detrimental to its photoactivity because excess dopants act as sites for charge carrier recombination, thus reducing photocatalytic activity. [15] These illustrations further suggested that such surface modifications would have a direct influence on photocatalytic activity, and that performance could be enhanced significantly through proper optimization of the photocatalyst surfaces.

1.3 Problem statement and aim

Although there has been much research effort devoted to enhancing photocatalyst performance by addressing the above-mentioned issues, the resolution of one problem often leads to the generation of another. There is also a lack of targeted effort and specialized knowledge in understanding the photocatalysis mechanism process, which is essential for the development of a photocatalyst with good visible light absorption, long lifetime charge carriers and high stability. Despite many semiconducting materials having been employed as a photocatalyst for H₂ generation, no single one has all these requirements. Hence, to this end, rational design of semiconducting materials at the nanoscale level is necessary for the development of highly efficient photocatalyst with enhanced H₂ performance. [16-18]

The aim of this research is to develop novel visible light responsive photocatalysts with good photocatalytic properties based on the rationale design of semiconductor nanocomposites and quaternary sulphide-based nanostructures. It is also our aim to further process these photocatalysts into a high performance photoelectrode to generate H₂ via a microbial

hybrid device. A detailed understanding of fundamental mechanisms involving the nanostructures and microorganisms contributing to H₂ enhancement in photocatalysis and the hybrid device was also a goal of this research.

1.4 Objectives

The overall objective of this thesis is to design, synthesize and characterize novel nanocomposites and nanostructures as photocatalysts, and to further process them into an efficient photoelectrode to generate H₂ via a hybrid device. The role behind the rational designing of photocatalyst and as well as the detailed fundamental mechanism of the hybrid device contributing to higher H₂ evolution will be further investigated and studied.

Specific goals are:

(a) The design of Au@TiO₂ core-shell hollow nanocomposites for high H₂ generation performance.

To improve the light absorption and promote charge separation of TiO₂ nanocomposites, gold nanoparticles (Au NPs) were incorporated into the hollow cavity of TiO₂, resulting in the formation of Au@TiO₂ core-shell nanocomposites. The synergistic effects of Au NPs as an electron trap together with its surface plasmon resonance (SPR) feature were responsible for the enhanced H₂ generation performance.

(b) Design of a solar microbial hybrid device for enhanced H₂ evolution.

To further improve the H₂ generation performance of the photoelectrochemical (PEC) cell, a microbial fuel cell (MFC) was connected

with the PEC cell to form a solar microbial hybrid device. In this system, microorganisms in the MFC oxidized organic matters to release bioelectrons, which were fed into the PEC cell via an external circuit for enhanced photocurrent output and H₂ generation. This enhancement was attributed to the bioelectrons originating from the MFC in the hybrid system.

(c) Surface characterization of octahedral-shaped nanocrystals for the understanding of different facets affecting H₂ generation performance.

To elucidate the relationship of photocatalytic activity to the exposed surface derived from a particular morphology, different shapes of sodium indium sulphide (NaInS₂) nanocrystals were synthesized and investigated for photocatalytic H₂ generation. The effect of atomic structures of the different NaInS₂ surfaces on the efficiency of photocatalytic H₂ generation was explained through computational models. Such understanding enables the design of highly efficient photocatalysts through crystal surface engineering.

(d) A facile cation-exchange template approach of preparing quaternary sulphide based photocatalyst for H₂ evolution.

To integrate the features of improved light absorption, charge separation, as well as stability into a single photocatalyst, a quaternary sulphide based nanocrystal was synthesized via a cation-exchange template strategy and investigated as a H₂ evolution photocatalyst. The flexibility of this approach

can also be employed to design and synthesize other types of quaternary sulphide based nanostructures.

1.5 Organization of the dissertation

This dissertation is organized as follows:

Chapter 1 briefly introduces the background and significance of using solar energy for H₂ generation, in particular via photocatalysis. It also highlights the overall motivations and objectives of this PhD research project.

Chapter 2 introduces the working principle and mechanism of photocatalysis and highlights some of the commonly used photocatalysts for H₂ generation. The different types of photocatalysts used for H₂ evolution are described. Strategies for enhancing the photocatalytic activity of nanostructures for H₂ evolution are highlighted.

Chapter 3 describes the experimental procedures for the fabrication of the semiconducting photocatalysts, and briefly introduces the chemicals and equipment used in the synthesis and characterization of the photocatalysts as well as the photocatalytic electrode.

Chapter 4 reports a facile method to prepare a well defined Au@TiO₂ core-shell hollow nanostructures for H₂ generation, and also investigates the SPR effect of Au NPs on its H₂ performance.

Chapter 5 reports a solar microbial hybrid device that can be used for H₂ generation. Different classes of conjugated oligoelectrolytes were employed to investigate the effect of charge transfer on the hybrid device for H₂ enhancement.

Chapter 6 reveals that the photocatalytic performance of a nanocrystal is strongly dependent on its surfaces derived from a particular morphology. Detailed computational studies were carried out to investigate and explain the correlation of the different NaInS₂ surfaces and H₂ photogeneration activity.

Chapter 7 discusses a simple cation exchange template approach to prepare an octahedral $\text{Ca-ZnIn}_2\text{S}_4$ nanocrystals for H_2 visible-light generation, which can also be adopted as a general strategy to fabricate other interesting quaternary-based semiconductors.

Chapter 8 provides a general conclusion and recommendation for future work.

2 Chapter 2 Literature review

2.1 Overview of photocatalysis

Driven by the growing environmental concerns and increasing demand for future energy consumption, much effort has been focused on the development of converting solar energy into another form of usable energy. With hydrogen (H_2) largely considered as an ideal fuel for the future owing to its clean and high-density energy characteristics, there has been a growing interest in developing new ways to generate H_2 using solar energy. [19] Photocatalytic water splitting is a promising strategy for generating H_2 mainly due to its simple and low cost design, as well as its mild operating conditions needed to drive the water splitting process. [20-23]

2.1.1 Configuration and working mechanism of photocatalytic water splitting

The typical setup of the photocatalytic approach is illustrated in Figure 2-1. The photocatalytic water splitting can be achieved by immersing powdered photocatalyst in water using a transparent quartz container. The container would have to be sealed properly to form a closed system to prevent leakage before the start of the reaction. When sunlight shines directly on the closed system, the photocatalyst present in the water solution will be activated and H_2 gas bubbles will be generated.

Figure 2-1: Schematic diagram of a photocatalytic system illustrating the possible pathways charge carriers can take within a semiconductor under light irradiation.

A semiconductor photocatalyst acts as a photosensitizer to absorb solar energy and provides active sites for the water splitting process to take place for H_2 evolution. A typical semiconductor possesses a void region where no energy level is available, which is significantly different from metals, where continuous electronic states exist. This void space found in semiconductors is commonly known as the band gap, which extends from the valance band (VB) to the conduction band (CB) level of the semiconductor. When an incident of light of wavelength equivalent to that of the band gap strikes the surface of the semiconductor, electrons will be promoted from the valance band (VB) to the conduction band (CB), leaving h^+ in the VB, forming an electron-hole pair as expressed in equation 1.

There are two major pathways that photo-induced charge carriers will take as they migrate to the semiconductor surface as illustrated in Figure 2-1. It has been reported that when species are pre-adsorbed onto the surface of the semiconductor, the electron transfer process would be more efficient than the transfer process for holes. [24] This causes the surface adsorbed species to easily accept electrons and undergo reduction (pathway C), while a hole will migrate to the surface and recombine with an electron from the donor species for oxidation of the species (pathway D). [25, 26] However, recombination between the charge carriers in the semiconductor can occur during the photocatalytic process and compete with the charge transfer process. (Figure 2-1) Charge recombination can take place within the bulk phase (pathway B) or on the surface of the semiconductor (pathway A), releasing energy in the form of heat or light. This recombination process will greatly limit the number of charge carriers participating in the water splitting reaction, directly affecting the efficiency of the semiconductor. [25, 26]

Studies have shown that the probability of charge recombination occurring within the semiconductor is strongly dependent on the crystal structure and particle size. For example, a highly crystalline material with little defects is less susceptible to charge recombination because defects serve as recombination centers for charge carriers to recombine. [27] If the particle size is small, the distance for the charge carrier to migrate to the surface is shorter, thereby reducing the charge carrier recombination probability. [14] Therefore,

the design and synthesis of nano-sized, highly crystalline semiconductors is desirable to improve the efficiency of a photocatalyst.

2.1.2 Fundamentals of photocatalytic water splitting

The overall water splitting process is a thermodynamically uphill reaction, which requires a large change of Gibbs free energy ($G = 238 \text{ kJ/mol}$) to break the chemical bonds of water molecules into H_2 and O_2 . Therefore, the photocatalytic property of semiconductors in achieving water splitting is strongly dependent on the electronic band structure.

Figure 2-2: Overall water splitting reaction on a semiconductor showing the water reduction and oxidation chemical potentials.

For water splitting to occur, the CB of the semiconductor must be more negative than the proton (H^+) reduction potential of H^+/H_2 (at 0 V vs. NHE) for H^+ to be reduced to form H_2 . (Figure 2-2) Similarly, the energy level of CB has to be more positive than the $\text{O}_2/\text{H}_2\text{O}$ (1.23 V vs. NHE) potentials for the oxidation of water molecules (H_2O) to form oxygen (O_2). Based on these parameters, a semiconductor with minimum band gap energy of 1.23 eV is required for driving the overall water splitting reaction, which corresponds to light with wavelength of $\sim 1100 \text{ nm}$. This means that about $\sim 70 \%$ of the solar

energy (light ~ 1100 nm) can theoretically be used for the photocatalytic of water splitting. [28]. When the semiconductor absorbs light photons with energies greater than its band gap, an electron is promoted from the VB to the CB, generating an electron hole pair in the process. These charge carriers will migrate from the bulk of the semiconductors to the active sites for water redox reactions to take place on the surface. Charge carriers that do not recombine will undergo reduction and oxidation with water to produce H_2 and O_2 gas respectively, as shown in equation 2 and 3.

The photocatalytic reaction of semiconductors for water splitting is usually performed in the presence of reducing (EDTA, alcohols) or oxidizing reagents (Ag^+ , Fe^{3+}) in order to drive either the water reduction or oxidation reaction. The half reaction principle of this photocatalytic reaction using sacrificial reagents is further illustrated in Figure 2-3.

Figure 2-3: Half reaction of water splitting in the presence of sacrificial reagents. [28] Copyright with permission from John Wiley and Sons.

Reactions that employ sacrificial reagents are widely known as half reactions of water splitting and are best suited for semiconductors with band energy levels that either satisfy the kinetic the thermodynamic requirements for H_2 or O_2 generation. It is important to note that reactions that uses redox reagents are not called water-splitting reactions because H_2 and O_2 are not evolved simultaneously.

2.2 Types of photocatalyst

Since the first discovery of water splitting on TiO_2 using light by Honda and Fujishima in 1972, over 130 semiconductors have been studied extensively and further tested for photocatalytic water splitting. Figure 2-4 shows some of the various semiconductors with their band edge positions aligned according to the redox potentials.

Figure 2-4: Relationship of the various semiconductor band structures with the redox potentials of water splitting.

The dotted lines represent the redox potential at 0 V and +1.23 V for H^+/H_2 and $\text{O}_2/\text{H}_2\text{O}$ respectively. The band gaps of Fe_2O_3 , WO_3 and MoS_2 are relatively low to absorb visible light, however, the conduction band of these materials is more positive than the chemical potential of H^+/H_2 . Electrons from these semiconductors will not have sufficient energy to reduce H^+ without the aid any external bias or co-catalyst. On the other hand, semiconductors such as ZrO_2 , TiO_2 , and ZnS have conduction band more negative than the H^+/H_2 potential. Unfortunately, they can only absorb light in the UV range, which corresponds to less than 5% of the sun energy spectrum. Although many semiconductors exhibited appropriate band edges for water splitting, the availability of visible light driven photocatalyst with appropriate band edges for water splitting are still lacking. Therefore, it is essential to tune the band gap in semiconductors to enhance its photocatalytic water splitting performance.

2.2.1 Titanium dioxide (TiO_2)

2.2.1.1 Pristine TiO_2

TiO_2 is the most extensively studied semiconductor for H_2 production due to its low cost, high stability and good photocatalytic properties. [29, 30] In addition, with its band edges extending across the chemical potentials of H^+/H_2 and $\text{H}_2\text{O}/\text{O}_2$, TiO_2 can be a good semiconductor to serve as a photocatalyst for H_2 production. [31] TiO_2 exists in three different crystalline structures, namely the anatase, rutile and brookite. Of the three TiO_2 structures, brookite phase is seldom reported due to its complex structure and difficulties in synthesizing its pure phase. Therefore, the anatase and rutile phases are more commonly used as photocatalyst for H_2 generation. [32, 33] The anatase phase of TiO_2 is a metastable, tetragonal structure with a band gap

of 3.2 eV, while the rutile phase is a more stable structure with a band gap of 3.0 eV. [34] The most obvious difference between anatase and rutile phase lies in their electronic structure as shown in Figure 2-5. [35]

Figure 2-5: The band structures of anatase and rutile TiO_2 at pH 0, 7 and 14.

Although both phases have similar VB positions, the CB of anatase phase is ~ 0.2 V more negative than its rutile phase, which provides the anatase phase with more driving force for water reduction, making the anatase phase more active than its rutile form. [36] To obtain a highly active TiO_2 photocatalyst, it is important to control the reaction conditions in a way such that the final TiO_2 structure consists of the anatase phase, without the formation of the rutile phase. This can be achieved by controlling the calcination temperature of the sol-gel process and reaction temperature of the hydrothermal conditions, as well as the pH of the solution. [37, 38] Over the years, many anatase TiO_2

nanomaterials have been developed and used as a photocatalyst for H₂ generation.

For example, Yang et al. synthesized ultra-thin anatase TiO₂ nanosheets as a photocatalyst for H₂ generation. [18] Figure 2-6 shows a TEM image of the TiO₂ anatase sheets with a well-defined rectangular shape. A lattice spacing of 0.235 nm can be clearly seen from the HRTEM image, from which it can be concluded that the as-prepared anatase nanosheets are exposed with {001} facets. It was reported that the high photocatalytic activity exhibited by the TiO₂ was attributed to the high crystallinity and the highly active {001} facets.

Figure 2-6: TiO₂ anatase nanosheets; a) Low Magnification image, b) HRTEM image. [18] Copyright with permission from Royal Society of Chemistry.

Xu et al. reported a single crystal anatase TiO_2 with exposed $\{111\}$ facets for H_2 evolution as shown in Figure 2-7. The large percentage of $\{111\}$ facets present on the TiO_2 nanosheets was achieved by using fluorine ions and ammonia as capping reagents during synthesis. Photocatalytic studies indicated that the enhanced performance was due to the large percentage of under-coordinated atoms present on the surface of the (111) plane. [39]

Figure 2-7: Single crystalline TiO_2 nanocrystals with $\{111\}$ facets. (a,b) SEM image, (c) Low magnification TEM image, (d) HRTEM image. [39]
Copyright with permission from American Chemical Society.

Jia et al. have successfully prepared anatase TiO_2 hollow spheres via a chemically induced self-assembly method. Figure 2-8 indicates that the TiO_2 hollow sphere is about 1 μm in diameter and the partially broken cavity clearly indicates that the TiO_2 has a hollow structure. The high H_2 photocatalytic performance (~ 0.477 mmol/h) could be attributed to the large surface area exhibited by the TiO_2 hollow spheres. [40]

Figure 2-8: SEM images of the TiO_2 hollow sphere. (a) Low magnification, (b) High magnification. [40] Copyright with permission with Royal Society of Chemistry.

Numerous high performance TiO_2 nanomaterials have been developed for H_2 generation. Unfortunately, due to its large band gap, TiO_2 can only be excited under UV light, which corresponds to a small fraction of the entire sun energy spectrum. Therefore it is important to extend its light absorption to the visible region to further enhance the H_2 performance of TiO_2 . This can be achieved by hybridizing TiO_2 with carbonaceous nanomaterials, semiconductor coupling and elemental doping.

2.2.1.2 Hybridization of carbonaceous nanomaterials with TiO₂

Figure 2-9: Structure of carbon nanotubes and graphene [41]. Copyright with permission from Elsevier.

Carbonaceous-based materials have gained tremendous attention over the past decade owing to their porous structure, good electronic properties and adsorption capacity. [42, 43] In particular, carbon nanotubes (CNTs) and graphene have attracted considerable attention due to their ability to improve the visible light absorption in photocatalysis (Figure 2-9). For example, Wang et al. have reported that the presence of multi-walled carbon nanotubes (MWNT) in TiO₂ can help enhance the photocatalytic activity by more than 10 times compared to pristine TiO₂. Its high performance can be attributed to the improved visible light absorption. [44] Apart from the improved light absorption, the incorporation of carbonaceous nanomaterials into TiO₂ can also increase its surface area and charge separation to further enhance the overall performance of the photocatalyst. Fan et al. had successfully prepared a reduced graphene oxide (RGO)/TiO₂ nanocomposite via a hydrothermal method. Their studies suggested that the intimate contact between RGO and TiO₂ can accelerate the electron transfer process to

suppress the charge recombination rate, thereby leading to higher H₂ photogeneration activity for the RGO/TiO₂ nanocomposite. [45] Mondal et al. successfully fabricated a highly active graphene/TiO₂ photocatalyst via a one-step soft template method and proved that the high surface area of graphene as well as the mesoporous morphology of TiO₂ played a key role in the enhancement of H₂ activity. [46]

2.2.1.3 Semiconductor coupling

Semiconductor composition is another common strategy to improve visible light absorption for enhanced H₂ performance. Coupling a semiconductor with a smaller band gap semiconductor forms a binary composite. In order for the small band gap semiconductor to act as a visible light sensitizer, it must first satisfy these two conditions. (1) It has to be responsive under visible light irradiation, and (2) also possess favorable band energy levels for electrons to be injected into the CB of the large band gap semiconductor, as illustrated in Figure 2-10. When a large band gap semiconductor is coupled with a small band gap material with higher CB energy level, electrons coming from the CB of the small band gap semiconductor will be injected into the large band gap semiconductor. In this way, the small band gap semiconductor can be used as a visible light sensitizer, to improve the visible light absorption of semiconductors.

Figure 2-10: Electron injection of electrons from CB small band gap into the large band gap semiconductor. [47] Copyright with permission from Elsevier.

One common semiconductor that has been used as a visible light sensitizer is zinc selenide (ZnSe). Thuy et al. found out that by coupling ZnSe and TiO_2 , the photocatalytic activity of ZnSe/ TiO_2 composite will be significantly enhanced, mainly due to its improved visible light absorption and reduced charge recombination rate.[48] Besides ZnSe, other small band gap semiconductors such as cadmium sulphide (CdS) and copper sulphide (CuS) are also commonly coupled with TiO_2 to reduce charge recombination rates and better utilize sunlight to maximize photocatalytic performance. For example Sun et al. successfully prepared CdS/ TiO_2 nanocomposite by depositing CdS quantum dots on the TiO_2 nanotube surface. Their results clearly demonstrated that the CdS quantum dots could act as a visible light sensitizer for TiO_2 and increase its charge separation between the two semiconductors for enhanced H_2 performance. [49]. Wang et al. reported that

the H₂ activity of CuS/TiO₂ nanocomposite is ~32 times higher than pure TiO₂. The excellent performance of CuS/TiO₂ can be attributed to the presence of CuS, which not only acts an electron trapper to reduce charge recombination, but also a co-catalyst to effectively reduce H⁺ into H₂ gas. [50]

2.2.1.4 Doped TiO₂

Elemental doping is often used as a common strategy to extend the light absorption of semiconductors into the visible range. Incorporating a foreign element into the crystal lattice of the host material results in the formation of a second-generation photocatalyst. Over the years, TiO₂ has been extensively doped with foreign elements, which can be categorized into two different groups; metal (cation) and non-metal (anion) elements. Cation doping mainly involves the use of transition metals, which includes vanadium (V) [51, 52], iron (Fe) [53, 54], cobalt (Co) [55] and molybdenum (Mo) [56]. The incorporation of such transition metals into the TiO₂ crystal lattice (substitute with Ti⁴⁺ sites) induces an intermediate band gap energy level (nearer to CB) within the band gap of TiO₂ and improves its visible light absorption for enhanced activity. However, heavy doping is detrimental to its photoactivity because excess cation dopants can act as centers for charge carriers to recombine. [15] Therefore, optimizing the concentration of the dopant within the photocatalyst is necessary for maximizing its performance. Besides dopant concentration, the electron configuration and the type of dopant metal would also affect the performance of the photocatalyst. For example, Dholam et al. found that the Fe doped TiO₂ exhibited higher activity for H₂ generation than Cr doped TiO₂, due to Fe ability to better trap

electrons. [54] Karakitsou et al. found out that the incorporation of cations with a valence higher than that of parent cation Ti^{4+} (W^{6+} , Ta^{5+} and Nb^{5+}) are more effective for water splitting reactions, while cations with lower valence number will result in a lower activity. [57]

Figure 2-11: Band structure of TiO_2 anion doping

Anion doping can also help to enhance the visible light response of TiO_2 . Anions such as nitrogen (N) [58], carbon (C) [59], sulphur (S) [60], fluorine, (F) [61] and Boron (B) [62] have been used as anion dopants to substitute the oxygen atoms in the TiO_2 crystal lattice. The incorporation of anions into TiO_2 will shift the VB upwards and narrows the band gap of TiO_2 , without changing the CB of TiO_2 as shown in Figure 2-11. Compared to cation doping, anion doping usually generates less recombination centers within the crystal lattice, which makes this strategy more effective for enhancing photocatalytic activity.

