Nanomaterials for sustainable hydrogen production by (photo)electrolysis

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**NANOMATERIALS FOR SUSTAINABLE
HYDROGEN PRODUCTION BY
(PHOTO)ELECTROLYSIS**

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2017

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HYDROGEN PRODUCTION BY
(PHOTO)ELECTROLYSIS**

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A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of
Doctor of Philosophy

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Date

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Student Name

Abstract

Global energy and environmental crisis have received enormous research attention for a long time. Fossil fuels as the primary energy source, comprised 86% of global energy consumption in 2015. However, the consumption of this nonrenewable resources brings about not only the environmental problem such as global warming, but also the economic problem since fossil fuels' price increased rapidly due to the limited recoverable reserves. With the inexhaustible irradiation from the Sun, solar energy is agreed to be the most promising renewable energy resource. Inspired by Mother Nature, converting solar energy to chemical energy has been intensively studied. Systems including photocatalytic and photoelectrochemical water splitting have been developed to fulfill the ultimate goal of high efficient solar-to-hydrogen conversion. The overall objective of this interdisciplinary research program is to improving the overall solar-to-hydrogen efficiency by rational design of catalytic nanomaterials.

Firstly, a new kind of photosensitizer were studied for improved light harvesting. A series of MOFs based on MIL-125 have been demonstrated as promising photosensitizers for PEC water oxidation. When applied MOFs/TiO₂ heterostructure materials as the photoanodes for solar water oxidation, the photocurrent of TiO₂ could be improved by nearly 100% under visible light through sensitization with aminated Ti-based MOFs. Incident photon-to-current conversion efficiency matches well with the UV-vis absorption of modified TiO₂ photoanodes, which confirm the sensitization of MOF materials. Highly porous structure of MOFs enables further tuning of light harvesting efficiency. By coupling with plasmonic Au nanoparticles, the light absorption could be further improved due to the LSPR effect.

Secondly, a new noble-metal free HER catalyst were synthesized for improved reaction kinetics. A general one step method to prepare ultra-small transition-metal carbide nanoclusters encapsulated in N, S co-doped graphene were developed, and used for all pH hydrogen evolution reaction. The as-prepared MoC_{1-x}/C materials possess ultra-small particle size (2.8 nm) with narrow size distribution (1.8 to 3.2 nm), which provides lots of catalytically active sites. The intimate interaction between transition-metal carbide nanoclusters and N, S co-doped graphene modifies the binding strength of protons on transition-metal carbides. The porous graphene supports enable quick charge transport and fast reactant/product diffusion. All of which contribute simultaneously, giving rise to the excellent HER performance of the transition-metal carbide/graphene composite catalysts.

Finally, photoelectrochemical reforming of biomass-derived alcohol oxidation has been developed for decreased overall energy consumption in solar-to-hydrogen system. In this new system, pure hydrogen and value-added chemicals were simultaneously produced driven by solar energy at room temperature. The hydrogen quantum efficiencies reach 80% across the entire visible region of the solar spectrum, leading to an ultrahigh hydrogen production rate of 7.91 $\mu\text{mol min}^{-1} \text{cm}^{-2}$ illumination area of a single-junction GaAs solar cell under AM 1.5G illumination. Moreover, by properly choosing the anodic catalyst, alcohols can be selectively converted to useful liquid chemicals with nearly 100% selectivity.

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Abbreviations

Abbreviations of chemical names

BDC 1, 4-benzenedicarboxylate

CdS Cadmium sulfide

CdSe Cadmium selenide

DMF Dimethylformamide

GaAs Gallium arsenide

HAuCl₄ Chlorauric acid

H₃BO₃ Boric acid

H₂SO₄ Sulfuric acid

HCl Hydrochloric acid

MeOH Methanol

MOF Metal-organic frameworks

MoS₂ Molybdenum disulfide

NaOH Sodium hydroxide

Na₂HPO₄ Sodium phosphate dibasic

NaH₂PO₄ Sodium phosphate monobasic

NaH₂PO₂ Sodium hypophosphite

NiSO₄ Nickel(II) sulfate

NH₄Cl Ammonium chloride

PBS Phosphate-buffered saline

PdCl₂ Palladium(II) chloride

Abbreviations

Pt Platinum

TBOT Tetra-n-butyl orthotitanate

TiO₂ Titanium dioxide

Abbreviations of Physical terms

IPCE Incident photon-to-electron conversion efficiency

J Current density

n Number of electrons transferred

PV Photovoltaic

R Reflectance

V Voltage

Z Impedance

ΔG Free energy change

λ Wavelength

Abbreviations of commonly used terms

Ag/AgCl Silver chloride electrode

AM Air mass

CB Conduction band

CE Counter electrode

CV Cyclic voltammetry

EDS Energy dispersive X-ray spectroscopy

Abbreviations

EIS	Electrochemical impedance spectra
FESEM	Field emission scanning electron microscope
FTO	Fluorine-doped tin oxide
HRTEM	High resolution transmission electron microscopy
ICP-OES	Inductively coupled plasma optical emission spectrometry
LSV	Linear sweep voltametry
RHE	Reversible hydrogen electrode
PEC	Photoelectrochemical
QD	Quantum dot
SCE	Saturated calomel electrode
VB	Valence band
WE	Working electrode
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