2.2.2 Other metal oxide based photocatalyst

Besides TiO_2 , traditional metal oxides such as zinc oxide (ZnO), iron oxide (Fe_2O_3) and tungsten oxide (WO_3) have also been widely studied because of their own specific advantages. However, these semiconductors have their limitations, especially when they are employed as a photocatalyst for H_2 generation. For example, ZnO was found to exhibit activity under light irradiation, however its inability to absorb visible light makes it an inefficient photocatalyst for H_2 generation. [63] Fe_2O_3 is a good visible light photocatalyst for O_2 evolution, but its low CB energy level is not sufficient to efficiently reduce H_2O to form H_2 gas. [64] WO_3 also faces the same problem as Fe_2O_3 , which further explains why these materials are seldom used as a photocatalyst for H_2 generation. [23]

Another metal oxide semiconductor that is worth highlighting is copper oxide (CuO). It is a p-type semiconductor with a narrow band gap of 1.4 eV, capable of utilizing the entire sun's energy spectrum. Since CuO is a very good visible light absorber with very high CB energy level, they are commonly used as a light sensitizer to improve the light absorption of large band gap materials. There have been a lot of works involving the coupling of CuO with other semiconductors for enhanced photocatalytic activity. For example, Xu et al. deposited CuO nanoparticles into TiO_2 nanotubes through a wet impregnation process for H_2 production. [65] Simon et al. have successfully synthesized vertically oriented CuO/ZnO nanorod arrays by a chemical vapor disposition method. Compared to pure ZnO , the CuO/ZnO nanorod arrays exhibit better charge separation with much improved stability, resulting in higher H_2 performance. [66] Wang et al. prepared a CuO/BiVO_4 heterogeneous

nanostructure through a hydrothermal method. It was reported that the presence of a p/n heterojunction within the nanostructure was crucial in increasing charge separation for enhanced water splitting performance. [67]

2.2.3 Sulphide based photocatalysts

Metal sulphide is another class of semiconductor that is considered as a good candidate for H_2 generation under visible light. The valance band of metal sulphide usually consists of 3p orbitals of S, which results in a higher VB energy level and a smaller band gap to that of metal oxide. (Figure 2-12)

Figure 2-12: The presence of 3p orbitals of S and 2p orbitals of O affecting band gap of semiconductors. [68] Copyright with permission from Royal Society of Chemistry.

2.2.3.1 Binary sulphide

One of the most well studied sulphide-based semiconductors is cadmium sulphide (CdS). CdS with a 2.4 eV band gap and is commonly used as a photocatalyst to generate H₂ under visible light in the presence of an electron donor. Although CdS possesses favorable band gap and band energy levels to achieve good H₂ activity under visible light, the presence of S²⁻ in the structure of CdS can be easily oxidized by the photo-induced holes, causing the entire structure to decompose into Cd²⁺ and S²⁻ species. For this reason, CdS alone is rarely employed as a photocatalyst due to its instability under photocatalytic conditions; instead, it is normally coupled with large band gap semiconductors for enhanced photocatalytic activity. For example, Huang et al. have developed CdS/ZnS core/shell nanocrystals to improve the stability and H₂ performance of the photocatalyst. [69] Kim et al. reported a new hybrid CdS/TiO₂ photocatalyst for visible light H₂ generation. Results have indicated that the presence of CdS quantum dots on the TiO₂ nanosheets surface will significantly increase its charge separation and visible light absorption, contributing to higher H₂ performance. [70]

Besides CdS, other transition metal sulphide semiconductors such as cobalt sulphide (CoS), [71, 72] nickel sulphide (NiS), [73-75] copper sulphide (CuS), [76] and molybdenum disulphide (MoS₂) [77, 78] have also been widely reported as cost-effective co-catalysts, with the aim of replacing noble metals (Pt) for photocatalytic H₂ generation. Recently, it was reported NiS/CdS photocatalyst (1.2 mol %) achieved a H₂ evolution rate of 2.18 mmol/h, which was 35 times higher than that obtained for pure CdS under visible light irradiation. This excellent H₂ rate can be attributed to the

presence of NiS acting as a co-catalyst to promote charge separation and to accelerate the reduction of H₂O for H₂ generation. [79] CuS is another co-catalyst that is commonly used to enhance the performance of the photocatalyst. For example, Zhang et al. prepared a CuS/ZnS photocatalyst via a facile hydrothermal cation exchange reaction. [80] The photocatalytic results indicated that the CuS/ZnS nanosheets achieved the highest H₂ evolution rate with 2 mol % of CuS loading, indicating the CuS co-catalyst is responsible for the enhanced performance mainly due to improved visible light absorption and increased charge separation between the electrons and holes.

Figure 2-13: Ball model of bulk-truncated hexagonal MoS₂ illustrating the exposed empty edges and under-coordinated surface. (Colour code: sulphur, yellow; molybdenum, blue) [81] Copyright with permission from Nature Publishing Group.

MoS₂ is another metal sulphide based catalyst that is widely known for its remarkable H₂ evolution reaction (HER) activity due to its highly active, empty edges and under-coordinated surface. (Figure 2-13) [82] Because of

its specific advantages towards H_2 evolution, MoS_2 was commonly used as an efficient co-catalyst on a variety of semiconductor photocatalysts. Li et al. deposited MoS_2 onto the CdS surface via the impregnation–sulfidation method and results have shown that the hybrid MoS_2/CdS photocatalyst exhibited remarkable H_2 activity (by 36 times). [83] It is believed that the intimate contact formed between MoS_2 and CdS is crucial for the excellent H_2 performance.

2.2.3.2 Ternary sulphide

Other than binary sulphide, ternary sulphide- based semiconductors such as sodium indium sulphide ($NaInS_2$), have also been tested and employed as a photocatalyst for H_2 generation. $NaInS_2$, which consists of alternating layers of Na^+ and InS_2^- , is a visible light active photocatalyst with a bandgap of 2.3 eV. Studies have shown that $NaInS_2$ can exhibit good H_2 photocatalytic activity ($\sim 28 \mu\text{mol/h}$) from a K_2SO_3 solution under visible light irradiation, even without the presence of any Pt co-catalyst. [84] The high H_2 activities of $NaInS_2$ is attributed to their unique two-dimensional (2D) layered structure, which can contribute to better charge separation and provide more active sites for H_2 evolution to take place on the surface of $NaInS_2$. To further enhance its photocatalytic activity, one of the ways is to reduce the band gap of $NaInS_2$. This can be achieved by doping it with transition metals such as Fe^{3+} , Ca^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , V^{4+} . [55, 85-89] For example, Zhang et al. have successfully prepared a Cu-doped $NaInS_2$ ($Cu-NaInS_2$) photocatalyst via a solvothermal method. [90] Results have shown that the H_2 evolution of $Cu-NaInS_2$ is ~ 3 times higher than that of pristine $NaInS_2$

and the H_2 enhancement is due to Cu doping. The incorporation of Cu into the crystal structure of $NaInS_2$ will help to reduce the band gap and also improve the mobility of the charges carriers in $NaInS_2$. Although the H_2 performance of $NaInS_2$ is good, the widespread application of $NaInS_2$ as a photocatalyst is still limited by its low stability, mainly caused by photo-corrosion.

Zinc indium sulphide ($ZnIn_2S_4$), on the other hand, have good chemical stability and is regarded as an eco-friendly, visible-light driven photocatalyst for H_2 evolution. Over the years, numerous $ZnIn_2S_4$ photocatalyst in various morphologies such as nanoparticles, nanotubes and microspheres have been developed. [91-94] For example, Chai et al. have prepared $ZnIn_2S_4$ microsphere via a template free hydrothermal method, and results have shown that the photocatalytic activity of $ZnIn_2S_4$ is highly dependent on the hydrothermal temperature. [95] This is because the specific surface area of the $ZnIn_2S_4$ microsphere will steadily increase with hydrothermal temperature, which will then provide more active sites on the surfaces of the photocatalyst for enhanced H_2 activity. Yu et al. have synthesized a $ZnIn_2S_4/CdIn_2S_4$ composite via a facile hydrothermal method and their H_2 performance was further investigated under visible light irradiation. It was found that the $ZnIn_2S_4/CdIn_2S_4$ composite exhibited a H_2 activity $\sim$ four times higher than pristine $ZnIn_2S_4$. The H_2 enhancement was attributed to the efficient movement of photo-generated charges from $ZnIn_2S_4$ to $CdIn_2S_4$, significantly suppressing the charge recombination on $ZnIn_2S_4$ and increase the surface density of electrons on $CdIn_2S_4$ for H_2 evolution. It was also reported that $ZnIn_2S_4/CdIn_2S_4$ exhibit good stability and the rate of H_2

evolution even increases after each run. [96]

2.2.4 Carbon nitrides

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) is a semiconductor that consists of carbon and nitrogen atoms. (Figure 2-14) Due to its superior properties over other materials, including high stability, low cost and relatively small band gap, $g\text{-C}_3\text{N}_4$ has been regarded as a good visible light driven, metal-free polymeric water splitting photocatalyst for H_2 production. Wang et al. demonstrated that $g\text{-C}_3\text{N}_4$ could be used as a photocatalyst for H_2 generation under visible light irradiation [97], but $g\text{-C}_3\text{N}_4$ itself has very low surface area and a high charge recombination rate. These problems have to be addressed to improve its H_2 photocatalytic activity.

Figure 2-14: Tri-s-triazine- based structure of $g\text{-C}_3\text{N}_4$. Colour scheme: C atoms: grey; N, blue [98]. Copyright with permission from American Chemistry Society

For example, Xiang et al. developed a composite photocatalyst by wrapping $g\text{-C}_3\text{N}_4$ with graphene using a chemical reduction strategy. [99] The presence of graphene on $g\text{-C}_3\text{N}_4$ can help to increase surface area and to provide a more

efficient electron movement within the composite for enhanced H₂ generation. Sun et al. successfully prepared g-C₃N₄ hollow spheres for the first time via a hard template process. It was reported that the hollow cavity within not only provide additional surface area for H₂O reduction to occur, it also induced multi-light reflection to improve the light absorption of the photocatalyst, thereby enhancing its photocatalytic activity. [100] Dong et al. prepared carbon-doped g-C₃N₄ via the calcination of melamine with absolute alcohol. [101] The effect of carbon in g-C₃N₄ can cause a significant change to the intrinsic electronic band structure through the formation of delocalized π bonds, thereby improving its visible-light absorption and electronic conductivity. [98]

2.2.5 Challenges

Although many types of semiconductors have been found to exhibit H₂ activity under light irradiation, rapid charge recombination, poor visible light absorption and instability of the photocatalysts are common problems contributing to their low H₂ photogeneration. Many surface modification techniques have been developed in recent years to improve the performance of photocatalysts by tackling the above-mentioned issues, however the resolution of one problem often results in the generation of another. For example, the deposition of noble metals, such as platinum (Pt) on a photocatalyst surface can help to inhibit charge recombination, but the use of excess Pt would reduce the photocatalyst exposure to light, greatly decreasing the amount of photo-induced charge carriers for H₂ generation. In addition, the extensive use of Pt in photocatalysis would decrease the competitiveness of this approach

due to its high cost. Elemental doping is also another effective way of enhancing the photocatalytic performance of photocatalysts by expanding its light absorption into the visible range through the formation of impurity energy levels. However, these dopants tend to become centers for charge carriers to recombine, which can be detrimental to the performance of the photocatalyst. Studies have shown that simply increasing the concentration of dopant and metal ion loading is not successful for photocatalytic improvement. Therefore, to effectively enhance the performance of photocatalysts, it is necessary to understand the charge transfer mechanism in heterogeneous photocatalysis and then develop new strategies based on rational design of nanomaterials.

2.3 Strategies for enhancing H₂ photocatalytic activity

For a semiconducting material to exhibit good H₂ photocatalytic performance, problems related to photocatalysis such as rapid charge recombination, poor visible light absorption and low stability have to be addressed accordingly. The following strategies have been employed to enhance H₂ photocatalytic performance, which includes the incorporation of efficient noble metals, development of a solar microbial hybrid device, morphological control of nanocrystals and the formation of quaternary-based nanostructures.

2.3.1 Incorporation of noble metals to nanostructures

2.3.1.1 Noble metals

Noble metals NPs have been recognized as an excellent material for harvesting light energy due to their ability to absorb a wide range of the sun

energy spectrum, including both visible and ultra violet light. These noble metals can exhibit a series of magnificent colors, which are mainly caused by the localized surface plasmon resonance (LSPR) effect.

2.3.1.2 Origin of surface plasmon resonance (SPR)

Figure 2-15: Surface plasmon resonance due to coherent interaction of the electrons in the conduction band with light.

Surface plasmon is a collection of free charges that occurs on the surface of a conducting material. When the wavelength of light (380 – 760 nm) is much larger than the size of the conducting material (noble metal NPs), free electrons present in the metal NPs will be polarized to one side, resulting in the formation of an electron plasmon cloud as illustrated in Figure 2-15. This light interaction allows noble metals to absorb some energy, and causes the electron plasmon cloud in the NPs to oscillate. The energy absorption will reach its maximum when the frequency of the incoming light wave is in resonance with natural frequency of the surface plasma, generating intense electromagnetic field at the surface of the NPs. This phenomenon is referred to as surface plasmon resonance (SPR). The frequency of this SPR effect can

be tuned by varying the geometry of the NPs such as particle size and shape. For example, Figure 2-16 shows the absorption profiles of the different gold (Ag) NPs with different diameter. It has been reported that Au NPs smaller than 5 nm do not exhibit any SPR feature, while Au NPs with a particle size range of 5-50 nm exhibit a SPR absorption band in the 520-530 nm region. Further increasing the size of the NPs will result in the shifting and broadening of the absorption band from the visible range (600-700 nm) to the infrared wavelength range (> 1000 nm).

Figure 2-16: Absorption spectra of gold nanoparticles in different sizes.
 [102] Copyright with permission from Royal Society of Chemistry.

Similarly, it is also possible to shift the SPR properties of silver from the UV range to the visible region by changing the shape of the NPs. Figure 2-17 displays the absorption spectra of Ag NPs in different morphologies (wires, spheres and cubes), with the Ag wires, spheres and cubes exhibiting SPR properties at 380 nm, 420 nm and 600 nm respectively. [103, 104]

Figure 2-17: Absorption spectra of silver nanoparticles in different morphologies. [102] Copyright with permission from Royal Society of Chemistry.

2.3.1.3 Localized SPR effect of noble metals

NPs such as gold (Au) and silver (Ag) are some examples of noble metals that exhibit distinct SPR absorption in the visible region. As such, researchers have exploited this SPR feature exhibited by noble metals as a common strategy for producing visible light responsive nanocomposites to enhance the performance of photocatalyst for H₂ generation. This can be achieved by coupling Au NPs with a wide band gap semiconductor, such as TiO₂, which results in the formation of an Au/TiO₂ composite photocatalyst. The SPR effect and the performance enhancement of Au/TiO₂ could be explained by an electron transfer mechanism as illustrated in Figure 2-18.

Figure 2-18: Diagram illustrating the SPR and charge transfer mechanism of Au NPs/TiO₂ composites under visible and ultra violet irradiation. [105]
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In an Au/TiO₂ composite structure, the plasmonic excitation of Au NP induced by the incident visible light can result in the injection of electrons from the Au NPs to the CB of TiO₂ and further reduces water for H₂ generation, while an electron donor will quench holes in the Au NPs. This indicates that the Au NP can act as a visible light sensitizer to improve the light absorption of wide semiconducting materials. When the Au/TiO₂ is exposed to UV light, electrons from TiO₂ will be promoted to the CB for H₂ generation. In addition, since the presence of Au NPs on the surface of TiO₂ can also act as an electron sink, electrons from TiO₂ will be transferred to the Au NPs, significantly improving the charge separation of the composite for enhanced H₂ performance.

2.3.1.4 Au-semiconductor based composites for H₂ evolution

With the presence of Au NPs on semiconductors facilitating visible light absorber and a electron trapper to enhance photocatalysis performance, many Au-semiconductor based photocatalysts have since been developed for H₂ generation. For example, ZnS nano-flowers decorated with Au NPs were successfully prepared via a simple hydrothermal method. The high H₂ performance of Au/ZnS can be attributed to the surface loadings of Au, which can significantly improve the visible light absorption and promote charge separation of the ZnS photocatalyst. [106] A ternary CdS/Au/ZnO core shell nanostructure was reported to exhibit H₂ activity about four times higher than that obtained for CdS/ZnO. It was found that the presence of Au at the interface of CdS/ZnO could serve as a bridge to effectively shuttle electrons from CdS to ZnO, contributing to higher H₂ activity. [107]

2.3.2 Solar microbial hybrid (PEC-MFC) device for enhanced H₂ generation

2.3.2.1 Photoelectrochemical cell

A photo-electrochemical cell (PEC) comprises two electrodes, namely a semiconductor electrode and a counter electrode. (Figure 2-19) The PEC cell is filled with 0.5 M Na₂SO₄ aqueous solution as electrolyte and it is partially separated by a nafion membrane for protons to easily diffuse between the anode and cathode chambers.

Figure 2-19: A typical PEC cell configuration

Under light illumination, the n-type semiconductor will be excited and electron-holes pairs will be formed. When the n-type semiconductor anode is submerged in the electrolyte, both CB and VB energy bands will start to bend upwards as shown in Figure 2-20. This upward bending of the VB enabled holes to be easily oxidized with H_2O to form O_2 gas, while the excited electrons in the CB will be easily transported to the counter electrode via an external bias for the reduction of H_2O to form H_2 . At present, the efficiency of most water splitting PEC systems remains relatively low and a more efficient photoanode needs to be developed in order to boost the performance of PEC cells for H_2 generation.

Figure 2-20: Schematic illustration of a n-type semiconductor photoanode.

[108] Copyright with permission from Elsevier.

2.3.2.1.1 Improving efficiency of photoanodes by elemental doping

Large band gap semiconductors, such as TiO_2 , can only be excited under UV light, which corresponds to a small fraction of the sun's energy spectrum. Because of this, it is important to extend light absorption by the TiO_2 photoanode to the visible region for improved PEC performance by elemental doping. For example, Xu et al. have successfully fabricated a Sn doped TiO_2 nanowire photoanode for PEC water splitting. [109] Results have shown that the PEC cell equipped with the Sn/ TiO_2 photoanode generated a photocurrent density of 2.0 mA/cm^2 , which was 8 times higher than pristine TiO_2 . The enhanced performance was attributed to the visible light response of the photoanode, as well as the increased density of carrier charges generated due to Sn doping. Zhang et al. demonstrated that PEC water splitting can also be feasible by using a N/Si co-doped single crystalline TiO_2 photoanode. [110] This PEC cell exhibited a photocurrent

of 1.77 mA/cm^2 with a solar to hydrogen (STH) efficiency of 1.1 %. This excellent PEC performance can be attributed to the effect of N and Si co-dopants, which provided enhanced light visible absorption, and improved charge transfer at the photoanode/electrolyte interface.