Abbreviations

Chapter 1

Introduction

This chapter presents a brief introduction to the thesis. First, the background and hypotheses of this thesis are described. Based on the proposed hypotheses, the scope and objectives of this thesis are then introduced. By following the description of the dissertation overview for each chapter in the thesis, the findings and outcomes of this thesis are summarized.

1.1 Background and Hypothesis

Global energy and environmental crisis have received enormous research attention for a long time. Fossil fuels as the primary energy source, comprised 86% of global energy consumption in 2015 according to the BP Statistical Review of World Energy June 2016. However, the consumption of this nonrenewable resources brings about not only the environmental problem such as global warming, but also the economic problem since fossil fuels' price increased rapidly due to the limited recoverable reserves. New renewable and clean energy resources (such as wind, geothermal, water, and solar energy) as the alternative energy resources are highly desired, which now only makes up 2.8% (BP Statistical Review 2016) of the world's primary energy resources.

The Earth receives an energy influx of 4.3×10^{20} J from the Sun each hour, which is even comparable with the total energy consumption in one year on our planet.^[1] Thus, solar energy is considered as the most promising renewable energy resource. The next question is how to convert the solar energy into usable energy. Currently, there are mainly three routes to utilize the solar energy, which are converting the solar energy into thermal energy, electric energy, and chemical energy. In which, electric and chemical energy as storable energy have gained much attention.

Photosynthesis is a natural energy conversion strategy adopted by plants, algae and certain bacterial species. In which, solar energy is harvested by the organism, and then stored in the form of chemical energy after multi-step chemical reactions. Inspired by the Mother Nature, lots of effort have been made to accomplish artificial photosynthesis. Dated back to early 1970s, Honda and Fujishima found how solar energy can be converted to chemical energy artificially, when they accidentally discovered water splitting into hydrogen and oxygen by titanium dioxide powder irradiated by UV light.^[2] Hydrogen is then recognized as a promising clean energy carrier, since after its combustion, water is produced as the sole product, which avoid

the green-house gas emission in the case of carbon containing fossil fuels, thereby solve the environment problems caused by combustion of fossil fuels. Since then, solar driven water splitting has attracted overwhelming attention and been intensively studied.

Hydrogen economy, proposed by Bockris and Justi in 1970s, provides a sustainable way to solve the forthcoming energy crisis.^[3] The Annual world demand of hydrogen is increasing by 3.5% (Freedonia group, 2014), and approximately 500 billion cubic meters hydrogen are produced annually for now.^[4] However, more than 90% of hydrogen is still produced from fossil fuels, such as natural gas or coal through steam reforming,^[5] which unfortunately produces CO₂ as a byproduct and is obviously not clean and sustainable in long term. Water covers 71% of the Earth's surface, which makes it the most abundant natural resource. Developing high efficient water splitting system driven by renewable energy resource plays a key role in future hydrogen economy.

Water splitting driven by solar energy can be accomplished by several routes. Firstly, photocatalytic water splitting, where catalyst materials adsorb light irradiation and generate charge carriers, namely photo-induced electrons and holes. The charge carriers are then separated and diffused to the catalysts surface, where redox reaction takes place and produces hydrogen and oxygen separately. With additional electronic energy input, water splitting can be accomplished by photoelectrochemical route. In which, catalysts are loaded on conducting substrate and fabricated as photoanode or/and photocathode. Under light irradiation, the separation of photo-generated charge carriers would be facilitated, since electrons can be transferred to the counter electrode through the circuit with the help of bias. In all the solar driven water splitting system, catalyst design plays a critical role which decide the efficiency of water splitting.

With numerous research in the past decades, many kinds of catalysts have been discovered. Besides TiO_2 , semiconductors based on transition-metal cation with d^0 (W^{6+} , Nb^{5+} , Ta^{5+} and Zr^{4+}) or d^{10} (Sn^{4+} , In^{3+} , Sb^{5+} , Ge^{4+} , and Ga^{3+}) electronic configurations are able to be used in photocatalytic water splitting.^[6] Besides the development of inorganic semiconductors, materials such as polymer semiconductors were also found to be active for photocatalytic water splitting (e.g. Poly(para)phenylene,^[7] carbonnitride ($\text{g-C}_3\text{N}_4$)^[8]).