2.3.2.1.2 Improving PEC performance by morphology control

Diffusion length is defined as the distance a charge carrier has to travel before it reaches the photoanode surface, where reaction occurs. A photoanode with a short diffusion length has low charge carrier recombination, and will exhibit higher efficiency than one with a longer diffusion length. It is important to note that the morphology of the photoanode would influence its charge carrier diffusion length. For example, photoanodes that possess a one-dimensional (1D) morphology (such as nanorods, nanotubes and nanowires) have shorter diffusion lengths relative to other conventional semiconductor photoanodes, which will help to enhance the H_2 performance for PEC systems. [111-115]

Photoanodes that possess a three-dimensional (3D) nanowire network can also exhibit good performance due to their large surface area, as well as their improved charge separation and fast electrochemical reactions. [116] Recently, Wang et al. developed a hierarchical TiO_2 -Si nanowire architecture based PEC photoanode for splitting water under visible light. [117] It was reported that these Si nanowires could act as conductive paths for fast electron transportation, while water oxidation occurs on the surface of the TiO_2 nanowires. The TiO_2/Si photoanode produced a photocurrent density of 2.7 mA/cm^2 , which was 9 times higher than that of a conventional TiO_2 photoanode.

2.3.2.2 Microbial fuel cell

A microbial fuel cell (MFC) is a bioelectrochemical system that relies on the inherent charge transfer mechanism(s) possessed by the bacterial strain to generate bioelectricity. [118, 119] A typical MFC is composed of an anode and cathode chamber separated by a proton exchange membrane (PEM), as shown in Figure 2-21. The biocatalysis of organic compounds by the bacterium would release electrons and flow from the anode electrode to the cathode electrode through an external circuit for electricity generation. Simultaneously, protons produced on the anode would reach the cathode chamber through the PEM and undergo reduction with O_2 to form H_2O .

Figure 2-21: Schematic diagram of a typical MFC cell. [120] Copyright with permission from Elsevier.

MFCs have attracted considerable attention in the past decade as a green technology, however the development of MFC technology has been largely hindered by the low power output generated by these systems. The poor performance in MFCs was mainly due to the low charge transfer efficiency of the anode. In order to enhance the performance in MFCs, researchers have increased (1) the specific surface area, (2) conductivity as well as the (3) extracellular electron transfer efficiency of the anode. [120, 121]

2.3.2.2.1 Increasing specific area

An anode with high specific area can provide more sites for more bacteria to be adhered to the anode surface, and consequently guarantee a large quantity of biocatalyst to be involved in the oxidation process for higher bio-electron output. For example, graphene based anodes have a specific surface area 500 times larger than woven carbon felt. [122, 123] The electricity generation for the MFC employing graphene-based anode was about 10 times higher to that of a regular carbon felt based anode. This result indicated that MFC performance was strongly dependent on the specific surface area of the anode. Anodes with higher surface area, such as graphene anodes, can achieve a thicker biofilm than a carbon felt anode (Figure 2-22), which enabled the graphene based MFC to produce more electrons for higher electricity output.

Figure 2-22: FESEM images of a) Graphene-biofilm, b) Carbon felt biofilm. [124] Copyright with permission from Wiley and Sons.

In order to further increase the specific area of the anode electrode, polyaniline (PANI) was electro-deposited on graphene to fabricate a 3D porous composite anode to obtain a porous anode. From the FESEM image in Figure 2-23, it can be seen that bacteria thrived on the surfaces of the porous PANI/graphene anode and a thick biofilm was formed. As a result of the improved bacterial loading, the PANI/graphene anode produced a power output density that was twice that of a regular graphene sheet anode. From the FESEM images, it was evident that high bacterial loading can help to improve the performance of MFCs. [125]

Figure 2-23: FESEM images of biofilm on the PANI/graphene anode.

[125] Copyright with permission from Royal Society of Chemistry.

2.3.2.2.2 Increasing conductivity

Carbon nanotubes (CNTs) are recognized as one of the electrode materials with the most potential not only due to their large specific surface area and high mechanical strength, but also for their excellent conductivity. Recently, researchers have discovered that anodes incorporating with CNTs can significantly improve the performance of the MFCs. For example, Qiao et al. have fabricated a CNT/PANI composite, as an anode material to generate electricity using a MFC. [126] It was found that the presence of CNTs could increase the electrical conductivity of the anode and improve its electron transfer capability for enhanced MFC performance. Sharma et al. developed a MFC using a carbon cloth as an anode that was deposited with multi-walled CNTs (MWCNTs) shown in Figure 2-24. It was reported that the power density generated by the MFC with MWCNTs was 6 times higher than the one with pure carbon cloth, indicating the critical role in

MWCNTS in facilitating electron transfer between the bacteria and anode.
[127]

Figure 2-24: FESEM image of the MWCNTS on carbon cloth. [127]
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2.3.2.2.3 Increasing EET efficiency

The low power density in MFCs was mainly caused by the poor electron transfer between the bacteria and the anode surface, and it was believed that increasing the anode EET (extracellular electron transfer) efficiency was one of the ways to enhance the performance of MFCs. Researchers have tested a variety of materials and eventually found that graphene oxide (GO) based anodes could improve its EET efficiency due to their surface rich oxygen functional groups. [128] Since then, many different types of GO based anodes have been developed. For example, Zhao et al fabricated a MFC equipped with a hybrid GO/CNT anode that could generate a maximum power density output of $97.9 \mu\text{W}/\text{cm}^2$, which is much higher

than the one obtained for pure carbon cloth ($6.5 \mu\text{W}/\text{cm}^2$). [124] It was reported that this novel anode architecture could greatly enhance the direct EET efficiency of the anode due to the strong adhesion between the bacteria and the anode surface, as well as the high conductivity of the CNTs and the large specific surface area of graphene. Lv et al. have developed a polypyrrole/GO (PPy/GO) composite anode (Figure 2-25) and it was reported that this PPy/GO MFC produced a maximum power density of $1326 \text{ mW}/\text{m}^2$. [129] This value was about 6 times more than that compared to the MFC employed with pure graphite felt ($166 \text{ mW}/\text{m}^2$), and its superior performance can be attributed to the high mechanical, electronic and biochemical properties of the PPy/GO anode.

Figure 2-25: FESEM of the PPy/GO anode. [129] Copyright with permission from Elsevier.

2.3.2.3 A hybrid PEC-MFC device

Wang et al. developed a self-sustained H_2 gas production hybrid device by connecting two independent platforms together as illustrated in Figure 2-26. [130] The hybrid device comprised of a photoelectrochemical (PEC) cell and microbial fuel cell connected in series. The MFC is partially separated by a semi permeable membrane (CEM), with the carbon cloth and Pt- carbon cloth used as an anode and cathode electrodes respectively. The MFC was then subsequently filled with wastewater and further inoculated with *Shewanella oneidensis MR-1*. The PEC cell was equipped with an n-type TiO_2 nanowire photoanode and a Pt counter electrode, filled with 0.5 Na_2SO_4 solutions as electrolyte. To form the hybrid PEC-MFC device, the MFC anode was connected to the counter-electrode of the PEC cell, while the photo-anode of the PEC cell was connected to the MFC cathode.

Figure 2-26: Schematic configuration of a PEC-MFC hybrid device. [130]

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This hybrid (PEC-MFC) device relies on both solar energy (from PECs) and the metabolism of microorganisms (in MFCs), to drive the water splitting reaction for H₂ generation, without the aid of any external bias. It was reported that the hybrid PEC-MFC device generated a photocurrent of 1.25 mA/cm² at zero bias, which was 90 times higher than the one obtained for the individual PEC device (0.013 ma/cm²) at the same potential. Results also confirmed that there was no obvious current drop in 6000 s, further indicating that the PEC-MFC device is stable and efficient for continuous operation. The hybrid device also generated large quantities of H₂ gas after a period of 24 h. These results points towards the possibility of employing various strategies to improve the PEC-MFC platforms for enhanced H₂ evolution.

2.3.3 Optimizing reactivity of NPs through morphological control

A surface is an important component of a solid-state material because many physical and chemical processes usually take place on surfaces. [131] In general, crystalline materials with different surfaces may possess different atomic electronic structures and exhibit different physiochemical properties. Studies have shown that the reactivity of a photocatalyst is strongly surface dependent because the different atomic rearrangement and coordination of a given surface will intrinsically affect the way molecular species interact, resulting in changes to its activity. [132] Given that atomic arrangement and coordination also changes with crystal facets in different orientations, the catalytic activity of a photocatalyst is therefore closely related to the enclosed crystal facet that is derived from a particular morphology. For this reason, the catalytic activity of a nanocrystal is sensitive to different morphologies, which

enables one to possibly maximize the activity of a photocatalyst through morphological control.

2.3.3.1 Co₃O₄ NPs

Shaped NPs has attracted intense research recently because it has being recognized as one of the strategies for optimizing the catalytic activity of NPs. This has led to the successful development of Co₃O₄ NPs in various shapes to be prepared for catalytic H₂ evolution by AB hydrolysis. [133-135] Co₃O₄ in the form of a cube and nanosheets have been fabricated and results have shown that Co₃O₄ nanosheets (0.35 mmol/min) exhibited higher H₂ activity than Co₃O₄ cube (0.22mmol/min). [136] The difference in H₂ activity between them is closely related to their unique surface atom alignment as illustrated in Figure 2-27. The surfaces of the Co₃O₄ cube were composed of (100) planes, while the Co₃O₄ nanosheets were dominated with {211} plane. The higher activity of the Co₃O₄ nanosheets is due to the high density of Co atoms exposed on the surface of the (211) plane.

Figure 2-27: Atoms alignment of Co_3O_4 cube at the (100) plane (a) Top view, (c) Side view and the (211) plane of the Co_3O_4 nanosheet (b) top view, (d) side view. Colour scheme: Co (white) and O (red). [137] Copyright with permission from American Chemical Society.

2.3.3.2 Cu_2O NPs

Besides Co_3O_4 , Cu_2O NPs with different shapes were also prepared. Cu_2O NPs with 50 facets, cube, octahedron and rhombicuboctahedron (RCO) (Figure 2-28) were decorated with Co_3O_4 NPs in a ratio of 1:5 and subsequently used for H_2 evolution to examine its catalytic activity. [138] The surface of the 50 faceted Cu_2O NPs were found to be enclosed with (100), (110), (111) and (311) planes which occupied about 14.7%, 39.1%, 11.3% and 34.9% of the total surface area, respectively. The surface of the RCO NPs was composed of (100), (110) and (111) surfaces, while the Cu_2O cube and octahedron were solely enclosed with (100) and (111) planes,

respectively. [139] Among the Cu_2O NPs evaluated, the 50 faceted Cu_2O NPs possessed the highest H_2 activity with a reported H_2 evolution rate of 0.78 mmol/g/s, which was more than the Cu_2O NPs obtained for the RCO (0.67 mmol/g/s), octahedral (0.56 mmol/g/s) and cubes (0.45 mmol/g/s). [138] The high performance of the 50 faceted Cu_2O NPs can be attributed to the higher density of Cu ions exposed on the (311) surface, compared to the surfaces of (100), (110) and (111) observed for the other morphologies. [140]

Figure 2-28: The crystal planes of the various shaped-controlled Cu_2O NPs.

[138] Copyright with permission from John Wiley and Sons.

2.3.3.3 TiO_2 NPs

Anatase TiO_2 NPs in the shape of decahedra were also prepared and employed as a photocatalyst for H_2 evolution by using methanol as a

sacrificial electron donor. [141] P25 was used as a reference for comparison. Amano et al. found that the surfaces of the decahedral was composed of $\{011\}$, $\{001\}$ and $\{101\}$ facets (Figure 2-29), while the P-25 contained no clear facets in any specific orientation. [141] Based on the H_2 evolution results obtained, the activity of decahedra TiO_2 NPs was about 50% higher than the one obtained for TiO_2 P25 NPs. The higher activity found in the decahedra NPs can be attributed to the under-coordinated Ti atoms (Ti_{5c}) exposed on the $\{011\}$, $\{001\}$ and $\{101\}$ facets, which can help to accelerate the water reduction process for enhanced H_2 production. [142]

Figure 2-29: Image of the decahedral TiO_2 NPs with the exposed $\{011\}$, $\{101\}$ and $\{001\}$ facets. [141] Copyright with permission from American Chemistry of Society.

2.3.4 Development of quaternary-based nanostructures

The structure of a semiconductor is an important aspect in material engineering when it comes to designing a photocatalyst for the efficient utilization of solar energy. In an effort to explore new material suitable for

photocatalysis, material scientists can no longer rely solely on conventional binary semiconductors to develop cheap and efficient visible light active photocatalysts for H₂ generation, due to the limitations of such materials. For this reason, the design of photocatalysts has been expanded to include more complex ternary and quaternary structures such as CuInS₂ and Cu₂ZnIn₂S₄. These copper based semiconductors were reported to possess very strong visible light absorption, large absorption coefficients and high photostability, and were recognized as the next generation of photocatalyst for H₂ evolution. [143, 144]

2.3.4.1 Cation exchange strategy

The formation of complex ternary and quaternary nanostructures can be achieved by using a cation exchange strategy. [145-148] This technique involves exposing the parent ionic crystal to new cations in solvated liquid form. During the cation exchange process, new cations enter into the parent crystal, while the original cations diffuse out and into the reaction medium as shown in the equation below, where, M is the new cation ion, and C and A are the parent crystal cation and anion.

The cation reaction technique has been recognized as an important strategy for post-synthetic chemical modification of nanocrystals due to their rapid reaction speeds. [149] A typical nanocrystal cation exchange reaction can be completed within seconds at room temperature, compared to other conventional methods (eg. hot injection), which could take more time at

elevated temperatures. [150] These mild and fast reaction conditions are attributed to the enhanced surface access and lower activation barriers for the diffusing ions. For example, Rivest et al. have fabricated CdSe/CdS dot-in-rod (dot/nanorods) heterostructures via the solvothermal method. It was reported that by reacting CdSe/CdS with Pb^{2+} at room temperature resulted in the formation of PbSe/PbS dot/nanorods, with no inter-diffusion of the Se and S atoms across the entire dot/nanorod heterojunction. (Figure 2-30) Their results indicated that the transformation of CdSe/CdS to a PbSe/PbS improved the optical light absorption of the dot/nanorods from visible to the near-infrared region (NIR), simply by cation exchange. It is also important to highlight that the size and shape of the dot/nanorod was well preserved during the cation exchange reaction. This allowed the CdSe/CdS nanostructure (parent crystal) to be used as a template to fabricate other types of interesting semiconductors based dot/nanorods, which was difficult to achieve using traditional methods. [151]

Figure 2-30: Cation exchange transformation of CdSe/CdS dot/nanorods to PbSe/PbS using Pb^{2+} ions. [151] Copyright with permission from Royal Society of Chemistry.

Recently, p-n type $CuInS_2/NaInS_2$ nanosheets were reported to efficiently produce H_2 under visible light irradiation. The high H_2 evolution rate exhibited by the nanostructure can be attributed to its efficient charge separation between the $CuInS_2/NaInS_2$ interfaces. [152] Apart from $CuInS_2$, quaternary semiconductors such as Cu doped $ZnIn_2S_4$ nanorings have also been prepared via a cation-exchange strategy. It was reported that the Cu- $ZnIn_2S_4$ nanorings not only exhibited a H_2 evolution rate ~ 16 times more than that for $NaInS_2$ nanoparticles, this material also had good stability without much loss in activity after each cycle. The good stability and H_2 performance of Cu- $ZnIn_2S_4$ can be attributed to the presence of Cu^{2+} ions incorporated into the $ZnIn_2S_4$ nanostructure. [153]

3 Research methodology

3.1 Chemical and materials

Titanium isopropoxide (97%), D-(+)-glucose, gold (III) chloride, P25- titania nanoparticles, sodium sulphide nano-hydrate, indium (III) chloride, zinc (II) chloride, calcium (II) chloride, bismuth (III) chloride, iron (III) chloride and Polyvinylpyrrolidone (MW= 10K) were purchased from Sigma. Hydrochloric acid (37 %), ethanol (99.8 %), methanol (99.8 %), acetic acid, terpineol and ethyl cellulose were supplied by Merck. Deionized (DI) water (18.2 MΩ) was obtained from a Millipore Q water purification system and used in all experiments. All chemicals and materials were used as received, unless otherwise stated.

3.2 Fabrication of nanoparticles

3.2.1 Synthesis of Au@TiO₂, and other core-shell hollow composites

A clear solution was prepared from 2 g of glucose and 30 ml water. It was stirred continuously and transferred to a 40 ml Teflon lined autoclave and maintained at 170 °C for 6.5 h. The brownish carbon nanospheres were harvested by centrifugation, cleaned by three cycles of centrifugation/washing/sonication in water and absolute ethanol and subsequently dried in vacuum for more than 8 h. Carbon nanospheres (200 mg) were dispersed into 20 ml of absolute ethanol and ultrasonicated (500 W, 230 V and 50 Hz) for about 10 min to ensure the carbon spheres were well dispersed. Subsequently, 0.05 ml of titanium isopropoxide (TIPP) was added into the brownish solution and allowed to age for about 18 h. After aging, the

solution was subjected to 3 cycles of centrifugation/ethanol wash/sonication and subsequently dried in a vacuum oven for more than 8 h. The resultant powder was placed in a furnace and heated to 550 °C in air at a heating rate of 16 °C min⁻¹ and maintained at 550 °C for 3 h. After this period, the TiO₂ hollow spheres were removed from the furnace immediately and left to cool to room temperature.

Au@TiO₂ hollow spheres (1 wt%, 2 wt%, 3 wt%) were prepared by adding various amount (0.01 ml, 0.02 ml, 0.03 ml) of HAuCl₄ (0.01 M) to glucose solutions to form Au@carbon spheres. Similar aging, washing and thermal treatment were used to obtain the Au@TiO₂ hollow spheres. The Au@TiO₂ hollow catalyst is denoted as Au@TiO₂-x in which x is the weight percentage of Au relative to TiO₂.

Pt@TiO₂ hollow spheres were prepared by changing the precursor from 0.01 M HAuCl₄ to 0.01 M H₂PtCl₆. Aging, washing and thermal processing procedure described above were used to synthesize Pt@TiO₂ hollow spheres. Au@Fe-carbon nanospheres were synthesized by aging the Au@carbon solution in an iron (III) chloride solution for about 18 h. Similar aging, washing and thermal treatment were used to obtain Au@Fe₂O₃ hollow spheres.

3.2.2 Preparation of Au-25 and Au-TiO₂

Control samples, Au-TiO₂ and Au-P25 (at 2 wt% over TiO₂) were synthesized via photo-deposition. Briefly, 0.01 ml of H₂AuCl₄ solution (0.01 M) was added into 100 mg of support catalyst (P25 or TiO₂ hollow spheres) and subsequently mixed with 5 ml of DI water and 5 ml of methanol. The

suspension was exposed to UV-vis light (MAX-302, Asahi Spectra, USA) for 2 h to photo-deposit Au ions onto the catalyst surfaces. The suspension was then subjected to 3 cycles of centrifugation/ethanol wash/sonication and subsequently dried in a vacuum oven for more than 8 h.

3.2.3 Synthesis of Octahedral NaInS₂ NCs and nanosheets

NaInS₂ NCs were prepared via a solvothermal method. InCl₃ (20 mg) was first dissolved in absolute methanol (15 ml) and then Na₂S.9H₂O (232 mg) was added into the solution to obtain a yellowish precipitate. The mixture was transferred into a 25 ml Teflon-lined autoclave and then sealed and maintained at 190 °C for 16 h. The resultant product was harvested and washed in water and absolute ethanol via three cycles of centrifugation, and subsequently dried in vacuum for more than 8 h. For the synthesis of NaInS₂ nanosheets, Na₂S.9H₂O (300 mg) was added to the aqueous solution (15 ml methanol with 20 mg of InCl₃) and then transferred and sealed in a 25 ml Teflon-lined autoclave. The same heating and washing procedure as described above was followed to obtain the NaInS₂ nanosheets.

3.2.4 Synthesis of NaInS₂ microspheres

For the synthesis of NaInS₂ microspheres, 200 mg of PVP (MW = 10K) was first added to 15 ml of absolute methanol to form a clear solution. The same amount of InCl₃ (20 mg) and Na₂S.9H₂O (300 mg) was subsequently added and further sonicated and stirred for 15 min to form a yellowish precipitate. The resultant precipitate was poured into a 25 ml Teflon-lined autoclave, sealed and maintained at 190 °C for 16 h. After the reaction was completed,

the products were recovered by washing thoroughly with distilled water and ethanol and dried in vacuum for more than 8 h.

3.2.5 Synthesis of octahedral Ca-ZnIn₂S₄ and Bi-ZnIn₂S₄ NCs

For the synthesis of octahedral Ca-ZnIn₂S₄ NCs, octahedral NaInS₂ nanoparticles (100 mg) and ZnCl₂ (20 mg) were mixed together with 15 ml of absolute methanol to form a yellowish precipitate. After stirring for 5 min, 0.5 ml CaCl₂ solution (5 mM) was subsequently introduced into the mixture and then carefully transferred into a 25 ml Teflon autoclave, which was then sealed and reacted at 190 °C for 16 h. The final yellow precipitate was recovered and washed in water and absolute ethanol via three cycles of centrifugation, and subsequently dried in vacuum for more than 8 h. For the synthesis of Bi-ZnIn₂S₄ NCs, 0.5 ml of BiCl₃ solution (5 mM) was introduced into the mixture and then transferred and sealed in a 25 ml Teflon-lined autoclave. The same heating and washing procedure was used as described above to obtain the Bi-ZnIn₂S₄ NCs.

3.3 Fabrication of photoelectrodes in a PEC cell

The photoelectrodes were fabricated via a screen-printing method known as the doctor blade technique. This technique consists of 2 main components. (1) The process of converting the nanocomposites (Au-TiO₂) into a smooth paste and applying it onto the surface of the FTO glass to make it into a photo-electrode (2) The as-prepared photo-electrode were calcinated at high temperatures for the removal of any impurities present on the electrode surface.

3.3.1 Preparation of Au-TiO₂ paste

In a typical procedure, 6 g of as-prepared Au-TiO₂ hollow spheres were transferred into an alumina mortar in powder form. Acetic acid (1 mL), water (1 mL) and ethanol (1 mL) were added to improve the stability of the paste from cracking. At each addition, the specific solvent was introduced drop-wise and the paste was further ground into fine particles using a mortar. After grinding for 15 min, 20 g of terpineol and 3 g of ethyl cellulose (10 % solution in ethanol) were added to the resultant powder, which was further processed into a smooth paste. [154]

3.3.2 Preparation of Au-TiO₂ photoelectrodes

Fluorine doped tin oxide (FTO) glass (15 Ω , 25 $\times$ 11 $\times$ 2.2 mm) was used as a current collector. The FTO glass was cleaned thoroughly by 3 cycles of ultrasonication, using water, acetone and ethanol. The as-prepared Au-TiO₂ paste was spread evenly onto the surface of the FTO glass via a doctor blade technique [154-156]. The electrode was dried for 5 min at room temperature and gradually heated in the muffle furnace at various conditions (325 $^{\circ}$ C/5 min, 375 $^{\circ}$ C/5 min, 450 $^{\circ}$ C/15 min, 500 $^{\circ}$ C/15 min) through a heating cycle (Figure 3-1) and subsequently left to cool to room temperature naturally to obtain the final product. The TiO₂ hollow spheres and P25 electrodes were synthesized with similar procedures.

Figure 3-1: Heating cycle for synthesizing electrode

3.4 PEC cell assembly

The PEC cell setup consisted of a two-electrode configuration system. A platinum wire was used as the counter and reference electrode. A Nafion proton exchange membrane (2 cm in diameter) was placed between the anode and cathode compartments to facilitate movement of protons within the cell. The working surface area of the PEC cell was $\sim 3.14 \text{ cm}^2$.

3.5 MFC assembly

All materials were used as received, unless otherwise stated. U-tube dual chamber MFCs were assembled according to literature. [157-159] Two 90° ball-to-plain-end and socket-to-plain-end glass tubes (17 mm O.D. $\times$ 1.8 mm wall thickness) (Spectra-Teknik, Singapore) were joined using a stainless steel pinch clamp (Spectra-Teknik, Singapore) and high vacuum silicone grease. The interface between both tubes was formed by a circular (diameter of 2 cm) piece of Nafion N117 proton exchange membrane (Ion Power, United States of

America). The dimensions of carbon-felt electrodes (3.18 mm thickness) (VWR Singapore Pte. Ltd. Singapore) were 5 cm × 2 cm (length × width). Titanium wire was connected to the electrodes by plastic screws and nuts (Spectra-Teknik, Singapore). The anode chamber was covered with a silicone septum and the titanium wire was threaded through, whereas the cathode chamber was covered loosely with an inverted glass vial to provide an aerobic environment. In addition, the cathode electrode was only partly submerged to allow oxygen reduction at the aerobic section of the device architecture. The glass tubes were then filled with ultrapure water and autoclaved for sterility. After sterilization and decanting the ultrapure water, the anode chamber was filled with 10 mL of lysogeny broth (LB) and 10 mL of bacterial culture. The cathode contained 20 mL of LB. The electrodes were then connected to 1 kΩ resistors and voltage was recorded with an eDAQ e-corder data acquisition system (Bronjo Medi, Singapore) at a rate of 1 point per 5 min. *E. coli* was cultured overnight in LB at 37 °C and adjusted to O.D₆₀₀ ~ 1.0 before inoculation into the MFC anode only.

3.6 Interconnection of the solar microbial hybrid system

The independent platforms are interconnected via wires to form a hybrid system (Figure 3-2). The MFC anode was connected to the counter-electrode of the PEC cell, whereas the photo-anode of the PEC cell was connected to the MFC cathode (connected via red wires). Robust interconnects were confirmed through probing by a multi-meter.

Figure 3-2: Photo of the solar microbial hybrid system

3.7 Synthesis of DSSN⁺ and DSTN⁺

The synthesis of 4,4'-bis(4'-(N,N-bis(6-(N,N,N-trimethylammonium)hexyl)amino)-styryl)stilbene tetraiodide (DSSN⁺) and 4,4'-thiophene-2,5-diylbis(ethene-2,1-diyl))bis(N,N-bis(6-iodohexyl)aniline) iodide (DSTN⁺) were performed according to literature. [160] [161]. DSSN⁺ and DSTN⁺ were produced through a series of organic synthesis reaction.

3.7.1 Synthesis of DSSN⁺

For the synthesis of DSSN⁺ (Figure 3-3), 4,4'-bis(diethylphosphonatemethyl)stilbene (0.5 g) and *N,N*-Bis(6'-iodohexyl)-4-aminobenzaldehyde (1.27 g) were mixed with THF (50 ml) in a three-necked flask until a homogenous solution is formed. Sodium tert-butoxide (0.21 g) was added to the solution, which results in an immediate color change to bright orange, followed by a gradual (over 5-20 min) transition to a light orange/yellow solution. The reaction was allowed to continue for another 24 h at room temperature and excess THF was removed via rotary evaporation. The crude product was further precipitated with ether and washed three times with brine to obtain the pure DSSN⁺ as a yellowish solid. (320 mg, yield: 67 %)

Figure 3-3: Chemical structure of DSSN⁺

Figure 3-4: NMR spectra for DSSN+

^1H NMR (500 MHz, CD_2Cl_2): 7.50 (d, $J = 8.5$ Hz, 4H), 7.47 (d, $J = 8.5$ Hz, 4H), 7.37 (d, $J = 8.7$ Hz, 4H), 7.12 (s, 2H), 7.05 (d, $J = 16.2$ Hz, 2H), 6.9 (d, $J = 16.2$ Hz, 2H), 6.63 (d, $J = 8.7$ Hz, 4H), 3.3 (t, 8H), 3.23 (t, 8H), 1.85 (m, 8H), 1.60 (m, 8H), 1.44 (m, 8H), 1.36 (m, 8H).

3.7.2 Synthesis of DSTN⁺

For the synthesis of **DSTN⁺** (Figure 3-5), thiophene (50 mmol, 4.2 g), paraformaldehyde (58.5 mmol, 1.75 g), and concentrated hydrogen chloride (6.4 mL) were added to a 100 mL three-necked flask at -5 °C to 0 °C. Gaseous dry hydrogen chloride was added slowly with stirring over a period of 2 h. The obtained brown oil was further reacted with 10 mL triethyl phosphite at 160 °C for 3 h. Excess triethyl phosphite was removed by vacuum distillation. Aldehyde (1.76 g, 3.25 mmol) in dry THF (50 mL) and potassium tert-butoxide (3.6 mmol, 0.4 g) were added in portions to the mixture for 8 h at room temperature. After the reaction was completed, the resultant mixture was further mixed with triethylamine for 10 h and excess THF was removed by rotary evaporation. The crude product was further precipitated with ether and washed three times with brine to obtain the pure DSTN⁺ as a brown solid (1.04 g, yield: 70 %).

Figure 3-5: Chemical structure of DSTN⁺

Figure 3-6: NMR spectra of DSTN+

^1H NMR (400 MHz, CDCl_3): δ = ^1H NMR (400 MHz, DMSO) δ 7.32 (d, J = 8.1 Hz, 4H, Ar-H), 7.04 (d, J = 16.0 Hz, 2H, Ar-H), 6.92 (s, 2H, Ar-H), 6.70 (d, J = 15.9 Hz, 2H, Ar-H), 6.61 (d, J = 8.0 Hz, 4H, Ar-H), 3.28 (m, 16H, $-\text{CH}_2-$), 3.02 (s, 36H, $-\text{CH}_3$), 1.65 (m, 8H, $-\text{CH}_2-$), 1.52 (m, 8H, $-\text{CH}_2-$), 1.31 (m, 16H, $-\text{CH}_2-$).

3.8 Material Characterization

- The morphologies of the obtained samples and the energy dispersive spectroscopy (EDS) measurements were conducted using a scanning electron microscope (JEOL JSM- 7600F) at 5 eV.
- The morphologies of the obtained samples, as well as the SAED and HAADF-STEM elemental maps were obtained using a transmission electron microscope (JEOL JEM-2100F) at a voltage 200 kV.
- The phases of prepared samples were identified by X-ray diffraction (XRD) analysis using a Shimadzu XRD-6000 X-ray diffractometer (Cu-Ka source)
- The light absorption of the samples were measured using a UV-vis spectrophotometer (Lambda 750 UV/Vis/NIR spectrophotometer) and BaSO₄ was used as a reference.
- The specific surface area of the samples was measured using a pore and surface analyzer (Quantochrome Autosorb-6B) and calculated using the Brunauer–Emmett–Teller (BET) equation.
- Crystal maker v9.0.3 was used for the crystal structure modeling and WinXmorph v1.54 was used to determine the facets for the obtained nanocrystals.
- Car Parrinello molecular dynamics (CPMD) simulations were carried out to investigate the interaction of water with the samples surfaces.

3.9 Performance evaluation

3.9.1 H₂ evolution measurement

The photocatalytic H₂ evolution measurement was carried out in a 25 ml quartz reactor at ambient conditions. In a typical measurement, 10 mg of the as-prepared photocatalyst was dispersed in a 15 ml aqueous solution in the presence of a sacrificial reagent. N₂ was bubbled into the solution for 30 min to remove traces of O₂ and H₂ in the sealed glass reactor. A 300 W Xe lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cut off filter ($\lambda > 420$ nm) was used as the light source. Analysis of the gaseous product was performed using gas chromatography (Agilent 7890A GC with TCD detector) and the gas was manually injected into GC at an interval of 30 min. For the stability study, the photocatalyst was filtered, washed with deionized water and re-dispersed in fresh aqueous solution after each cycle.

3.9.2 Electrical characterization

Linear sweep voltammograms (LSV) of stand-alone PEC cells and PEC-MFC hybrid systems were measured in a two-electrode configuration with platinum wire as the counter and reference electrode. For the PEC-MFC hybrid system, the Au-TiO₂ hollow spheres, TiO₂ hollow spheres and standard P25 electrodes functioned as the working electrode. All electrical characterization was performed using a CHI 660D electrochemical workstation (CH Instruments) at a scan rate of 20 mV/s. The electrolyte was 0.5 M Na₂SO₄ solution (pH 7.0). The effective surface area of the working electrode was 0.2 cm². The light source was simulated from a 150 W xenon solar simulator (96000, Newport Corp.) using a solar filter with a measured intensity equivalent to standard AM1.5 sunlight (100 mW/cm²).

3.9.3 Electrochemical impedance spectra (EIS)

The EIS measurements were carried out by using an automated potentiostat (Metrohm Autolab) in a three-electrode electrochemical system under 1 sun illumination at 1.23V vs. RHE from 100000 to 0.1 Hz. The semiconductor based FTO, platinum mesh and Ag/AgCl served as the working, counter and reference electrodes, respectively. The electrolyte was 0.5 M Na₂SO₄ solution (pH 7.0).

4 A strategy for in-situ synthesis of well-defined core-shell Au@TiO₂ hollow spheres for enhanced photocatalytic H₂ evolution¹

4.1 Introduction

Chapter 4 investigates how core-shell hollow composites (Au@TiO₂), with Au NPs encapsulated within the core of the hollow TiO₂ shell, could be a new class of nanostructures that could potentially contribute significantly towards H₂ generation. The Au@TiO₂ hollow nanocomposites were prepared via a facile in-situ hydrothermal reduction hard template strategy, with the amount of Au NPs encapsulated controlled by the concentration of Au precursor used during synthesis. The plasmonic Au NPs encapsulated in the core-shell composites were used as a visible light sensitizer and an electron trapper to improve its charge separation and visible light absorption of the photocatalyst for enhanced H₂ generation. The stronger, localized SPR effect exhibited by the Au@TiO₂ was also further confirmed through control experiments. It was also demonstrated that by using appropriate precursors, this approach could also be used as a general strategy for synthesizing other types of core-shell metal oxide based hollow structures with well-defined morphology. Such core-shell metal oxide hollow nanostructures can be further explored for other emerging applications.

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4.2 Results and discussion

The Au@TiO₂ hollow spheres (Au@TiO₂) were prepared via a carbonaceous hard template strategy as displayed in Figure 4-1A. This can be divided into 3 steps; the formation of Au@carbon templates, the adsorption of Ti ions and the removal of template via calcination. In this approach, glucose solution acted as a carbon source and a reducing agent to hydrothermally reduce Au ions (HAuCl₄) into Au nanoparticles. Under hydrothermal conditions, glucose solution undergoes aromatization and carbonization and the Au NPs were encapsulated within the core of the carbonaceous spheres forming Au@carbon templates. Interestingly, we found that by manipulating the concentration of Au added to the glucose solution, carbonaceous spheres with different numbers of Au cores can be obtained.

Figure 4-1: Synthesis of (A) Au@TiO₂, (B) Au@Fe₂O₃, (C) Pt@TiO₂ hollow spheres

Figure 4-2 shows the TEM images of the Au@carbon-x with different H₂AuCl₄ concentrations (x denoted as % weight content of gold over carbon). Without the addition of Au to the glucose solution, pure carbonaceous spheres with a diameter of 100 nm were obtained, as shown in Figure 4-2a. However, as Au content was increased to 1 wt%, only some of the carbonaceous spheres (Figure 4-2b) encapsulated Au NPs. When concentration was increased to 2 wt% and beyond, every individual carbon spheres encapsulated Au NPs, as shown in Figures 4-2c and 4-2d.

Figure 4-2: TEM images of Au@carbon-x spheres with different Au content with x denoted as the weight percentage of Au over carbon (a) 0 wt %, (b) 1 wt %, (c) 2 wt %, (d) 3 wt %.

The surfaces of the Au@carbon templates are rich in negatively charged functional groups such as O-H and C=O, therefore enabling positive metal ions to be attracted onto it. [162] Because of strong electrostatic interactions, positive

Ti ions can be easily adsorbed onto the surfaces of the Au@carbon templates to form Au@carbon/Ti composites as indicated in Figure 4-1A. These composites were further annealed in air to remove the carbon templates and the adsorbed Ti ions were converted into a TiO₂ shell, obtaining Au@TiO₂-x hollow spheres (with x denoted as % wt content of Au over TiO₂). Inset images in Figure 4-2 show the corresponding schematic diagram of the Au@TiO₂-x hollow spheres after calcination, implying the number of Au NPs found in the TiO₂ hollow cavity is dependent on the number of Au cores encapsulated in the Au@carbon templates.

Figure 4-3: 2 wt% Au@TiO₂ hollow spheres (a) SEM image; (b) TEM image; (c) Close up TEM image; (d) and (e) HRTEM images of Au@TiO₂-2; (f) SAED pattern.

The field emission scanning electron microscopy (FESEM) image in Figure 4-3a shows that 2 wt% Au@TiO₂ (Au@TiO₂-2) have an average size of about 70-90 nm, while the transmission electron microscopy (TEM) image (Figure 4-3b) reveals that Au NP is within the interior cavity of the hollow sphere, i.e. a core-shell Au@TiO₂ hollow sphere. The detailed structural information of the Au@TiO₂-2 was further investigated by TEM and high-resolution TEM (HRTEM) images. Figure 4-3c shows the TEM image of an individual Au@TiO₂-2 with the Au NP located within the hollow cavity measuring about 12 nm. The HRTEM images shown in Figure 4-3d and 4-3e further disclose that the Au@TiO₂-2 are highly crystalline with an interplanar spacing of 0.25 nm and 0.35 nm, corresponding to the (200) plane of metallic Au and (101) plane of anatase TiO₂ phase respectively. The selective area electron diffraction (SAED) pattern in Figure 4-3f was taken from the same Au@TiO₂ hollow sphere, revealing that the obtained Au@TiO₂-2 has a polycrystalline structure. The concentric rings were attributed to (200) planes of Au and (101), (004) and (105) planes of TiO₂ anatase.

To determine the temperature required for the template removal, a thermogravimetric analysis (TGA) experiment was performed on the Au@carbon and Au@carbon-Ti composites spheres. The samples were heated at a rate of 20 °C min⁻¹ from room temperature to 750 °C in air and two weight loss steps were observed (Figure 4-4a). The first weight loss step in the region from 40 °C to 300 °C regions was associated with moisture losses in both samples. Beyond 300 °C, a significant weight decrease in both samples indicated the decomposition of carbon templates. A plateau region from 550 °C to 700 °C was observed for both TGA curves suggesting that no further weight

loss was observed for both samples and the final weight discrepancy between both curves is attributed to the newly formed Au@TiO₂ hollow spheres, which constitute about 2.3 % weight of the Au@carbon/Ti composites. This result implies that a temperature of 550 °C is sufficient to remove the carbon templates and convert Au@carbon/Ti composites into Au@TiO₂ hollow spheres.

Figure 4-4: (a) TGA curves for Au@carbon and Au@carbon/Ti composites, Au@carbon and Au@TiO₂ (b) XRD pattern, (c) EDS spectrum.

It should be noted that the Au@TiO₂ hollow sphere does not contain any traces of carbon after calcination at 550 °C. To confirm this, X-Ray Diffraction (XRD) patterns of the Au@carbon and Au@TiO₂ were analyzed. The amorphous nature of the carbon templates is characterized by a broad diffraction peak at around 21° as shown in Figure 4-4b, while the other diffraction peaks can be ascribed to the (111), (200), (220) and (311) faces of Au (JCPDS No. 65-8601).

In contrast to XRD pattern of Au@carbon, the Au@TiO₂ XRD pattern (Figure 4-4b) has newly formed diffraction peaks ascribed to the TiO₂ phase (JCPDS No. 86-1157) without any carbon peaks detected. This result provides evidence that the Ti ions formed the TiO₂ shell and the carbon templates were completely removed. The complete removal of carbon templates is also evidenced from Energy Dispersive X-Ray spectroscopy (EDS) analysis and Figure 4-4c shows the EDS spectrums for Au@carbon and Au@TiO₂. By comparing both EDS spectra, it can be observed that the intensity of the carbon peak for Au@TiO₂ is greatly reduced and only traces of carbon can be found in Au@TiO₂. This trace of carbon in Au@TiO₂ can also be attributed to the contamination of the equipment itself and may not be due to the incomplete removal of the carbon templates.

Figure 4-5: N_2 adsorption/desorption isotherms and pore size distribution (inset) of (a) $Au@TiO_2-2$, (b) $Au-P25$ (c) XRD patterns of the $Au@TiO_2-x$ (x denoted as % weight content of gold), (d) UV-Vis spectra of (0) $Au@TiO_2-0$, (1) $Au@TiO_2-1$, (2) $Au@TiO_2-2$, and (3) $Au@TiO_2-3$.