However, most of these semiconductors catalysts can only absorb UV light due to their wide band gaps. To harvest the visible lights which occupy most (40%) of the sunlight energy compared to UV light (3-5%), materials with proper band structure are in great needed. The photo-induced charge recombination is another problem. Due to high charge recombination rate, the utilized portion of incident irradiation is quite low, i.e. low quantum yield. It is important to develop catalyst that possess the capability to support rapid electron/hole transport to the surface. The intrinsic catalytic activity of catalyst is one of the most critical parameters that decide the solar-to-hydrogen efficiency.

Nanotechnology provides researcher with great opportunity to tune the structure and performance of catalytic materials. When size of materials decreased to nanoscale range, unexpected properties are presented. Owing to the rapid advancement of nanotechnology over the past three decades, nanostructured materials are now playing critical roles in the development of energy conversion devices. However, the current efficiency of the solar-to-hydrogen conversion is still far from satisfactory, there is urgent needed to develop a high efficiency catalyst with the help of nanotechnology. In this PhD program, our leading motivation is to enhance the efficiency of solar-to-hydrogen systems by optimizing the photo/electro-catalytic materials using nanotechnology. New catalytic materials and system with wide adsorption of solar irradiation spectra, fast charge separation and transfer, enhanced

catalytic activity will be developed. The formation mechanisms of the advantageous nanostructured materials will be revealed, and the underneath reaction kinetics within these systems will be explored and discussed in details.

1.2 Objectives and Scope

Based on the background and motivation described above, the objectives and scope of this thesis are listed below:

(a) For efficient visible light harvesting, metal-organic frameworks (MOFs) will be studied as a new kind of photosensitizer.

Despite the intensive efforts of research on traditional photosensitizer including dye molecules and quantum dots, visible light absorption in current solar driven water splitting system is still far from satisfactory. We intend to find alternative photosensitizer based on the newly found photoactive MOF materials. First, TiO_2 nanoarray will be synthesized on conducting substrate using a hydrothermal method. Then a series of semiconductor/MOFs heterostructures will be fabricated and used as photoanodes. The as-prepared materials will be characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), dark-field scanning TEM (DF-STEM) and UV-visible spectra (UV-Vis). Then the photoelectrochemical properties of these photoanodes will be tested under visible light irradiation. The study of MOF as photosensitizer provides opportunities to broaden the applications of MOFs, more importantly, provide a new kind of photosensitizer materials for visible light harvesting thereby enhance the efficiency of photoelectrochemical water splitting systems.

(b) For efficient electrocatalytic activity, a new strategy will be developed to synthesize noble-metal-free hydrogen evolution reaction (HER) catalyst.

The intrinsic catalytic activity is critical for the overall water splitting efficiency. Noble metal catalysts (e.g. Pt) show excellent activity towards HER, but their practical application is greatly restricted due to their scarceness. A new noble-metal-free catalyst based on transition metal carbide will be synthesized and studied as HER catalyst. The product will be characterized by XRD, TEM, HRTEM, DF-STEM, X-ray photoelectron spectroscopy (XPS), N₂-sorption isotherms and Raman spectroscopy. Then the electrochemical properties of these catalyst will be tested.

(c) Efficient solar-to-hydrogen system design based on biomass-derived alcohols.

The overall splitting of water is a strong uphill reaction, which has a standard reaction potential of 1.23 eV^[9], the energetic convenience of water splitting is severely limited by the oxidation half reaction. Considering the abundance of oxygen in the atmosphere, replacing oxygen evolution reaction with reactions consume less energy provide an effective way to enhance the overall solar-to-hydrogen efficiency. Alcohol electrooxidation catalyst will be loaded on conducting substrate and used as anode. Catalyst will be characterized by means mentioned before. The overall solar-to-hydrogen efficiency will be evaluated and compared to solar driven water splitting system.

1.3 Dissertation Overview

This thesis contains six chapters and organized as follows:

Chapter 1 describes a rationale analysis for the research. The background, motivation, objectives, and scope of the thesis are introduced.

Chapter 2 reviews the literature concerning the current research progress on the solar-to-hydrogen system (including photocatalytic, photoelectrochemical and electrochemical water splitting system). Introduce basic principles, techniques and fundamentals, then summarize up-to-date research progresses regarding catalysts development.

Chapter 3 elaborates the fabrication of semiconductor/MOFs heterostructures, evaluates the photoelectrochemical water splitting catalytic activity using the as-prepared materials as photoanode. Reveals the possible application of MOF materials as photosensitizers.

Chapter 4 introduces a novel strategy to synthesize noble-metal-free HER catalyst. Tests the performance of these catalysts in acidic, neutral and alkaline electrolytes respectively, reveals the outstanding activities of these catalysts in electrolytes with a wide pH range.