The N_2 adsorption measurement of the $Au@TiO_2-2$ hollow sphere in Figure 4-5a shows a typical type IV isotherm with a hysteresis loop in the high-pressure region (0.8-1.0), implying the $Au@TiO_2$ is mesoporous after calcination. [163] In addition, the pore-size distribution curve (inset of Figure 4-5a) obtained from the desorption branch reveals that the pores of the $Au@TiO_2$ shell have a relatively wide range of about 8- 20 nm. Owing to their mesoporous hollow structure and highly porous shell, a high Brunauer-Emmett-Teller (BET)

specific surface area of $107 \text{ m}^2 \text{ g}^{-1}$ was achieved for Au@TiO₂-2, which is approximately 2.5 times higher compared to Au-P25 ($42 \text{ m}^2 \text{ g}^{-1}$, Figure 4-5b).

Three different Au@TiO₂ with varying amount of Au loadings (Au@TiO₂-1, 2 and 3) were fabricated using the same conditions and their crystal structures were investigated by XRD as shown in Figure 4-5c. The XRD profiles of all three Au@TiO₂ products (1-3 wt%) were quite similar and exhibited strong diffraction peaks at 25.3° , 37.9° , 48.1° , 54.0° , 62.7° and 76.1° corresponding to (101), (004), (200), (105), (204), and (301) faces of anatase of TiO₂, respectively (JPCDS No.21.1272), with minor rutile diffraction peaks also detected at 27.4° and 41.2° corresponding to (110) and (200) (JCPDS No. 76-1940). [164, 165] It was noted that all Au@TiO₂ hollow spheres (1-3 wt%) exhibited a mixture of anatase and rutile phases. The presence of the rutile phase could be due to the high temperature that was required for the complete removal of the carbon templates based on results obtained from TGA. [166] In addition, the Au@TiO₂ hollow spheres showed one characteristic peak at 44.5° corresponding to Au (200) and the peak intensity increases with Au loading from 2 wt% to 3 wt%. No obvious peak was observed for the XRD pattern of the 1 wt% sample, which is largely due to the low concentration of Au that is beyond the instrument detection limit.

Figure 4-5d shows the UV-Vis diffuse reflectance spectra for the different Au@TiO₂ (0-3 wt %) composites. An intense UV absorption band was observed at wavelengths shorter than 390 nm and can be assigned to the intrinsic band gap of TiO₂ (E_g : 3.2 eV, assumed to be mainly anatase phase based on XRD data). [167] However, in contrast to the pure TiO₂ sample, the Au@TiO₂ nanocomposites (1-3 wt%) exhibited broad absorption bands at ~ 580

nm arising from the SPR feature of the Au NPs, with the intensity of the peak increasing with Au loading. It should be noted that the SPR wavelength for Au@TiO₂ has apparently red-shifted compared to that of free Au particles of similar sizes (520 – 530 nm for 15 nm Au nanoparticles). [168] This is attributed to the fact that the localized SPR of Au NPs is highly sensitive to the dielectric environment. [169, 170] Since TiO₂ has a higher refractive index (n=2.49) compared to water (n=1.33), direct contact of encapsulated Au on the TiO₂ matrix would cause a shift in the SPR band.

Figure 4-6: Photocatalytic H₂ evolution rates of Au@TiO₂ hollow spheres with different Au contents (a) in 0.1 M ascorbic acid solution under visible light irradiation; (b) in 0.1 M aqueous methanol solution under UV irradiation.

The Au@TiO₂ hollow spheres were tested for photocatalytic H₂ evolution under visible light (≥ 420 nm) irradiation and L-ascorbic acid (0.1 M, pH =4.0) was used as the sacrificial reagent as shown in Figure 4-6a. No H₂ was detected over the Au@TiO₂-0 sample because there is no light absorption in the visible light region, whereas a significant increase in H₂ evolution rate was observed for the Au@TiO₂ (1-3 wt%) samples, confirming that Au NPs are visible light sensitizers and responsible for the photocatalytic activities under visible light irradiation. The H₂ evolution rate for Au@TiO₂ reaches a maximum rate of 40.25 mmol g⁻¹ hr⁻¹ at 2.0 wt% Au loading, while increasing the Au loading to 3 wt% will lower its H₂ evolution rate to 18.69 mmol g⁻¹ hr⁻¹. It is interesting to note that although Au@TiO₂-3 has the strongest intensity absorption band at 580 nm, the H₂ evolution for Au@TiO₂-3 is reduced significantly compared to that of Au@TiO₂-2. These results suggest that the H₂ evolution does not solely depend on intensity of the SPR peak, but also the different amounts of Au loading. It has been mentioned previously that the Au concentration will affect the morphology of the Au@carbon and increasing Au loading from 2-3 wt% will result in more Au NPs encapsulated within the hollow cavity of Au@TiO₂-3. These excessive Au NPs encapsulated in the hollow spheres may serve as centers to promote the recombination of electron-hole pairs, thereby lowering the photocatalytic activity of the Au@TiO₂-3. [105, 171]

The photocatalytic performances of the Au@TiO₂ hollow spheres were further evaluated by measuring the amount of H₂ generation under ultra-violet (UV) irradiation as shown in Figure 4-6b. Methanol was used as the sacrificial reagent to quench the photo-generated holes. Control experiments in the absence of either methanol or Au@TiO₂ showed no H₂ production. In

comparison to pure TiO₂ hollow spheres that exhibit the least amount of H₂ (12.04 mmol g⁻¹ hr⁻¹), all Au@TiO₂ (1-3 wt%) exhibited higher H₂ evolution rates. Among them, a 4 fold enhancement (69.77 mmol g⁻¹ hr⁻¹) was achieved for the Au@TiO₂-2 while the H₂ evolution rates for Au@TiO₂-1 and Au@TiO₂-3 are 47.07 mmol g⁻¹ hr⁻¹ and 37.16 mmol g⁻¹ hr⁻¹ respectively. It can be observed that the trend of results obtained in Figure 4-6a and 4-6b are quite similar and Au@TiO₂-2 exhibited the highest performance for both UV and visible light irradiation. Increasing Au loading to 3 wt% resulted in a distinct decrease in H₂ production, which further indicates that excess amount of Au NPs existing within the hollow spheres would have a detrimental effect on its photocatalytic performance. This is most probably due to the high recombination rate between the charge carriers. It is important to note that methanol and ascorbic acid were used as sacrificial reagents to evaluate the photocatalytic activities of the Au@TiO₂ hollow spheres under UV and visible light respectively. Preliminary H₂ evolution results (not shown) indicate that methanol is a good sacrificial reagent to generate high H₂ yields. [42] However, when methanol was used as sacrificial reagent under visible light, no H₂ was detected. This result implies that although methanol can efficiently oxidize the holes on TiO₂ under ultra-violet light, it can hardly oxidize the holes of gold under SPR excitation. [172] Therefore, ascorbic acid (pH 4), a common sacrificial reagent for Au-TiO₂ composites, was used for H₂ evolution studies under visible light.

Figure 4-7: Schematic illustration of proposed mechanism for H₂ evolution (a) in 0.1 M ascorbic acid solution under visible light ($\lambda > 420$ nm) irradiation, and (b) in 0.1 M aqueous methanol solution under ultra violet light ($\lambda > 320$ nm) irradiation.

In addition, it is also interesting to note that the Au@TiO₂ hollow spheres exhibited a huge difference in H₂ evolution rate under two different light sources (visible light and UV irradiation). This suggests that the mechanism of Au@TiO₂ for H₂ evolution differ from one another under different light illumination, directly affecting the photocatalytic H₂ evolution rates. The proposed mechanism of the Au@TiO₂ hollow spheres for photocatalytic H₂ generation is illustrated in Figure 4-7. When the Au@TiO₂ hollow spheres were illuminated by visible light, plasmon excited electrons in Au will be injected into TiO₂ to further reduce H⁺ into H₂, [173] while holes in the Au nanoparticle will be quenched by ascorbic acid. Since the electrons in TiO₂ are not excited under visible light, the main contribution of the photoactivity of Au@TiO₂ is the injected plasmon-excited electrons from gold, therefore resulting in a low H₂

evolution rate. However, when the Au@TiO₂ hollow spheres were exposed to UV irradiation, electrons in TiO₂ will be excited to the conduction band (CB). [174] In addition, since Au NPs encapsulated within the hollow cavity can act as an electron sink, electrons from TiO₂ will be easily transferred to Au, significantly improving its charge separation within the Au@TiO₂ structure for enhanced H₂ generation. [175] It is probable that the enhanced charge separation as well as the high density charge carriers generated by the excitation of TiO₂ are responsible for the higher H₂ evolution rates observed under UV irradiation. To prove that the core-shell Au@TiO₂ hollow spheres could be efficient photocatalysts, the photocatalytic performance of the as-prepared Au@TiO₂-2 was further compared with Au-TiO₂, Au-P25 and P25. It is important to note that Au-TiO₂ and Au-P25 were synthesized by photo-deposition with the same Au content as Au@TiO₂-2 (see experimental section). Figure 4-8a and 4-8c shows the TEM image of the Au-P25 and Au-TiO₂ at 2 wt% respectively. Figure 4-8b and 4-8d is a magnified image of the red region (in Figure 4-8a and 4-8c), which further reveals that Au NPs were grown and anchored onto the surface of P25 and TiO₂ hollow spheres after photo-deposition. Au@TiO₂-2, Au-TiO₂, Au-P25 and P25 samples were tested for photocatalytic H₂ evolution under solar light irradiation using methanol as the electron donor and their H₂ evolution rates are shown in Figure 4-8e. It was found that the core-shell Au@TiO₂-2 hollow spheres (69.77 mmol g⁻¹ hr⁻¹) are more photocatalytic active than Au-TiO₂ (37.80 mmol g⁻¹ hr⁻¹), Au-P25 (9.68 mmol g⁻¹ hr⁻¹) and P25 (3.5 mmol g⁻¹ hr⁻¹). The higher H₂ evolution rates for Au@TiO₂-2, Au-TiO₂ and Au-P25 compared to P25 is largely due to the presence of Au NPs incorporated in the TiO₂. It is understood that when

Au@TiO₂ is exposed to UV irradiation, electrons from the conduction band (CB) of TiO₂ will be transferred to Au NPs until equilibrium is attained between them. The accumulation of electrons trapped within the Au NPs from TiO₂ will cause the net Fermi level to shift to a more negative level during Fermi-level equilibrium leading to better charge separation and enhanced photocatalytic performance. [175-177] This could explain why the photocatalytic activities for Au@TiO₂-2, Au-TiO₂ and Au-P25 experienced much higher H₂ evolution rates compared to P25.

Figure 4-8: TEM image (a) and (b) Au-P25, (c) and (d) Au-TiO₂ hollow spheres (e) H₂ evolution profiles of P25, Au-P25, Au-TiO₂ and Au@TiO₂-2 in in

0.1 M aqueous methanol solution under UV irradiation. (f) Recycle study on Au@TiO₂-2 in 0.5 M aqueous methanol solution under UV-visible irradiation.

It is also interesting to note that although Au@TiO₂-2 and Au-P25 have the same Au content (2 wt%), the photocatalytic performance for Au@TiO₂-2 is about 7 times higher compared to Au-P25. This improved performance could be attributed to the unique core-shell hollow structure of Au@TiO₂-2. The void space and highly porous shell in Au@TiO₂-2 will contribute to higher surface area of the photocatalyst (107 m² g⁻¹), offering more active sites for more H⁺ ions to be captured and reduced into H₂ compared to Au-P25. Furthermore, the mesoporous structure will also provide additional pathways and channels for more reactants to diffuse into and out of the photocatalyst, which explains for the enhanced performance observed for Au@TiO₂-2 relative to that of Au-P25 (9.68 mmol g⁻¹ hr⁻¹) under similar conditions. [178] Finally, although Au@TiO₂-2 and Au-TiO₂ hollow spheres have similar Au content and surface areas, the photocatalytic activity for Au@TiO₂-2 is about double that of Au-TiO₂. This superior performance of the core-shell hollow spheres may be attributed to the presence of the Au NPs encapsulated within the core of hollow cavities as well as the multiple light reflection effect of Au@TiO₂-2. It is well known that hollow spheres are good photocatalysts as light is able to penetrate through the shell of the hollow sphere and continually reflect off the walls of the hollow interior to induce a multi-light reflection effect within the cavity. [17, 41] This multiple-light scattering effect will increase the degree of light absorption by the encapsulated Au NPs through multiple light scattering, inducing a stronger localized SPR (LSPR) effect on Au@TiO₂-2. [179-181] The enhanced LSPR effect will generate more photoelectrons in the TiO₂ shell

matrix, explaining the higher photocatalytic activity observed for Au@TiO₂-2 than for Au-TiO₂.

To investigate the stability of the core-shell photocatalyst against poisoning, a stability test was performed on the Au@TiO₂-2 samples under solar light irradiation as shown in Figure 4-8f. Au@TiO₂-2 sample was subjected to three consecutive cycles of use, with the samples recovered by centrifugation and subsequently re-dispersed in fresh methanol solution after each cycle. The results clearly show that there is no significant loss in activity after each cycle, which is attributed to the high stability of Au NPs in the core-shell hollow structure. This indicates that the core-shell hollow structure Au@TiO₂ is an excellent photocatalyst and the core-shell hollow spheres Au@TiO₂ can be reused with little loss in photocatalytic activity.

The current proposed carbonaceous hard template strategy is not restricted to the synthesis of Au@TiO₂ hollow spheres; it can also be employed for the fabrication of other noble metal core-shell hollow composites such as Au@Fe₂O₃ and Pt@TiO₂ hollow spheres. Figure 4-1B illustrates the synthesis of Au@Fe₂O₃ hollow structure: after encapsulating the Au NPs into carbon templates under hydrothermal conditions. Fe ions are adsorbed onto the surface of the Au@carbon and subsequently annealed in air for template removal to obtain the Au@Fe₂O₃ hollow structure.

Figure 4-9: TEM images of (a) Au@Fe₂O₃ and (b) Pt@TiO₂ hollow spheres, (c) XRD patterns of Pt@TiO₂ and Au@Fe₂O₃.

The synthesis of Pt@TiO₂ hollow composites follows a similar approach as shown in Figure 4-1C: the only difference is that the Pt precursor was mixed with glucose solution to form Pt@carbon through a hydrothermal reaction. The Pt@carbon templates were exposed to Ti ions and further annealed to form Pt@TiO₂ hollow spheres. Figure 4-9a and 4-9b shows the TEM image of Au@Fe₂O₃ and Pt@TiO₂ hollow spheres respectively. From these images, it is evident that Au and Pt NPs were embedded into the core of these hollow

spheres. The hollow shell material encapsulating the Pt and Au NPs were confirmed by XRD patterns as shown in Figure 4-9c. The diffraction peaks of Au (200) and Pt (200) at 44.5° with their respective crystalline $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 phases indicate the successful formation of $\text{Au@Fe}_2\text{O}_3$ and Pt@TiO_2 hollow spheres. These results support the flexibility of this method for producing different types of core-shell hollow spheres. The key behind the successful fabrication of the different core-shell hollow spheres using this approach is due to: 1) The *in-situ* hydrothermal reduction of glucose that can effectively reduce noble metal ions into metallic NPs, which can subsequently serve as nuclei for the formation of M@carbon spheres ($\text{M} = \text{Au, Pt}$). As such, Au@carbon and Pt@carbon spheres can be synthesized easily using their respective Au and Pt precursors. [182] 2) The rich functional groups ($-\text{OH}$ and C=O) on the surface of M@carbon templates can readily adsorb any metal ions (Fe^{3+} , Ti^{4+}), forming an outer layer and producing a wide range of metal oxide hollow spheres after calcination. By combining both of these features together and employing appropriate noble metal (eg. $\text{M} = \text{Pt, Au}$) and metal ion precursors (eg. $\text{W} = \text{Fe}^{3+}$, Mg^{2+} , Ti^{4+} , Cu^{2+} , Zn^{2+} , Co^{2+}), different types of noble metal core-shell metal oxide hollow structures ($\text{M@W}_x\text{O}_y$) can be achieved.

4.3 Summary

In summary, a simple approach of combining an *in-situ* hydrothermal reduction technique with the adsorption of Ti^{4+} ions onto carbon templates was successfully developed to prepare uniform and well-defined core-shell hollow structure Au@TiO_2 NPs with different Au loadings. Among them, the 2 wt%

Au@TiO₂ exhibited the highest photocatalytic activity for H₂ evolution under both visible light and solar light irradiation. The photocatalytic performance of Au@TiO₂-2 was further compared with P25 under UV irradiation and results indicated that the Au@TiO₂-2 was about 7 times more active than Au-P25. This remarkable enhancement for Au@TiO₂-2 can be attributed to three factors. Firstly, the Au NPs can act as an electron trap, increase charge separation within the Au@TiO₂ matrix for enhanced activity. Secondly, hollow cavity and mesoporous shell provide additional active surface pathways and channels for more reactants to be reduced to H₂. Lastly, Au encapsulated within the core-shell hollow structure can absorb more visible light and induce a stronger SPR effect on the Au NPs for more electrons to be transferred to TiO₂ to reduce water into H₂. In addition, Au@TiO₂-2 had exhibited good photostability. Other types of noble metal core shell hollow spheres (Pt@TiO₂ and Au@Fe₂O₃) can also be fabricated by using appropriate metal ion precursors. This work paves the way for the development of other types of core-shell hollow (M@W_xO_y) photocatalysts based on the manipulation of the metal oxide shell and the noble metal inner core.

5 Enhancement in H₂ evolution using Au-TiO₂ hollow spheres with microbial devices modified with conjugated oligoelectrolytes²

5.1 Introduction

Based on the good photocatalytic properties exhibited by the Au-TiO₂ hollow spheres as reported in chapter 4, these photocatalyst were further processed and fabricated into an electrode, and then employed as a photoanode to generate H₂ gas in a photoelectrochemical (PEC) cell using solar energy. Although PEC water splitting is an attractive strategy to generate H₂, this phenomenon needs to be driven by an external bias, which decreases the competitiveness of this platform. In order to demonstrate a self-sustaining water splitting device driven by solar energy, a continual supply of external energy must be provided. To address this issue, researchers have developed a new type of solar-microbial cell (SMC), comprising of a PEC and a microbial fuel cell (MFC) by connecting the two devices in series. This hybrid device was designed to be self-sustaining by utilizing both solar energy (from PECs) and the metabolism of microorganisms (in MFCs), to drive the water splitting reaction for H₂ generation. Recently, studies have reported that the use of conjugated oligoelectrolytes (COEs) can help to enhance the performance of MFCs. [159, 183] These amphiphilic COEs, built from electronically delocalized π -conjugated aromatic backbones with pendant ionic groups, were able to intercalate spontaneously into the membrane of the microorganisms and improve the charge collection of the MFCs for increased electrical current output.[159, 184, 185] Although these chemically modified MFCs have shown significant performance enhancement through the

use of COEs, it has yet to be employed together with a PEC cell as a hybrid system for H₂ generation.

In this chapter, an integrated PEC-MFC hybrid platform was employed to demonstrate enhanced H₂ evolution (1) using Au-TiO₂ hollow spheres to improve the photoabsorption capabilities of the photo-anode through enhanced surface plasmon resonance effect in PEC cells, and (2) chemical functionalization of *E. coli* with two novel COEs, i.e. 4,4'-bis(4'-(N,N-bis(6''-(N,N,N-trimethylammonium)hexyl)amino)-styryl)stilbene tetraiodide (DSSN⁺) and 4,4'-thiophene-2,5-diylbis(ethene-2,1-diyl))bis(N,N-bis(6-iodohexyl)aniline) iodide (DSTN⁺), to enhance extracellular charge transfer in MFCs.

² Reproduced from [C.K. Ngaw, V.B. Wang, Z. Liu, Y. Zhou, S. Kjelleberg, Q. Zhang, T.T.Y. Tan, S.C.J. Loo, npj Biofilms And Microbiomes, 2015, 1, 15020] with permission from the Nature Publishing Group.