Chapter 5 presents the design of a new solar-to-hydrogen system with photoreforming of biomass-derived alcohols. Elaborates the fabrication of electrodes, and the assembling of device. Evaluates the solar to hydrogen efficiency under simulated AM1.5G irradiation and natural sunlight.

Chapter 6 summarizes the whole thesis, and elaborates the reconnaissance studies which could be conducted in the near future.

1.4 Findings and Outcomes

This research leads to several novel outcomes:

1. A series of Ti-based MOFs have been demonstrated as promising photosensitizers for PEC water splitting. First, a series of Ti-based MOFs based on MIL-125 were fabricated on TiO₂ nanowire array photoanodes. When applied these Ti-based MOFs/TiO₂ as the photoanodes for solar water oxidation, the photocurrent of TiO₂ nanowire photoelectrode could be improved by nearly 100% under visible light through sensitization with aminated Ti-based MOFs. By coupling with plasmonic Au nanoparticles, the visible light absorption efficiency could be further improved due to the localized surface plasmon resonance effect.

2. A general one step method has been developed to prepare transition-metal carbide nanoclusters encapsulated in graphene as noble-metal-free electrocatalysts for hydrogen evolution. High density MoC_{1-x} (2.8 nm) nanoclusters encapsulated in nanoporous N, S co-doped graphene matrix has been obtained. This catalysts showed outstanding catalytic activity in all pH electrolytes with great durability. The synthesis method can be extended to prepare WC_{1-x} (2.0 nm) nanoclusters encapsulated in nanoporous N, S co-doped graphene, which again showed great HER activity in all pH electrolytes.

3. A new strategy for simultaneous hydrogen and chemicals production driven by solar energy via photoelectrochemical reforming of biomass-derived alcohols has been developed. The hydrogen quantum efficiencies reach 80% across the entire visible region of the solar spectrum, leading to an ultrahigh hydrogen production rate of $7.91 \mu\text{mol min}^{-1} \text{cm}^{-2}$ illumination area of a single-junction GaAs solar cell under AM 1.5G illumination. Moreover, by properly choosing the anodic catalyst, the alcohols can be selectively converted to useful liquid chemicals with nearly 100% selectivity.

Chapter 2

Literature Review

This chapter reviews the current solar-to-hydrogen system including photocatalytic water splitting system and photoelectrochemical water splitting systems. The fundamentals of these systems are first introduced, and the research progress focused on the catalysts design and synthesis in each area are reviewed. In addition, electrochemical water splitting as an important part of solar-to-hydrogen conversion is also reviewed.

2.1 Overview of Solar-to-Hydrogen Systems

The Earth receives an energy influx of 4.3×10^{20} J from the Sun each hour, with the inexhaustible irradiation from the Sun, solar energy is considered to be the most promising renewable energy resource. Converting solar energy into storable energy sources such as electric energy and chemical energy have gained much attention. After the discovery of photolysis of water in 1970s by Honda and Fujishima, numerous researches has been conducted, numerous candidate materials have been reported, and great achievements have been achieved. In this chapter, we will first introduce the fundamentals of current solar driven water splitting systems and then review the catalysts research progress in each area.

2.2 Photocatalytic Water Splitting System

2.2.1 Fundamental of Photocatalytic Water Splitting

Reaction processes of photocatalytic redox reactions is shown in Figure 2.1. Under light irradiance, photons with energy larger than the bandgap of semiconductors would be adsorbed by the semiconductor, electrons at valence band (VB) will be excited to the conduction band (CB), while leave holes at the valence band (i); then the photo-generated charge carriers will diffuse to the catalyst surface separately or recombine and release heat or light (ii); separated electrons and holes meet with substrate molecules at the surface (may couple with co-catalysts), and redox reaction will take place there (iii).

Figure 2.1 Reaction illustration of photocatalytic water splitting on a semiconductor photocatalyst coupled with co-catalysts. Reprinted with permission of ref. ⁽¹⁰⁾ Copyright (2014) The Royal Society of Chemistry.

During the photocatalytic water splitting process, protons are reduced by photo-generated electrons, while water molecules are oxidized by photo-generated holes. Four electron-hole pairs need to be separated which will generate two hydrogen molecules and one oxygen molecule respectively. Overall splitting of water into hydrogen and oxygen need an input energy of 237.2 J/mol (Eq. 2-1), which corresponds to $\Delta E^\circ = 1.23$ V per electron transferred according to the Nernst equation. In order to drive photocatalytic water splitting, a semiconductor should possess a bandgap larger than 1.23 eV with its conduction band and valence band-edges straddle the redox potentials of hydrogen (H^+/H_2) and oxygen (O_2/H_2O).