5.2 Results and discussion

The Au-TiO₂ hollow spheres was employed as the working electrode in the PEC cell due to its favorable band position for PEC water splitting, good chemical stability and low cost. [186-188] In addition, AuNPs embedded within the TiO₂ hollow spheres can improve charge separation within the electrode by reducing recombination reactions. The Au-TiO₂ hollow spheres were prepared *via* a carbonaceous hard template strategy. [189] The field emission scanning electron microscopy (FESEM) image shows that the Au-TiO₂ hollow spheres have an average size of ~50 - 70 nm (Figure 5-1a and 5-1b). Transmission electron microscopy (TEM) images revealed the formation of hollow spheres with an average diameter of ~60 nm and the presence of AuNPs encased within the internal cavity of the hollow spheres (Figure 5-1c). The Au-TiO₂ hollow spheres were then processed into a smooth paste and deposited onto the surface of a FTO glass substrate by the doctor blade technique. [154] The FESEM image collected from the thin film on the FTO surface reveals a densely packed array of nanoparticles with an average diameter of ~60 nm (Figure 5-1d).

Figure 5-1: *Au-TiO₂ hollow spheres. (a) FESEM image. (b) TEM image. (c) Enlarged TEM image of Au-TiO₂ hollow spheres. (d) FESEM of Au-TiO₂ hollow spheres electrode.*

Optical absorption spectroscopy was performed to further analyze the fabricated electrodes (Figure 5-2a). All the electrodes exhibited an intensive absorption band at wavelengths shorter than 390 nm, which is consistent with the intrinsic band gap reported for TiO₂ (~3.2 eV). [167] However, in contrast to the TiO₂ hollow spheres and P25 standard electrodes, the Au-TiO₂ hollow spheres electrode exhibited a characteristic plasmonic absorption band at ~580 nm. This is attributed to the SPR effect of the AuNPs, whereas the TiO₂ hollow spheres and P25 standard electrodes do not exhibit such peaks. In addition, X-ray diffraction (XRD) spectra from the respective electrodes were collected (Figure

5-2b). TiO₂ hollow spheres and P25 standard films showed similar XRD profiles and exhibited strong diffraction peaks at 25.3°, 37.9°, 48.1°, 54.0°, and 62.7°, which correspond to the anatase faces of (101), (004), (200), (105) and (204) of TiO₂ respectively (JPCDS No. 21.1272).

Figure 5-2: (a) Optical absorption spectroscopy and (b) X-ray diffraction patterns of various electrodes used in PEC cells.

Minor diffraction peaks were also detected at 27.4° and 41.2°, which correspond to the rutile faces of (110) and (200) of TiO₂ respectively (JCPDS No. 76-1940). Collectively, these results reveal that the crystal structures of TiO₂ hollow spheres and P25 standard films exhibit a mixture of anatase and rutile phases. In contrast to the XRD patterns of TiO₂ hollow spheres and P25 standard films, the XRD pattern of Au-TiO₂ hollow spheres exhibited additional diffraction peaks at 44.5°, 68.4° and 77.5°, which can be attributed to the (111), (220) and (311) faces of Au (JCPDS No. 65-8601). This analysis indicates the successful incorporation of AuNPs within the TiO₂ hollow spheres.

Electrical performances of individual PEC cells were analyzed to investigate the role of photo-anode modification in PEC water splitting. Linear sweep voltammograms (LSV) of the various photo-anodes were performed in 0.5 M Na₂SO₄ electrolyte under 1 sun illumination (AM1.5, 100 mW/cm²) (Figure 5-3a). At 0 V, the Au-TiO₂ hollow spheres produced the highest photocurrents (~0.04 mA/cm², orange trace), whereas TiO₂ hollow spheres produced ~0.02 mA/cm² (blue trace). Lastly, the system employing standard P25 produced ~0.005 mA/cm² (red trace). LSV under dark condition (black trace) exhibited a horizontal line and negligible current density was generated at 0 V, indicating that current does not increase significantly when swept under dark conditions. Collectively, these results validate the choice of Au-TiO₂ hollow spheres as the best material, amongst these candidates, for the photo-anode. Amperometric on-off current-time curves further corroborate these observations (Figure 5-3b).

Figure 5-3: (a) Linear sweep voltammograms and (b) Amperometric current-time curves of stand-alone PEC cell employing different photo-anodes under one sun illumination (100 mW/cm²). Na₂SO₄ solution (0.5 M, pH 7.0) was used as an electrolyte.

The observed photocurrent for P25 standard increased from $\sim 0.005 \text{ mA/cm}^2$ to $\sim 0.02 \text{ mA/cm}^2$ for TiO_2 hollow spheres. The enhanced photocurrent generation ($\sim 4\times$) is attributed to the hollow sphere morphology, as it is a favorable architecture for photocatalytic activities. [171, 190, 191] Photons penetrating through the shell reflect from the walls of the sphere to induce sustainable reflection within the hollow cavity. This enhances the probability of light absorption by the TiO_2 for better efficiency. In addition, it is interesting to observe that incorporating AuNPs into the TiO_2 hollow spheres can further improve the photocurrent generation to $\sim 0.04 \text{ mA/cm}^2$. This enhanced performance is attributed to the presence of AuNPs encased within the cavity of the hollow spheres. The AuNPs not only induce SPR effect, which generates more photoelectrons for higher photocurrent output, [179, 181, 192] they can also function as electron sinks [193, 194] to ensure reduced charge recombination within the Au- TiO_2 architecture for enhanced photocatalytic effect. No H_2 gas was produced at the Pt wire for the stand-alone PEC cell, which is due to the low photocurrent output produced at zero bias (0 V vs. Pt).

Currently, two hypotheses exist to account for the enhanced extracellular charge transfer afforded to COE-modified bacterial systems – (1) direct charge transfer across the conjugated molecular backbone of the intercalated COEs which are functioning as nanowires within the cellular membrane; [160, 184] (2) membrane perturbation after COE intercalation in the cellular membrane, causing concomitant leakage of intracellular redox active component, which contributes to extracellular charge transfer. [183, 195, 196] Although the specific mechanism(s) remain in contention, MFCs employing such chemically modified *E. coli* shows enhanced electrical output. The independent MFCs

employing *E. coli* as the biocatalyst without chemical modification exhibited a maximum power density of $\sim 1.5 \times 10^{-16} \text{ W/cm}^2$. The addition of $10 \mu\text{M}$ DSTN+ and DSSN+ improved the electrical output to $\sim 2.5 \times 10^{-16} \text{ W/cm}^2$ and $\sim 3.5 \times 10^{-16} \text{ W/cm}^2$ respectively (Figure 5-4a). In an attempt to improve charge transfer by employing such COEs, the chemical backbone of DSTN+ has been modified by replacing one of the benzene ring, as seen in DSSN+, with a thiophene moiety, which is hypothesized to have better charge transfer capabilities.

Figure 5-4: (a) Power density vs. time of MFC inoculated with *E. coli* chemically modified with DSSN+ and DSTN+. (b) Scanning electron microscopy image of *E. coli* biofilm colonized on a carbon fiber electrode surface.

Scanning electron microscopy (SEM) image clearly revealed biofilm colonizing on the electrode surface, which has been retrieved from the anode chamber of the MFC (Figure 5-4b). The cells are rod-shaped (width of $\sim 0.5 \mu\text{m}$ and length of $\sim 2 \mu\text{m}$), which are typical morphologies of *E. coli*. Upon COE incorporation into the cellular membrane of *E. coli*, enhanced charge transfer will occur *via* one or both of the aforementioned hypotheses. Either proposed mechanism can

be the major route for enhanced charge facilitation, however, this specific investigation does not fall within the scope of this study, and is independent of the conclusions in this work.

The combined effects of COE-incorporated *E. coli* and modified photo-anodes were investigated in the SMC hybrid system. In order to gain deeper insight, three different types of photo-anodes (Au-TiO₂ hollow spheres, TiO₂ hollow spheres and P25 standard) were fabricated as PEC cells. MFCs employing chemically modified *E. coli* were interfaced to the different PEC cells in series by connecting the MFC anode electrode to the Pt cathode in the PEC cell and subsequently, the MFC cathode electrode to the photo-anode in the PEC cell. Since the MFCs will only reach its maximum power density after 36 h (Figure 5-4a), all electrical measurements performed on the SMC hybrid system commenced after 36 h from the point the MFC was inoculated with *E. coli*. LSV data were collected from the SMC hybrid systems modified with different COEs and photo-anodes in the dark and under 1 sun illumination (Figure 5-5a). It is interesting to note that the LSV for the SMC hybrid system in dark condition (black trace, Figure 5-5a) generated a photocurrent of $\sim 0.08 \text{ mA/cm}^2$ at zero bias (0 V vs Pt).

Figure 5-5: (a) Linear sweep voltammograms and (b) Amperometric current-time curves of hybrid SMC system employing different photo-anodes and *E. coli* chemically modified with DSTN+ and DSSN+. Electrochemical measurements were performed at zero bias under one-sun illumination (100 mW/cm²), and Na₂SO₄ solution (0.5 M, pH 7.0) was used as an electrolyte.

This value is substantially larger than that for individual PEC cells (black trace, Figure 5-3a) at the same potential. This enhancement is attributed to the liberated electrons originating from the MFC in the hybrid system. *E. coli* oxidizes organic matter in the anode media and releases electrons which will flow through the external circuit to the Pt wire of the PEC cell, hence producing current in the process. This demonstration validates the hypothesis that integrating a MFC to a PEC cell can enhance the performance of the resultant hybrid system, which shows promise in liberating H₂ gas at zero bias (0 V vs. Pt). The P25 standard photo-anode used in the SMC hybrid system without COE modification exhibited a photocurrent of ~0.12 mA/cm² at zero bias (0 V vs. Pt) (Figure 5-5a). This enhancement is ~30× larger than the photocurrent obtained for the stand-alone PEC cell employing the same photo-anode (~0.005

mA/cm^2 , red trace in Figure 5-3a) at the same potential. This further confirms the validity of the adopted SMC hybrid platform. It is noteworthy to mention that the photocurrent of the SMC hybrid system employing P25 standard photo-anode increases from $\sim 0.12 \text{ mA}/\text{cm}^2$ to $\sim 0.16 \text{ mA}/\text{cm}^2$ and $0.18 \text{ mA}/\text{cm}^2$ after changing the photo-anode to TiO_2 hollow spheres and Au- TiO_2 hollow spheres respectively. This observed trend in increased photocurrent is in line with changes in the hollow spheres architecture as well as the reduced recombination mechanism afforded by employing AuNPs, as reported in literature. [181, 197]

Figure 5-6: (a) Linear sweep voltammograms and (b) Amperometric current-time curves of hybrid SMC system employing different photo-anodes and *E. coli* chemically modified with DSTN+ and DSSN+. Electrochemical measurements were performed at zero bias under one-sun illumination ($100 \text{ mW}/\text{cm}^2$), and Na_2SO_4 solution (0.5 M, pH 7.0) was used as an electrolyte.

In comparison to the SMC hybrid system employing unmodified *E. coli*, higher photocurrents were observed across all three photo-anodes in systems employing chemically modified *E. coli* at zero bias (Figure 5-5a and 5-6a). This illustrates the effect of such COEs in significantly enhancing the photocurrent generation in the modified hybrid systems through improved performance in the

modified MFCs. The hybrid system employing Au-TiO₂ hollow spheres in the PEC cell and DSSN+ in the MFC generated the highest photocurrent (~ 0.35 mA/cm²) through an additive effect at zero bias (0 V vs. Pt). This enhancement is $\sim 9\times$ larger than the photocurrent obtained for the stand-alone PEC cell employing only Au-TiO₂ hollow spheres (~ 0.04 mA/cm², orange trace in Figure 5-3a) at the same potential. It is worth mentioning that a lower photocurrent (~ 0.23 mA/cm²) was observed for the SMC hybrid system employing Au-TiO₂ hollow spheres/DSTN+ relative to Au-TiO₂ hollow spheres/DSSN+ (~ 0.35 mA/cm²). The reason for the inferior performance of DSTN+ relative to DSSN+ is unknown at this point and is subject to future investigations. However, it should be pointed out that COE modification of *E. coli* resulted in enhanced performances in the hybrid systems. Amperometric on-off current-time curves corroborate these observations (Figure 5-5b and 5-6b). These data further confirm earlier observations that COE-modified *E. coli* MFCs produce higher power density, especially so in the DSSN+ modified bacterial system, and Au-TiO₂ hollow spheres absorb the most photons as compared to systems using TiO₂ hollow spheres and P25 standard photo-anode. In addition, the stability of the SMC hybrid system employing Au-TiO₂ hollow spheres and DSSN+ was investigated by measuring the photocurrent of the system over time under 1 sun illumination (100 mW/cm²). It was found that the hybrid system demonstrated reproducible photocurrent values without any significant drop within 4000 s (Figure 5-7). This result clearly shows that the adopted system and various modifications are stable and efficient for continuous operation without any zero bias (0 V vs. Pt).

Figure 5-7: Stability study of the SMC hybrid system employing Au-TiO₂ hollow spheres and DSSN+ was performed at zero bias under one-sun illumination (100 mW/cm²). Na₂SO₄ solution (0.5 M, pH 7.0) was used as an electrolyte.

H₂ concentration was quantified in the modified SMC hybrid system after 36 h to elucidate the effects of the modifications on H₂ evolution (Figure 5-8). The H₂ evolution rate of the SMC hybrid system employing Au-TiO₂ hollow spheres photo-anode and DSSN+-incorporated *E. coli* was the highest (~3.4 μmol/h) at zero bias. Consequently, the system employing only a P25 standard electrode (without any modification) exhibited a H₂ evolution rate of ~1.0 μmol/h at the same potential. This result strongly suggests that the amount of H₂ produced is highly dependent on the photocurrent generated by the SMC hybrid system.

Figure 5-8: *H₂ evolution profile of the various hybrid SMC systems after 36 h with chemically modified photo-anodes and COE-incorporated *E. coli*. H₂ measurements were carried at zero bias under one-sun illumination (100 mW/cm²), with the Na₂SO₄ solution (0.5 M, pH 7.0) acting as an electrolyte.*

In addition, the solar-to-hydrogen efficiencies (STH) of the SMC hybrid systems employing Au-TiO₂ hollow spheres photo-anode/DSSN+-incorporated *E. coli* and P25 standard electrode were calculated using the following equation, where V is the potential difference between the photoanode and Pt cathode, j (mA/cm²) is the photocurrent density at the specified voltage, P_{sun} is the irradiance intensity at 100 mW/cm² (AM 1.5 sunlight). [198]

$$\text{STH} = \frac{j \times (1.23 - V)}{P_{\text{sun}}} \quad [5]$$

The P25 standard electrode in the hybrid system produced an efficiency of 0.19% at zero bias (0 V vs. Pt), while the SMC hybrid system employing Au-TiO₂ hollow spheres photo-anode/DSSN+-incorporated *E. coli* achieved an improved efficiency of 0.44% at the same potential. Faradaic efficiencies for the hybrid systems (Au-TiO₂ hollow spheres photo-anode/DSSN+-incorporated *E. coli* and P25 standard electrode) producing H₂ gas were also calculated to be 78.9 and 75.4% respectively. This observation suggests that the amount of H₂ evolved was less than expected and can be attributed to the charge recombination occurring at the Au-TiO₂ hollow spheres photo-anode. When the electrode was illuminated, energetic plasmonic electrons from AuNPs will be injected into the conduction band of TiO₂, while energetic holes will be transferred to the AuNPs, forming a separation of charges at the Au-TiO₂ interface. However, due to the close proximity of the charges at the interface, holes from the AuNPs may recombine quickly with the electrons in the conduction band of TiO₂. This charge recombination process will lead to less H₂ generated, resulting in a lower faradic efficiency observed for the Au-TiO₂ hollow spheres photo-anode/DSSN+-incorporated *E. coli* hybrid system. [199]

The working mechanism in the modified SMC hybrid system is proposed (Figure 5-9). Upon illumination by a light source, electron-hole pairs are generated in the TiO₂ photo-anode at the PEC cell [200, 201]. The introduction of the hollow sphere morphology allows for a higher probability of photon absorption, which directly increases the number of photo-generated electrons. The presence of metallic AuNPs facilitates charge separation and movement by minimizing back flow of the photo-generated electrons (Figure 5-9a).

Figure 5-9: Working mechanisms in SMC hybrid system with chemically modified photo-anode and *E. coli*. (a) Schematic representation of charge separation and movement in Au-TiO₂ hollow sphere photo-anode. (b) Mechanistic diagram of the PEC-MFC hybrid system. (c) Schematic representation of DSSN⁺ and DSTN⁺ incorporation in lipid membranes of *E. coli*.

By employing AuNPs, the visible light photoabsorption capability is also accentuated at ~580 nm. Green dots represent photo-generated electrons liberated during PEC water splitting at the Au-TiO₂ hollow sphere photo-anode. These electrons then move through an external circuit to the MFC cathode, where they reduce the dissolved oxygen to water at the aerobic MFC cathode (Figure 5-9b). In the MFC anode chamber, exogenously added COEs (DSSN+ and DSTN+) interact extensively with the cellular membrane of *E. coli*. This is attributed to their amphiphilic nature which is realized by the hydrophobic portion of the delocalized π -conjugated aromatic backbone and long hydrophilic side chains[160]. In addition, the pendant ionic end groups aid in solubility in aqueous media. The COEs intercalate and self-assemble in the cellular membrane of *E. coli* and facilitate enhanced extracellular charge transfer (Figure 5-9c) *via* either aforementioned mechanism. The blue dots represent electrons liberated by *E. coli* during metabolism of the organic source and interaction with COEs. These electrons move towards the platinum counter electrode in the PEC cell to reduce protons (generated from PEC water splitting at the photo-anode) to form H₂ gas. Based on collective data, successful incorporation of solar energy with oxidative breakdown of organic substrates by microbial catalytic mechanisms was demonstrated to achieve PEC water splitting at zero bias.

5.3 Summary

In summary, by interfacing two seemingly independent platforms, the combined SMC hybrid system demonstrated significant improvement in photocurrent and H₂ generation relative to the independent PEC cell. The data presented herein

points towards the novel application of COE-modified biofilms, with DSSN⁺ and DSTN⁺, and a unique photo-anode composition/morphology in Au-TiO₂ for enhanced microbial electrohydrogenesis in a modified SMC hybrid system. The successful demonstration using these dual strategies provides exciting insights and paves the way forward for new technologies towards a sustainable hydrogen economy.

6 Surface and site-dependent visible-light photocatalytic H₂ evolution of octahedral NaInS₂ nanocrystals

6.1 Introduction

Chapter 6 investigates how the catalytic properties of a photocatalyst can be enhanced by morphological control, and further demonstrates that maximizing the exposure of reactive facets exposed is highly desirable in improving the overall performance of a photocatalyst. A one-pot solvothermal approach was used to synthesize NaInS₂ nanostructures with different morphologies, including octahedral nanocrystals (NCs), nanosheets and microspheres, simply by adjusting the conditions of the solvothermal reaction. Using the three as-prepared NaInS₂ nanomaterials as photocatalyst, the effect of morphologies on the performance for H₂ evolution was investigated by performing Car-Parrinello molecular dynamics (CPMD) simulations on the obtained NaInS₂ photocatalysts. *Ab initio* molecular simulations and electrostatic potential mapping were carried out on the different NaInS₂ nanostructures to further validate the principles behind the enhanced H₂ photocatalytic activity.

6.2 Computational methods

To investigate the interaction of water with the NaInS_2 crystal facets, *ab initio* molecular dynamics simulations of the NaInS_2 crystal in aqueous environments were performed, implementing Car Parrinello molecular dynamics [202] in the CPMD package [31]. NaInS_2 {012} and NaInS_2 {001} facets were modeled as periodic slabs, with water above the surfaces. The CPMD simulations with plane-wave pseudopotential implementation of Density Functional Theory (DFT) [203, 204] were performed using the Perdew-Burke-Ernzerhof (PBE) [205] exchange correlation functional and norm conserving Troullier Martins [206] pseudopotential with a plane wave expansion cut off of 80 Rydberg (Ryd.). All the atoms of the crystal were kept frozen during the simulations and all water molecules were completely free to move. The temperature of the simulation system was maintained constant at 300 K with the Nose-Hoover [207, 208] chain thermostat. The volumetric density maps of water molecules, averaged over the trajectory length of ~ 4 ps was calculated and visualized using the Visual Molecular Dynamics package. [209]

To further quantify the interaction of water molecules with various facets of the NaInS_2 crystal, calculations were performed using the *ab-initio* total-energy and molecular-dynamics program VASP (Vienna *ab-initio* simulation program) developed at the Fakultät für Physik of the Universität Wien. [210] The simulations were performed under the generalized gradient approximation within DFT using the PBE exchange correlation functional and the projector

augmented wave [211] (PAW) method for treatment of the inner core, with a plane wave cutoff energy of 400 eV. All the surface models of the crystal facets were generated from the optimized bulk crystal with lattice constant $a=3.87$, $b=3.87$, $c=20.14$ (all in Å) which is in good agreement with reported values. The interaction energies of water molecules with the surface at various sites on the NaInS_2 , $\{012\}$ and $\{001\}$ facets were calculated. Electrostatic potential maps of the different facets of NaInS_2 crystals were also generated using electrostatic potential calculations in VASP.