Noticeably, the band structure of semiconductor is just the thermodynamic requirement for photocatalytic water splitting. Actually, an activation energy is needed due to the transportation of photo-generated electron/holes, electron/holes recombination, thermodynamic losses, and kinetic losses. Thus the ideal bandgap of a photocatalyst should be between 2.0 to 2.2 eV. ^[11]

Co-catalysts also play pivotal roles for improving the activity of photocatalytic water splitting. First, the photo-generated electrons and holes migrated to redox co-catalysts would facilitate the charge separation, suppress recombination of the charge carriers; secondly, lower activation energy of redox reaction on the co-catalysts would greatly enhance the solar-to-hydrogen efficiency; last but not least, transfer of photo-generated holes to the co-catalyst can suppress the corrosion of catalysts, thus improve the durability of catalysts.

2.2.2 Advancements in Photocatalytic Water Splitting

Numerous semiconductors have been developed as photocatalysts for water splitting in the past decades (Figure 2.2).^[9] Among the existing catalysts, some semiconductors are applicable only for half reaction either hydrogen evolution reaction (e.g. CdSe, Si) or oxygen evolution reaction (e.g. WO₃, Fe₂O₃) due to their improper band structure. Although a lot of semiconductors can be used for overall water splitting (e.g. TiO₂, ZrO₂), most of them can only absorb UV light ($\lambda < 400\text{nm}$) due to the large bandgaps (usually larger than 3.0 eV).

Figure 2.2 Semiconductor materials used in solar water splitting system. Reprinted with permission from ref. (9). Copyright (2009) The Royal Society of Chemistry.

Visible light occupies most (53%) of the sunlight energy while Ultra-Violet light takes only 4%. Assume a quantum efficiency of 100%, a maximum efficiency of solar energy conversion is only 2% for UV utilization theoretically, when a catalyst can absorb and utilize light with wavelength up to 800nm, the conversion efficiency can increase to 32%.^[12] In order to harvest the visible light, studies nowadays focus on the developing of new catalysts with narrower bandgap, as well as narrowing the band gap of existing semiconductors through different strategies.

Figure 2.3 UV/vis spectra and digital photographs of transition metal-doped TiO_2 . Reprinted with permission from (13). Copyright (2013) The American Chemical Society.

Doping is an effective strategy to narrowing the bandgap of semiconductors. Doping TiO_2 with transition metal (e.g. Rh, Cr, Mn) can effectively reduce the bandgap with controllable manner.^[13] By using titanium alkoxide as precursors and low temperature annealing process post-synthesis, Liu and coworkers have obtained carbonate doped TiO_2 porous particles.^[14] Density of states of doped TiO_2 showed 0.2 eV smaller bandgap compared to undoped TiO_2 . Narrowed bandgap extend the light absorption of the as-synthesized catalyst from the UV to the visible light region, corresponding to the brown color of catalysts.

Another effective way to optimize the band structure is to synthesize solid solution of two semiconductors with different bandgap. The bandgap of solid solution prepared with GaN (band gap 3.4 eV) and ZnO (band gap 3.2 eV) can be reduced to 2.58 eV,^[15] this solid solution showed stable overall water splitting under UV as

well as visible light irradiation. A series of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solutions with controllable band structure can be prepared by coprecipitation method. CdS has a bandgap of 2.4 eV, while ZnS has a wide bandgap of 3.9 eV, the bandgap of the solid solution can be tuned from 2.20 eV to 3.12 eV by varying the component concentration.^[16] Noticeably, only semiconductors with similar crystal structure can be used to prepare solid solution. Although this method can prepare semiconductors with desired bandgaps, the quantum efficiency is still quite low due to high defect density in the structure.

Photocatalysts with heterostructure composed of two or more semiconductors provide another effective strategy to harvest visible light. CdS ^[17, 18], CdSe ^[19], CoS ^[20], Cu_2S ^[21] with small bandgaps but only applicable for half reaction (hydrogen evolution reaction) can be used as sensitizer for wide bandgap semiconductor. In this heterostructured photocatalysts system, visible light can be absorbed by narrow bandgap semiconductor, then photo-generated electrons will diffuse to the adjacent wide bandgap semiconductors.

Besides traditional semiconductors, new materials such as graphitic carbon nitride ($\text{g-C}_3\text{N}_4$)^[22], metal-organic frameworks (MOFs)^[23] are emerging as promising photocatalysts. MOFs are a kind of microporous materials, the structures consist of metal ion or cluster (known as node) and rigid organic ligands (known as linkers) through coordination bond to form 3-D networks. Some MOFs (such as MOF-5) are recognized as semiconductors with bandgaps between 1.0-5.5 eV.^[24] Due to the versatility of MOFs, band gaps of these kinds of MOFs can be tunable by simple design of the structures, in order to harvest the sunlight, such as combination of different components, structure design of the metal clusters or chemical functionalization of the linkers.^[25-27]

Several strategies can be used to fabricate photoactive MOFs. First strategy is to integrate useful components (metal-oxo, ligands) into MOFs structures.