6.3 Results and discussion

The octahedral NaInS_2 NCs were obtained through a solvothermal reaction in absolute methanol solution using an appropriate amount of InCl_3 and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, at 190°C for 16 hr. (see chapter 3.2.3) The as-prepared octahedral NCs were analyzed via field emission scanning electron microscope (FESEM) and X-Ray diffraction (XRD). The low-magnification FESEM image (Figure 6-1a) confirms that the NaInS_2 NCs are nearly 100 % octahedral shaped with well-defined edges and smooth surfaces. The magnified FESEM image (Figure 6-1a inset) reveals that the individual NCs have an average apex-to-apex length (L) of ~ 800 nm and an edge-to-edge width (W) of ~ 600 nm. Figure 6-1b displays the XRD spectrum of the octahedral NCs, which can be indexed to a pure hexagonal NaInS_2 phase with cell constants of $a = 0.3803$ nm and $c = 1.989$ nm (JCPDS No. 74-0135).

The structure of the as-prepared NaInS_2 octahedral NCs was further examined by transmission electron microscopy (TEM). Figure 6-1c shows a representative TEM image of the individual octahedral NCs in low magnification with an L/W ratio of about 1.3. The diamond-shaped outline and structural dimensions of the individual NCs were consistent with FESEM observations. The close-up high-resolution TEM (HRTEM) image (Figure 6-1d) of the same particle reveals a clean and perfectly crystalline surface with a lattice spacing of 0.38 nm, which corresponds to the (220)-plane distance of the NaInS_2 crystal. Figure 6-1e shows a TEM image of the octahedral particle and the inset is the corresponding selected area electron diffraction (SAED) pattern. The SAED pattern can be

indexed to the [100] zone axis of the NaInS₂ product, indicating a single crystalline structure.

Figure 6-1: Octahedral NaInS₂ NCs a) Typical SEM image, b) XRD pattern. c) Low-magnification image, d) High-resolution image, e,f) TEM image and Schematic model along [100] direction, g,h) TEM image and schematic model along [001] direction

The apex angles between the two side faces were measured to be 108.2° and 71.8° respectively, and this agrees well with the model of octahedral NaInS₂ projected along the [100] direction as shown in Figure 6-1f. To further confirm the identity of the octahedral NaInS₂ NCs, the same particle was rotated from the [100] to the [001] zone axis, as shown in Figure 6-1g. It can

be observed that the outline and structural angles of the octahedral particle still corresponded well with the octahedral NaInS_2 model projected along the $[001]$ direction (Figure 6-1h). On the basis of the similar structural features observed from the TEM images and structural modeling analysis, it was proposed that the as-prepared NaInS_2 octahedral NCs were enclosed with both two- $\{001\}$ and six- $\{012\}$ facets. The corresponding 3D model of an ideal octahedral NaInS_2 crystal (eight facets) is shown in Figure 6-2.

Figure 6-2: a) Schematic 3D illustration of octahedral NaInS_2 enclosed with eight high-energy facets, b) The corresponding 3D model of the ideal NaInS_2 nanoparticle

The formation of octahedral NaInS_2 NCs was investigated by removing the samples at different reaction times and further analyzing using FESEM and XRD. Figure 6-3 shows the FESEM images and XRD spectra of the NaInS_2 NCs sampled at 1, 6, 10 and 16 h respectively. No distinct XRD diffraction peaks and morphology were observed at $t = 1$ h, indicating that the NaInS_2 nuclei were still amorphous in nature and growth was still at its primitive stage. Small NaInS_2 octahedral NCs began budding out from the surface after 6 h,

signifying the start of the octahedron nanoparticle evolution (Figure 6-3b). At $t = 10$ h, octahedral NCs continued to bud out from the surface, while small octahedral NCs grew larger in size. This could explain the existence of both large and small NCs as shown in Figure 6-3c. By $t = 10$ h, XRD diffraction peaks (Figure 6-3d for 10 h) ascribed to NaInS_2 phase became more obvious, indicating that the NCs were more crystalline as it grew larger in size. Octahedral shaped NCs with well-defined edges became more evident when the reaction was prolonged to 16 h. At this stage, small particles ($<$ critical size) diminished for the growth of larger octahedral NCs through an Ostwald ripening process. (Figure 6-3d) [212, 213] No obvious structural changes were observed beyond 16 h and highly crystalline NaInS_2 octahedral NCs were obtained, as evidenced by the FESEM images and XRD profiles.

Figure 6-3: FESEM images of octahedral NaInS₂ at different reaction times; a) 1 h, b) 6 h, c) 10 h, d) 16 h; e) XRD patterns of octahedral NaInS₂ NCs at different reaction times

Based on the above XRD and FESEM analysis, it is proposed that the octahedral NaInS₂ NCs was achieved via an Ostwald ripening process and the main evolving steps are schematically illustrated in Figure 6-4. At first, tiny NaInS₂ nuclei would be generated in a supersaturated solution. When a sulphur precursor concentration of 0.8 mM was used, the overall reaction rate for crystal growth decreased. The slow nucleating NaInS₂ atoms provided sufficient time

for three-dimensional crystal growth, allowing tiny budding of octahedral NaInS_2 crystals to take shape. Due to the different solubility between relatively larger and smaller particles, the large octahedral NCs would eventually grow bigger in size at the expense of the smaller ones and ultimately mature into larger octahedral NCs via Ostwald ripening.

Figure 6-4: Schematic illustration for the formation of NaInS_2 octahedral NCs

The successful preparation of the octahedral NaInS_2 NCs provided a good opportunity to investigate the surface-dependent photocatalytic activity of NaInS_2 . For comparison NaInS_2 nanosheets and microspheres were also prepared. In this study, the photocatalytic performance of all NaInS_2 products was investigated by measuring the amount of H_2 evolved under visible light ($\lambda > 420 \text{ nm}$) and is shown in Figure 6-5. The octahedral NaInS_2 NCs demonstrated the highest photocatalytic evolution rate of $\sim 67 \mu\text{mol/g/hr}$, which was about 6.1 and 2.3 times higher than that, for microspheres ($11 \mu\text{mol/g/hr}$) and nanosheets ($29 \mu\text{mol/g/hr}$) respectively.

Figure 6-5: *H₂ evolution rate of the as-prepared products: NaInS₂ microspheres, nanosheets and octahedron NCs, performed in 0.1 M ascorbic acid solution (pH 4.0) under visible light ($\lambda > 420$ nm) irradiation.*

Brunauer-Emmett-Teller (BET) measurements indicated that the nanosheets exhibited the largest surface area of 51.23 m²/g, followed by 28.1 m²/g and 2.67 m²/g for the octahedral NaInS₂ and microspheres respectively. Microspheres exhibited the lowest performance probably due to two reasons: (1) Low surface area – providing few active sites for H⁺ ions to be reduced to H₂, (2) Higher recombination rate due to its polycrystalline structure – providing additional surface defects for charge carriers recombination. In general, photocatalytic performance was affected by surface area and a larger surface usually leads to better photocatalytic properties. However, in this case, although NaInS₂ octahedral NCs had a lower surface area than nanosheets, their photocatalytic activity still out-performed nanosheets. This further suggests that higher photocatalytic performance exhibited by the octahedral NCs in this case was not

due to surface area but more closely related to the surface exposed facets of the octahedral NCs and nanosheets.

The crystal structure of NaInS_2 is composed of alternating Na^+ (cation) and InS_2^- (anion) layers. These anion layers consist of edge-shared InS_6 octahedral with the Na^+ cation co-existing between the anion layers, stacked on top of one another (S-In-S Na S-In-S Na S-In-S) along the c axis to form a layered structure. [84, 214] Based on structural modeling analysis, the NaInS_2 NCs was enclosed with six $\{012\}$ facets and two $\{001\}$ facets. Further analysis of the octahedron model revealed obvious differences of the atomic arrangement between the $\{001\}$ and $\{012\}$ facets. The $\{012\}$ facet is terminated with Na and In atoms, where each surface In atom is coordinated to three sulphur atoms. (Figure 6-6a) However for the $\{001\}$ facet, its surface may be terminated with Na atoms or InS_2 blocks, as shown in Figure 6-6b and 6-6d. It was determined that the hexagonal shaped NaInS_2 nanosheets were bounded with $\{001\}$ facets only.

During photocatalytic reactions, electrons are transferred from the photocatalyst surface to the reactant species and thus such species must have intimate contact with the surface before photocatalytic reactions can occur. When a photocatalyst surface is exposed to reactant species (in this case water), water molecules close to the surface will be photo-reduced by high-energy electrons. [25, 215] In principle, the smaller the separation between the surface and water molecules, the easier will it be for the water molecules to be reduced into H_2 gas. [216] The interaction between the water molecules and the surface are closely related to its proximity, which may be determined by the coordination number of surface atoms as well as the unique atomic arrangement of the

different crystal facets. [216] Since the predominant surface in the octahedral NCs is the $\{012\}$ facet, Car-Parrinello molecular dynamics simulations were performed to investigate the interaction of water with this facet. The simulation performed at 300 K suggests that water molecules have great affinity with the surface, with a preference to interact with the exposed In atoms on the surface, compared to the Na atoms.

Figure 6-6: Representation of structure a) $\{012\}$ facet b) Na terminated $\{001\}$ facet as viewed from the side c) Na terminated $\{001\}$ facet, d) InS_2 terminated $\{001\}$ facet e) InS_2 terminated $\{001\}$ facet

The volumetric density map of water molecules (Figure 6-7a) further supports this. Here, the volumetric density of water, averaged over the trajectory length

of 4 ps is plotted as an isosurface. The isosurface suggests greater localization of water molecules along the rows of surface In atoms, while the localization near the surface Na atoms is comparatively less and further away. CPMD simulation of the NaInS_2 {001} facet terminated with Na atoms in an aqueous environment was also performed. The simulation suggests uniform distribution of water over the Na atoms, as can be seen from Figure 6-7b.

Figure 6-7: CPMD simulations of a) NaInS_2 {012} facet b) NaInS_2 {001}.

It is known that different surface atomic arrangements in facets can lead to differences in the surface charge and thereby the distribution of adsorbates at the interface. [217] To understand the possible origins of this distinction in interaction of water with the surface atoms on the different facets of NaInS_2 NCs, the electrostatic potential of the two facets was calculated. The topology of the electrostatic potential over the NaInS_2 {012} surface at an isovalue of 4 (positive potential), shown in Figure 6-8a, suggests the formation of a corrugated potential wall over the surface with a pattern of alternating ridges and furrows over the Na and InS_2 blocks, respectively. The dense arrangement

of water over the In rows, seen in Figure 6-7a, suggests that the water molecules are localised in the furrows over the InS₂ blocks and above the ridges on the Na atomic rows, as shown in Figure 6-8a. The term “wall” used here is indicative of the spatial region over the surface of the crystal, corresponding to the topology of the potential surface, giving an estimate of the distance of approach of the water molecules to the surface. This offers an explanation to the localisation pattern seen in Figure 6-7a. The existence of the furrows over the rows of In atoms could be explained based on its coordinate unsaturation as they are bonded to only three sulphur atoms compared to the In atoms in the bulk, which are six coordinated. However, the electrostatic potential of the {001} facet terminated with Na atoms shown in Figure 6-8b shows a uniformly flat potential wall with marginal depressions around the Na bridge sites. This possibly explains the uniform distribution of water over this surface as seen in Figure 6-7b. The potential wall over the InS₂ terminated {001} facet shown on Figure 6-8c is similar to that on the Na terminated surface, but at a much larger distance from the surface. Thus, the potential walls, as seen here, may limit the approach and interaction of water with specific sites on the surface, based on its topology.

Figure 6-8: The electrostatic potential wall over a) $\text{NaInS}_2 \{012\}$ facet b) $\text{NaInS}_2 \{001\}$ c) $\text{NaInS}_2 \{001\}$ facet

To extract quantitative information on the interaction of water molecules with NaInS_2 surfaces, we performed additional DFT calculations simulating the interaction of individual water molecule with the different crystal facets of NaInS_2 . The binding energy of water to the different surfaces of NaInS_2 crystals was calculated using equation 6 and is presented in Table 1.

$$E_{\text{binding}} = E_{(\text{surf} + \text{water})} - (E_{\text{surf}} + E_{\text{water}}). \quad [6]$$

It was observed that the $\text{NaInS}_2\{012\}$ facet which exposes only In and Na atoms at the surface in alternate rows, has the strongest interaction with water with binding energy of -1.28 eV on the In top site, -1.2 eV on the In bridge site and -0.83 eV on the Na bridge site (Table 1). This allows very close and intense spatial localisation near the surface, as seen in the CPMD simulation performed on this facet (Figure 6-7a). In contrast, the interaction of water with both, the Na terminated and InS_2 terminated, $\{001\}$ facet is much weaker as can be seen from the binding energy values of -0.76 eV and less on this surface (Table 1).

The $\{001\}$ facet, when terminated by InS_2 , exhibited much weaker interaction with water compared to the Na terminated $\{001\}$ facet. Thus, the octahedral crystal with six $\{012\}$ facets and two $\{001\}$ facets can be assumed to be much better in its interaction with water. This could possibly enhance the probability of water splitting due to preferential interaction with water and thereby the evolution of hydrogen upon photoexcitation. The nanosheet is predominantly exposed with the $\{001\}$ facet which exhibits much lower interaction with water molecules. This could be a possible explanation for the significantly higher hydrogen evolution rate observed on the octahedral crystals $\{012\}$ and $\{001\}$ facets compared to the nanosheets $\{001\}$ facet.

Table 1: Binding energy of water molecules at different sites on the NaInS₂ crystal facets.

Interaction site on the surface	Binding energy (ev)
NaInS ₂ {012}- In top site	-1.2838
NaInS ₂ {012}- In bridge site	-1.1977
NaInS ₂ {012}- Na bridge site	-0.8293
NaInS ₂ {012}- hollow site	-0.7665
Na terminated NaInS ₂ {001}- Na bridge site	-0.7293
Na terminated NaInS ₂ {001}- Na top site	-0.6609
Na terminated NaInS ₂ {001}- Na-hollow site (over In)	-0.6246
Na terminated NaInS ₂ {001}- Na hollow site (over S)	-0.5422
NaInS ₂ {012}- Na top site	-0.5422
InS ₂ terminated NaInS ₂ {001}- S bridge site	-0.3264
InS ₂ terminated NaInS ₂ {001}- S hollow site (over In)	-0.297
InS ₂ terminated NaInS ₂ {001}- S top site	-0.2857
InS ₂ terminated NaInS ₂ {001}- S hollow site (over S)	-0.2251

6.4 Summary

In summary, single crystalline octahedral NaInS₂ nanocrystals were successfully synthesized for the first time via a simple, one-pot solvothermal strategy. It was found that sulphur content and the addition of structure directing surfactants could affect the solvothermal crystal growth process, resulting in different NaInS₂ NCs morphologies. Octahedral NaInS₂ photocatalyst exhibited excellent visible-light photocatalytic performance and its H₂ evolution rate was about ~ 2.3 times higher than that of nanosheets. This enhancement is due to the presence of {012} facets on the surface of octahedral NCs. CMPD simulations were performed on both {012} and {001} facets, and these results demonstrate that water molecules have greater affinity on {012} than {001} facets. The binding energy of water molecules to the different surface sites, obtained from DFT calculations, confirming that the surface atomic arrangement of a {012}

facet will interact strongly with water molecules. This promotes the reduction of H^+ to H_2 , and will increase the reactivity of octahedral $NaInS_2$ NCs for enhanced H_2 evolution. The successful development of octahedral $NaInS_2$ NCs will open a new dimension for designing other interesting sulphide-based NCs with high percentage of reactive facets for photocatalysis and other applications.

7 Synthesis of highly reactive quaternary sulphide-based octahedral nanoparticles via a cation exchange template strategy

7.1 Introduction

Chapter 7 reports the formation of a quaternary sulphide ($\text{Ca-ZnIn}_2\text{S}_4$) based material synthesized from a ternary compound (NaInS_2) via a cation-exchange template strategy. Because the morphology and the crystallinity of the NCs were well preserved during the cation-exchange reaction, these obtained quaternary $\text{Ca-ZnIn}_2\text{S}_4$ NCs possessed new properties, while inheriting properties from the parent ternary NaInS_2 structure. Our results have indicated that the quaternary $\text{Ca-ZnIn}_2\text{S}_4$ NCs not only exhibited higher activity than ternary NaInS_2 microspheres, but also were very stable under photocatalytic conditions. The enhanced performance can be attributed to the incorporation of the Ca^{2+} and Zn^{2+} cations in the NaInS_2 structure, which results in a significant improvement to its light absorption, charge separation and stability of the material. The cation exchange template approach can be used as a general strategy to fabricate other quaternary-based nanomaterials with unique morphologies and enhanced functions.

7.2 Results and discussion

The NaInS₂ nanocrystals (NCs) were prepared via a solvothermal route at 190 °C and 16 h, by adding appropriate amounts of InCl₃ and Na₂S·9H₂O. (see chapter 3.2.3) The as-prepared products were first analyzed using X-Ray Diffraction (XRD) and field emission scanning electron microscopy (FESEM). Figure 7-1 show a typical XRD pattern of the as-prepared NCs, which can be indexed to a hexagonal NaInS₂ phase (JCPDS No. 74-0135), indicating the products obtained were of pure NaInS₂. FESEM images (Figure 7-2a and 7-2b) revealed that the NaInS₂ products were octahedral-shaped and bounded with eight smooth surfaces. From the magnified FESEM image of Figure 7-2b, it can be observed that the shape of the octahedral NCs were well defined with an average edge-to-edge length of ~800 nm. To further examine the structural information of the octahedral NCs, transmission electron microscopy (TEM) was performed. Figure 7-2c displays a high-resolution TEM (HRTEM) image of the clean NaInS₂ nanocrystal surface with a lattice spacing of 0.38 nm. This lattice spacing corresponds to the (220)-plane distance of NaInS₂ crystal, which is consistent with earlier XRD observations as shown in Figure 7-1. The selected area electron diffraction (SAED) pattern (Figure 7-2d) can be indexed to the [100] zone axis of hexagonal NaInS₂, confirming the obtained octahedral NaInS₂ NCs is a single crystalline structure. This analysis indicates the successful preparation of uniform single crystalline NaInS₂ octahedral NCs via a solvothermal method.

Figure 7-1: XRD pattern for the NaInS₂ octahedral NCs

Figure 7-2: Characterization of NaInS₂ octahedral NCs; a,b) FESEM images, c) HRTEM image, d) SAED pattern

It is interesting to highlight that the as-prepared NaInS₂ NCs (ternary sulphide) can be further transformed into a quaternary sulphide NCs via a simple cation-exchange approach. [149, 153, 218] The formation of quaternary sulphide NCs can generally be divided into two stages as illustrated in Figure 7-3. Stage I involved the decomposition of NaS₂ and InCl₃ at high temperatures and metal ion species (Na⁺, In³⁺ and S²⁻) from these precursors, which will react with each other to form NaInS₂ nanoparticles. [219] These nanoparticles grew larger in size under solvothermal conditions and slowly evolved into a NaInS₂ octahedral nanocrystal, through an Ostwald ripening process as shown in Figure 7-3. These as-prepared NaInS₂ octahedral NCs were further reacted with other metal ions

(eg. R or M= Mg^{2+} , Ca^{2+} , Cu^{2+} , Zn^{2+}), leading to the formation of quaternary sulphide ($\text{R-M}_x\text{In}_y\text{S}_z$) NCs, via a cation exchange reaction. It should be noted that the feasibility of the cation-exchange process is dependent on the solubility of the involved materials and it is crucial for the final compound to be less soluble than the initial one for subsequent cation-exchange reaction to occur. [220] For example, $\text{Ca-ZnIn}_2\text{S}_4$ NCs can be obtained by further reacting the initial NaInS_2 octahedral NCs with Zn^{2+} and Ca^{2+} cations (Stage II). Since the solubility of Na^+ ions is higher as compared to Zn^{2+} and Ca^{2+} , Na^+ originated from its parent NaInS_2 structure will be replaced with Zn^{2+} and Ca^{2+} and quaternary $\text{Ca-ZnIn}_2\text{S}_4$ NCs will be obtained at the end of Stage II.

Figure 7-3: Schematic illustration of the formation process of $\text{Ca-ZnIn}_2\text{S}_4$ octahedral NCs.

FESEM and TEM images (Figure 7-4a & 7-4b) revealed that the obtained $\text{Ca-ZnIn}_2\text{S}_4$ NCs after reaction were octahedral-shaped with an edge length of ~ 800 nm. The clear fringes of the HRTEM image in Figure 7-4b (inset) illustrate that the $\text{Ca-ZnIn}_2\text{S}_4$ NCs is a single-crystalline structure and the lattice spacing of 0.38 nm corresponds to the (220) interplanar distance of ZnIn_2S_4 . To further examine the structure and elemental compositions of the final product, XRD

and energy dispersive X-ray spectroscopy (EDS) were performed on the Ca-ZnIn₂S₄ NCs. Figure 7-4c displays the XRD pattern for NaInS₂ (green) and Ca-ZnIn₂S₄ NCs (red). By comparing both XRD patterns, it is evident that major structural transformation of the NaInS₂ NCs had taken place during the cation-exchange reaction. The XRD pattern for Ca-ZnIn₂S₄ (red) can be indexed to the cubic phase of ZnIn₂S₄ (JCPDS-00-048-1778), implying the NaInS₂ have successfully transformed into Ca-ZnIn₂S₄ NCs and the cation-exchange reaction was complete. EDS analysis (Figure 7-4d) also further confirmed the elemental composition of the Ca-ZnIn₂S₄ products after the cation-exchange reaction. Although the above XRD and EDS results confirmed the successful transformation of NaInS₂ to Ca-ZnIn₂S₄, peaks pertaining to Ca were not observed probably due to the weak signal beyond the instrument detection limit. To verify Ca ions were present in the final product, HAAF-STEM elemental mapping was performed on the Ca-ZnIn₂S₄ NCs. EDS elemental maps (Figure 7-4e,f,g,h,i) clearly show that the final octahedral NCs were composed of Zn, In, S and Ca and these elements were uniformly distributed into these octahedral NCs.

Figure 7-4: Octahedral $\text{Ca-ZnIn}_2\text{S}_4$ a) FESEM image, b) TEM image, c) XRD pattern, d) EDX spectra e,f,g,h,i) Elemental mapping

The photocatalytic performance of NaInS_2 and $\text{Ca-ZnIn}_2\text{S}_4$ octahedral NCs were evaluated by measuring the amount of H_2 evolved. For comparison, NaInS_2 microspheres were prepared and also tested. The photocatalytic H_2 evolution

test was performed under visible light irradiation ($\lambda > 420$ nm) using L=ascorbic acid (0.5 M, pH = 4.0) as the sacrificial reagent. Figure 7-5a displays the visible light H_2 evolution rates of the as-prepared octahedral NCs ($NaInS_2$ and $Ca-ZnIn_2S_4$) and $NaInS_2$ microspheres. $Ca-ZnIn_2S_4$ octahedral NCs exhibited the highest H_2 evolution rate of $\sim 131 \mu\text{mol/g/hr}$, which is about ~ 12 , and ~ 1.9 times higher than that, for $NaInS_2$ microspheres ($\sim 13 \mu\text{mol/g/hr}$) and octahedral $NaInS_2$ ($\sim 62 \mu\text{mol/g/hr}$) respectively. It is not surprising that $NaInS_2$ microspheres exhibited the lowest photocatalytic activity possibly owing to its low surface area. In addition, its polycrystalline structure is likely to promote electron-hole recombination within the microspheres and thereby reduces its photocatalytic activity. A change in the morphology of the $NaInS_2$ products, from a microsphere ($\sim 13 \mu\text{mol/g/hr}$) to an octahedral NC ($\sim 62 \mu\text{mol/g/hr}$) had enhanced its photocatalytic performance further by ~ 4.7 times. This enhancement is largely attributed to the reactive facets exposed by the $NaInS_2$ octahedral NCs. In comparison to $NaInS_2$ microspheres without any specific facets and orientation, the $NaInS_2$ octahedral NCs were enclosed with six $\{012\}$ and two $\{001\}$ facets. It has been reported that these reactive surfaces possess unique atomic arrangements and can interact strongly with water molecules, accelerating the water reduction process for higher H_2 evolution. [221-226]

Figure 7-5: Comparison of performance evaluation and characterization of the as-prepared products a) H_2 evolution rates of the products, b) Nyquist plots, c) UV-vis spectra, d) Stability study. H_2 measurement and stability study was carried out in a 0.1 M ascorbic acid solution (pH 4.0) under visible light ($\lambda > 420$ nm) irradiation.

It is important to observe that although both $\text{Ca-ZnIn}_2\text{S}_4$ (quaternary) and NaInS_2 (ternary) are octahedral shaped, the H_2 evolution rate for $\text{Ca-ZnIn}_2\text{S}_4$ was still double that of NaInS_2 . Since the morphology of $\text{Ca-ZnIn}_2\text{S}_4$ was derived from NaInS_2 , it is likely that $\text{Ca-ZnIn}_2\text{S}_4$ would also inherit similar reactive facets from its parent octahedral NaInS_2 , suggesting that these surfaces may play a minor role for the higher photocatalytic activity observed for $\text{Ca-ZnIn}_2\text{S}_4$. This would mean that majority of the photocatalytic enhancement could be attributed to its improved charge transfer properties found in Ca-

ZnIn₂S₄ relative to NaInS₂. [188, 227] There is also a high possibility that the bulk enhancement could be due to the transformation of NaInS₂ to pristine ZnIn₂S₄ and not by Ca²⁺ doping, since the charge transfer properties of a material is strongly dependent on its electronic structure. In order to exclude this effect, octahedral ZnIn₂S₄ was prepared and used as a reference for comparison. The intrinsic electronic and charge-transfer properties of the three samples were investigated by using electrochemical impedance spectroscopy (EIS) measurement as shown in Figure 7-5b (Nyquist plot). It can be observed that the diameters of the semi-circle for both octahedral NaInS₂ and ZnIn₂S₄ samples are the same, implying that the charge interfacial transfer between them is quite similar. However, when 2 wt% of Ca was loaded into ZnIn₂S₄, the diameter of the semicircle become much smaller than that of ZnIn₂S₄. These results indicate that the incorporation of Ca²⁺ to ZnIn₂S₄ can significantly improve the charge interfacial transfer within the Ca-ZnIn₂S₄ system, decreasing the recombination rate between the charge carriers and the electronic structure of ZnIn₂S₄ itself does not contribute to the enhancement. [15, 228] Figure 7-5c shows the UV-vis diffuse reflectance spectra for the Ca-ZnIn₂S₄, ZnIn₂S₄ and NaInS₂ products. Although all of the octahedral products displayed light absorption in the visible range, the UV-vis spectra for Ca-ZnIn₂S₄ was shifted slightly to higher wavelengths. This proved that the light absorption for Ca-ZnIn₂S₄ was improved due to Ca²⁺ doping, resulting to higher H₂ production rate. Based on the similar trends of characterization results observed from the Nyquist plots and UV-vis spectra respectively, it could be inferred that the Ca²⁺ doping was responsible for the improved H₂ evolution rate observed for Ca-ZnIn₂S₄ as compared to that for ZnInS₂. The proposed mechanism of this H₂

enhancement is further illustrated in Figure 7-6. When the $\text{Ca-ZnIn}_2\text{S}_4$ photocatalyst is exposed to visible light illumination, electrons at the valance band (VB) are promoted to the conduction band (CB), leaving behind holes in the VB to be quenched by ascorbic acid (sacrificial reagent). The incorporation of Ca^{2+} ions into the ZnIn_2S_4 photocatalyst allows for a higher probability of photon absorption, which directly increases the number of photo-generated electrons in the CB. [88, 229] The presence of Ca^{2+} dopants can also reduce the recombination rate of the photo-excited electron and holes. [89] The enhanced charge separation as well as the high density of electrons generated on the surface of the photocatalyst will promote the reduction of H^+ to H_2 , and hence increases the H_2 evolution rate of $\text{Ca-ZnIn}_2\text{S}_4$.

Figure 7-6: Schematic illustration of the proposed mechanism for photocatalytic H_2 generation over $\text{Ca-ZnIn}_2\text{S}_4$.

The stability of the synthesized octahedral $\text{Ca-ZnIn}_2\text{S}_4$ and NaInS_2 photocatalysts was investigated by recycling the sample under visible light irradiation as shown in Figure 7-5d. Both octahedral samples were repeated for

three successive cycles of use, with the sample recovered by centrifugation and re-dispersed in fresh 0.1 M ascorbic acid after each cycle. No significant loss in H_2 evolution rate was observed for the Ca-ZnInS₄ NCs, while the octahedral NaInS₂ NCs experienced a sharp decrease in H_2 activity over time in between runs with no H_2 evolution rate observed at the end of the third cycle. This clearly indicated that the Ca-ZnInS₄ NCs are more stable than the NaInS₂ NCs under photocatalytic conditions, and the transformation of the NCs from a ternary (NaInS₂) to a quaternary (Ca-ZnInS₄) compound can help to improve the stability of the photocatalyst. Taken together, these results clearly show that the replacement of Na⁺ with Ca²⁺ and Zn²⁺ cations in the NaInS₂ structure can significantly enhance the stability and photocatalytic activity of the NCs, and the current cation-exchange synthesis strategy of novel quaternary nanomaterials may greatly improve the development of high performance photocatalyst.

Figure 7-7: a) Schematic diagram of the cation template strategy, $\text{Bi-ZnIn}_2\text{S}_4$ NCs b) FESEM image, c) Elemental mapping

From the above FESEM and TEM images, it can be observed that the size and structural features of $\text{Ca-ZnIn}_2\text{S}_4$ NCs (Figure 7-4a, 7-4b) were similar to the one obtained for NaInS_2 (Figure 7-2a, 7-2c). These observations confirmed that both morphology and single crystalline structure of the final products were well preserved after the cation-exchange reaction, and the morphology of the final product was dependent on the starting material (octahedral NaInS_2 NCs). This also meant that the octahedral NaInS_2 NCs could be used as a template to fabricate other types of quaternary sulphide octahedral-shaped products, via the cation-exchange strategy.

To prove that the cation-exchange template strategy does not only restrict the synthesis of octahedral Ca-ZnIn₂S₄ NCs, other quaternary sulfide octahedral-shape products such as Bi-ZnIn₂S₄ NCs were fabricated. Figure 7-7a illustrates the formation Bi-ZnIn₂S₄ NCs via the cation-exchange strategy, which follows a similar approach shown previously in Figure 7-3. The only difference was that BiCl₃ precursor was added together to the ZnCl₂ and octahedral NaInS₂ NCs to form a solid solution and subsequently transferred into a Teflon-lined reactor for further reaction. With the solubility of Na⁺ is higher than Bi³⁺ and Zn²⁺ metal ions, Na⁺ originated from the NaInS₂ template will be replaced with Bi³⁺ and Zn²⁺, resulting in the formation of Bi-ZnIn₂S₄ NCs. The XRD pattern of the Bi-ZnIn₂S₄ NCs obtained (Figure 7-8) show that the diffraction peaks can be indexed to cubic ZnIn₂S₄ phase (JCPDS No. 74-0135).

Figure 7-8: XRD pattern of 2% Bi-ZnIn₂S₄ octahedral NCs

From the FESEM image in Figure 7-7b, it can be clearly seen that the morphology of the Bi-ZnIn₂S₄ NCs was preserved and the EDS elemental maps (Figure 7-7c) also revealed that the chemical composition of the final product was uniformly distributed with Zn, In, S, Bi. From the above analysis, it can be confirmed that Bi³⁺ and Zn²⁺ were incorporated into the structure of Bi-ZnIn₂S₄ and these results support the flexibility of this strategy to fabricate other interesting quaternary sulfide based nanomaterials. The reason behind the successful formation of quaternary sulfide nanomaterials using this approach can be due to two aspects. 1) The cation-exchange-induced synthesis exploits the principle that the final compound should be less soluble than the initial one. Since the solubility of Na⁺ ions species from the initial compound (NaInS₂) is higher than other metal ion species (Mg²⁺, Ca²⁺, Bi³⁺, Zn²⁺), Na⁺ can be easily substituted with other metal ions during the ion-exchange reaction, resulting in the formation of quaternary sulphide-based product (eg. Ca-ZnIn₂S₄ and Bi-ZnIn₂S₄). 2) In addition, the morphology and the structural features of the final products were preserved during the cation-exchange process. As such, other types of interesting shaped quaternary NCs can be synthesized easily (not limited to octahedral-shaped NCs), since the morphology of the final product is derived from its parent structure.

7.3 Summary

In summary, single crystalline octahedral Ca-ZnIn₂S₄ NCs were successfully fabricated via a facile cation-exchange template approach. The obtained octahedral Ca-ZnIn₂S₄ NCs demonstrated high photocatalytic performance with good stability and its H₂ evolution rate is about ~12 times higher than that for

NaInS₂ microspheres. Our results demonstrated that enhanced H₂ photocatalytic activity by elemental Ca²⁺-doping could be attributed to the improved visible light absorption and reduced charge recombination of the photocatalyst. More importantly, with the morphology of final product well preserved during cation-exchange reaction, this strategy can be employed to design and fabricate other interesting well-defined reactive quaternary sulphide alloys for enhanced performance in photocatalysis, gas sensors and other optoelectronic devices.

8 General conclusion and recommendation for future directions

8.1 General conclusion

In this dissertation, semiconducting materials were rationally designed, synthesized and employed as a photocatalyst for H_2 generation. The catalytic activity of these photocatalysts was enhanced through the incorporation of noble metals, morphological control and the development of novel quaternary-based nanoparticles. These photocatalysts were further prepared into efficient photoanodes to produce H_2 by integrating a PEC and MFC together to form a SMC hybrid system. The working mechanism of the SMC hybrid system, as well as the principles of photocatalysis and strategies involved in the development of highly active photocatalysts were thoroughly reviewed and discussed.

Some specific conclusions derived from this dissertation are:

- a) Incorporation of Au NPs into TiO_2 provided performance enhancement for the photocatalyst for H_2 generation. The plasmonic Au NPs on the surface of semiconductors served as a visible light sensitizer and an electron trapper to improve its charge separation and visible light absorption.
- b) By encapsulating the Au NPs into the cavity of the core-shell TiO_2 hollow sphere, the performance of the photocatalyst was further enhanced. The multiple light reflection effect within the hollow cavity increased the degree of light absorption by the encapsulated Au NPs

through multiple light scattering and induced a stronger localized SPR effect for higher H₂ generation.

- c) H₂ enhancement was achieved via a SMC hybrid device, by connecting the MFC and PEC cells together in series. The integration of these two independent devices enabled additional bioelectrons originating from the MFC hybrid device to flow through the external circuit to the PEC cell to produce more electrons for enhanced H₂ generation.
- d) The overall performance of the SMC hybrid device was enhanced by the addition of conjugated oligoelectrolytes (COEs) to the bio-anode of the MFC. The SMC hybrid system employing Au-TiO₂ hollow spheres photo-anode/COE-modified *E. coli* produced higher current output compared to those with unmodified *E. coli*. The enhancement was attributed to the amphiphilic nature of COEs, which enabled them to interact extensively with the cellular membrane of *E. coli* to facilitate enhanced extracellular electron transfer.
- e) The photocatalyst performance was enhanced through morphological control because the surface atomic arrangement and configuration, which determines the catalytic activity of a given surface, was closely related to the enclosed facets derived from a particular morphology. Octahedral-shaped NaInS₂ NCs exhibited higher H₂ catalytic activity than NaInS₂ nanosheets. The good H₂ performance was attributed to the presence of highly active facets enclosed on the octahedral NCs.
- f) Car-Parrinello molecular dynamics simulations have shown that the surface of the octahedral NaInS₂ NCs were rich in under-coordinated In atoms, which provided more active sites with stronger interaction with

the water molecules. The intimate contact between the surface and water molecules promotes the reduction H^+ to H , accelerating the H_2 evolution rate in water splitting.

- g) A quaternary sulphide based nanocrystal ($Ca-ZnIn_2S_4$) was successfully prepared by replacing the Na^+ from the structure of $NaInS_2$ with Ca^{2+} and Zn^{2+} ions via a cation-exchange template approach. Our results have shown that the incorporation of Ca^{2+} and Zn^{2+} was behind the excellent H_2 performance and stability, which can be attributed to the improved light absorption and charge separation of the $Ca-ZnIn_2S_4$ photocatalyst.
- h) The morphology of the NCs was well preserved during the cation-exchange reaction, which enables researchers to exploit this strategy in producing other novel quaternary-based photocatalysts with enhanced activity and stability.

8.2 Recommendations for future directions

As described in Chapter 5, the integration of two seemingly independent platforms (PEC and MFC) into the SMC hybrid device has exhibited significant improvement in photocurrent and H_2 generation relative to the standalone PEC-cell. The integration of these two independent devices enabled additional bioelectrons originating from the MFC hybrid device to flow through the external circuit to the PEC cell to produce more electrons for enhanced H_2 generation. It is also important to point out that the SMC hybrid device is self-sustainable in nature, because it utilizes both solar energy (from PECs) and the metabolism of microorganisms (in MFCs), to drive the water splitting reaction for H_2 generation. Besides being self-sustainable, this hybrid device also represents an environmental friendly approach for generating H_2 , by addressing the increasing demands for clean energy as well as the need for wastewater treatment.

The SMC hybrid device is recognized as a future technology in achieving a H_2 economy, but widespread use of this hybrid technology has been limited by its relatively low power output, mainly caused by its poor extracellular electron-transfer (EET) of the bioanode and quantum efficiency of the PEC photoanode. In order to further enhance the performance of this hybrid technology, the following recommendations for future work are put forward:

- 1) It was reported in chapter 7 that the octahedral $Ca-ZnIn_2S_4$ NCs exhibited good H_2 photocatalytic performance with good stability. The excellent performance was attributed to the improved light absorption

and charge separation of the Ca-ZnIn₂S₄ photocatalyst due to the presence of Ca²⁺ and Zn²⁺ incorporated into the NaInS₂ nanostructure during the cation exchange reaction. To take advantage of these good photocatalytic properties, the Ca-doped ZnIn₂S₄ octahedral NCs developed can be further processed into a photoanode via the doctor blade technique to enhance the performance of the hybrid system.

- 2) One-dimensional (1D) nanomaterials can also be employed for the fabrication of the PEC photoanode, to further enhance the performance of hybrid systems. Examples of such nanomaterials include nanorods, nanotubes and nanowires. Studies have proved that these 1D-nanomaterials have shorter diffusion lengths and will induce a lower charge carrier recombination compared to other conventional nanomaterials. When these photoanodes prepared from 1D nanomaterials are further employed in the PEC cell of the hybrid system, high photocurrent output will be produced for enhanced H₂ generation.
- 3) Other than 1D nanomaterials, photoanodes prepared from multi faceted nanoparticles may also be a promising approach in improving the performance of a hybrid system. It was reported in chapter 6 that a multi faceted NaInS₂ nanoparticle, in a shape of an octahedron, exhibited higher H₂ evolution than nanosheets due to the strong binding energies of water molecules on the {012} facets. This clearly indicates that reactivity of a photocatalyst is strongly dependent on the surface morphology of the nanoparticle. When photoanodes were prepared from

these highly reactive octahedral NaInS_2 photocatalysts, it is likely that the photoanode will also possess good reactivity, which will be effective in enhancing the performance of the hybrid system.

- 4) Besides modifying the photoanode of the PEC cell, the overall performance of the hybrid system can also be enhanced by increasing the surface area and conductivity of the MFC anode. Anodes with high specific surface area can increase the performance of hybrid systems because large amounts of bacterial cells can adhere onto these surfaces and oxidize organic matter to release more bio-electrons for higher current output. Besides high surface, which results in higher bacterial loading, an anode with high conductivity can also significantly improve the direct extracellular electron transfer (EET) between the bacteria and electrode for performance enhancement. An example of an anode with high surface area and conductivity is a CNT/GO composite. It is expected that the employment of CNT/GO composites as an anode in the MFC of the hybrid system can help to further improve the performance of this hybrid technology.

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