The traditional semiconductors such as Fe_2O_3 have limited photocatalytic activities because the high recombination rates of the photo-generated charge carriers,^[27] semiconductors with nanoscale structures can enhance the separation of charge carriers by reducing the distance to the active sites on the surface. While MOFs with metal-oxo clusters provide even smaller size of photo-responsive structures, limited recombination rate and higher photocatalytic activities are expected. Maarten Roelfaers^[28] tested the photocatalytic properties of several Fe-oxo clusters based MOFs. Compared to the commercial Fe_2O_3 nanopowder which has no photocatalytic activities, all MOFs with Fe-oxo clusters are observed with high photocatalytic activities under visible-light irradiation.

Another component (ligand) used in MOFs structures are also highly responsible for the visible light harvesting, the rigid molecule linkers not only provide the possibility of 3D net structures of MOFs, but also incorporate the visible-light harvesting properties within the MOFs, as the π -electrons of conjugated system are easy to be irradiated by light.^[29] Matthew J. Rosseinsky and co-workers developed a water-stable porphyrin-based MOF,^[30] they tested its photocatalytic hydrogen evolution rate under visible-light irradiation with EDTA as sacrificial reagent and Pt as co-catalyst, results showed a hydrogen evolution rate at 200 $\mu\text{mol}/(\text{gh})$ after an induction period of about 3h.

Doping MOFs with metal can incorporate new catalytic sites in the structures, providing another strategy in photocatalytic MOF design. Lin and his coworkers used a mix-and-match synthetic strategy to dope several kinds of metal ions within UiO-67.^[31] The parent ligand of UiO-67 is BPDC (para-biphenyldicarboxylic acid), they synthesis six different ligands by modifying BPDC with Ir, Re, and Ru ion

complexes, due to the same ligand length, these metal ions can be doped through incorporation of the modified ligands into UiO-67 structures. Photocatalytic activities are observed in the doped UiO-67, however they did not explain the detail process of charge transfer in these photoreactions. Later on, two kinds of the UiO-67 doped with Ir were used for hydrogen evolution with Pt as co-catalyst and TEA as sacrificial reagent.^[32] They further discussed the charge transfer process in these reactions, and claimed that the doped Ir moiety can be irradiated by visible light to a ¹Metal-to-Ligand Charge Transfer (¹MLCT) excited state, which transitions to a ³MLCT state through intersystem crossing, the long-lived ³MLCT state then returns to the ground state leading to phosphorescence emission. The life time of the ³MLCT state in MOFs last 51.8 ns and 110.3 ns compared to 11.1 ns and 89.0 ns in the ligands respectively, they believe the prolonged emission lifetimes of MOFs are due to the rigidity of the MOF frameworks. The hydrogen evolution amount from this doped MOF is about 100 nmol after 12 h reaction.

Ligand functionality is another efficient way to fabricate visible-light responsive MOFs. MIL-125 with a band gap about 3.6 eV is now a well-known photocatalytic MOF, which is constructed by Ti-oxo cluster and 1,4-benzenedicarboxylate (BDC) ligands. Hermenegildo Garcia and his coworkers observed the photoinduced charge transfer in the MIL-125.^[33] Christopher successfully controlled the band structures of MIL-125 through ligand functionalization.^[26] Yu and Masaya tested the photocatalytic properties of this MOF.^[34, 35] They fabricate MIL-125-NH₂ and further deposit Pt nanoparticles onto the surface as co-catalyst through a photodeposition process. UV-Visible spectrum shows this MOF can absorb visible light with wavelength up to 500nm. When TEOA used as the sacrificial reagent, MIL-125-NH₂ is able to produce about 0.33 umol/(gh) hydrogen from water splitting, and this activity last for at least three runs (every run lasts for 3 hours). In this MOF, the charge transfer process is LMCT, which means when exposed to visible light,

the BDC-NH₂ ligands absorb the light and photo-generated electrons then migrate to the metal cluster, H⁺ finally get the electrons from the reaction site (co-catalyst Pt) to produce hydrogen. Also, this MIL-125-NH₂ can be used to photocatalytic reduce CO₂ to formate with TEOA as a sacrificial reagent.^[36] Another sample of ligand functionality is aminated UiO-66, which can photocatalytic oxidize alcohols and reduce Cr(VI) thus convert solar energy to chemical energy.^[37]

Compared to previous design, post-synthetic modification is another way to realize photocatalytic MOFs. Pt used as co-catalyst usually appears as nanoparticles or colloidal, but with modification of Pt-containing complex onto the ligands of MOF-253 by post-synthetic modification, Xu and co-workers found this MOF can serve as photosensitizer and photocatalyst at the same time.^[38] They studied the hydrogen evolution under different conditions, such as the concentrations of MOFs, TEOA sacrificial reagent, and the types of solvent. The photocatalytic H₂ evolution rate increased along with the concentration of MOFs. At 440 nm, highest quantum efficiency can be obtained (1.63%) when CH₃CN/H₂O was chose as co-solvent. They further discussed the charge transfer mechanism, including ³MLCT, proton-coupled electron transfer (PCET), they believe the Pt-Pt interaction within the structure is the key reason for the improvement of photocatalytic activity.

2.3 Photoelectrochemical Water Splitting Systems

When the photocatalysts are deposited onto electrodes and immersed in electrolyte with external circuit connection, a photoelectrochemical water splitting system is formed. After immersing photoelectrode in electrolyte, charge transfer will occur between electrolyte and electrode until equilibrium (Figure 2.4), an interfacial electric field is thus developed and results in the band bending at the surface of photoelectrode, which leads photo-generated holes (electrons) to move to the surface of photoanode (photocathode) under irradiation.^[39]

Figure 2.4 The band energetics of a photoelectrode/electrolyte contact (A) before equilibration; (B) after equilibration in the dark; (C) in quasi-static equilibrium under steady state illumination. Reprint with permission from ref. (39). Copyright (2010) American Chemical Society.

Figure 2.5 shows three setups of PEC water splitting system. A photoanode and photocathode can be tandem connected to form PEC water splitting system (Figure 2.5a).^[40] The actual working condition of this system can be obtained by plotting respective J - V curves of photoanode and photocathode together, working potential and maximum current density are revealed at the intersection point. Thus photoelectrode are usually studied separately. N-type semiconductors with valence band edge more positive than the oxygen evolution potential can be used as photoanode. Under irradiation, photo-generated holes are used for oxygen evolution reaction, while photo-generated electrons will be transferred to the counter electrode via external circuit and consumed in hydrogen evolution reaction (Figure 2.5b). A p-type semiconductor with conduction band edge more negative than hydrogen evolution potential can be used as photocathode (Figure 2.5c). Under irradiation, the

potential of counter electrode is equal to the Fermi level of photoanode/photocathode. An external bias is needed to drive HER/OER at the counter electrode.

Figure 2.5 Energy diagrams of PEC water splitting using (a) tandem connected photoanode and photocathode, (b) photoanode with a counter electrode and (c) photocathode with a counter electrode. Redraw with permission from ref. (40). Copyright (2014) Royal Society of Chemistry.

In photoelectrochemical water splitting systems that require an external bias to drive the electrolysis, the conversion efficiency η can be calculated using Eq.2-2:

$$\eta = \frac{J_{mp}(1.23 - V_{app})}{P_{in}} \quad (2-2)$$

where V_{app} is the applied bias measured between the photoanode (OER) and the photocathode (HER), J_{mp} is the measured current density, and P_{in} is the power density of the photo-irradiation.

Another important criterion in designing photoelectrochemical water splitting system is the thermodynamic stability of the photoelectrode materials. Candidate materials must possess excellent durability in the aqueous electrolyte solutions to avoid degradation. To fulfill this requirement, the material's reductive/oxidative

decomposition potentials must be more negative/positive than the semiconductor's band-edge for hydrogen evolution/water oxidation. However, very few materials found to date show excellent stability in electrolyte for both water oxidation and reduction at the same time. ^[41]

2.3.1 Advancement of Photoanode Research

An n-type semiconductors with valence band edge more positive than the oxygen evolution potential can be used as photoanode. Under irradiation, photo-generated holes are accumulated at the interface of photoanode/electrolyte and used for oxygen evolution reaction (Eq.2-3).

Photoanode materials have to be stable under oxidizing conditions, and this rigorous restriction makes metal oxides and oxometalates (anions of metal oxides) the most investigated photoanode materials. In these materials, the valence band is made up with O 2p orbitals, while the conduction band is consisted of the valence orbitals of the metal elements. As a result, the valence band edges of most metal oxides and oxometalates, such as ZnO, TiO₂, WO₃ and Fe₂O₃ are stabilized at 2.5 ~ 3.5 eV vs. NHE. ^[42]

In this section, we will introduce several routes which leads to the enhancement of PEC water oxidation efficiency including the nanostructure design and fabrication of photoanode, doping of photoanode catalyst as well as sensitization by quantum dots.

2.3.1.1 Nanostructure Design of Photoanodes

Nanostructure of photoelectrode is critical for charge separation and transfer. Several kinds of photoanode structures have been developed, such as polycrystalline/nanoparticle thin film (Figure 2.6a), nanotube array (Figure 2.6b), or

nanowire/nanorod array (Figure 2.6c) on conductive substrate.^[43] Mechanical strength is usually poor in nanoparticle electrode, and large resistance were commonly existed in polycrystalline materials as well as between the catalyst and substrate. Among these, single crystal nanowire/nanorod array growth on conductive substrate offers direct electrical pathways for photo-generated electrons. Without grain boundary inside, the transport rate of charge carriers could be greatly increased.

Figure 2.6 Nanostructures for photoelectrodes in PEC water splitting systems. (a) polycrystalline/nanoparticle thin film, (b) polycrystalline nanotube. (c) single-crystal nanowire/nanorod array. Redraw with permission of ref. (43). Copyright (2009) SPIE.

Using a hydrothermal method followed by a calcination process, Liu has prepared single crystalline anatase TiO_2 nanowires on Ti foil.^[44] Firstly, through an alkali hydrothermal growth and ion-exchange reaction, bititanate nanowires were grown on titanium foil, then after a heat treatment, single crystalline anatase TiO_2 nanowires can be obtained with 2-50 μm length. Transparent conductive fluorine-doped tin oxide (FTO) has a small lattice mismatch with rutile TiO_2 , thus can be used as substrate to grow rutile TiO_2 nanowire array. Changing of the synthesis parameters enables fine tuning of the density, length and diameter of the nanowires.^[45] This two single crystalline TiO_2 nanowire array materials were used as photoanode and showed good performance.

Figure 2.7 Scheme of a fully integrated nanosystem of semiconductor nanowires for direct solar water splitting. Reprint with permission from ref. (46). Copyright (2013) American Chemical Society.

Yang's group reported a fully integrated system using TiO₂ nanowire as photoanode and Si nanowire as photocathode, which can utilize UV and visible light respectively. Due to large surface area, efficient charge transfer and co-catalyst loading, the obtained solar-to-fuel conversion efficiency can reach 0.12% under simulated sunlight.^[46]

ZnO nanowire arrays on substrate is usually fabricated with a seed-growth protocol. ZnO seeds on substrate are synthesized by decomposition of zinc salts at 200–350 °C, in the following vapor/solution phase growth process, ZnO nanowires can be obtained through a preferential growth on the pre-existing seeds.^[47, 48]

Besides directly growth, a template method can also been used for nanorod array growth on substrate. Al₂O₃ is the most commonly used hard template. Ta₃N₅ nanorod arrays can be obtained by nitridation of Ta₂O₅ which were previously grown on Ta foil through Al₂O₃ template.^[49]

2.3.1.2 Doping of Photoanode Catalysts

In order to harvest visible light, band engineering is widely studied to narrow the bandgap of semiconductors. The conduction band edge of photoanode materials can be tuned with metal ions, either as dopants or bulk matrix. The adjustment of conduction band edge position will further tune the bandgap of the oxides and oxometalates.^[42] The bandgap of many oxides and oxometalates, which possess d^0 or d^{10} configuration, can be decreased using different strategies, hence improving their responses towards visible light illumination. Metal ions, especially those possess strong polarizing ability, can be used to form M-O bonds that produce oxygen-to-metal charge transfer absorption, which lies in the visible region of the light spectrum.^[50] In addition, the conduction band and valence band edges can be tuned by the introduction of transition metals and incorporation of anion species (N^{3-} or S^{2-}), respectively.

Transition metal dopants are reported to decrease the bandgap of TiO_2 , but the stability and poor charge transfer remain problems. N dopant were introduced to fabricate stable visible-light responsive TiO_2 in Asahi's^[51] and Khan's^[52] group, the maximum photo-conversion efficiency of 8.35% can be obtained at an applied bias of 0.3V. C dopant can be introduced by a high-temperature annealing process at 500-800 °C in CO atmosphere.^[53] Compared to the pristine TiO_2 photoanode, the modified photoanodes exhibited apparently improved photoresponses towards visible-light irradiation. Annealing in hydrogen atmosphere leads to H doped TiO_2 , the dark-green color reveal the visible light absorption of photoanode.^[54]

Nitrogen dopants can also be introduced into ZnO crystals through a two-step thermal annealing approach.^[55] ZnO was first treated at 530°C under ammonia environment, followed by annealing at the same temperature under N_2 atmosphere for 30 min. N-doped ZnO exhibits an order of magnitude improvement in photocurrent compared to the pristine ZnO.

NaTaO₃ has a perovskite structures and possess a tunable bandgap of (~ 4.0 eV). Kudo et al. have enhanced the performance of NaTaO₃ with a 2% doping of La. They found that the surface area of the crystal was increased by 8 times, and the La-doped NaTaO₃ exhibited improved activity with a breakthrough oxygen evolution rate of 9.7 mmol/hr under the illumination of 400 W-Hg light source in pure water.^[56]

2.3.1.3 Quantum Dots Sensitization of Photoanode

Fabrication of heterostructures with different band gap semiconductors is an effective way to enhance the overall efficiency of photoanode. There are three types of band gap alignments: straddling (type I), staggered (type II), and broken (or misaligned, type III) shown in Figure 2.8.^[57] A type II configuration is favorable, since under irradiation, photo-generated electrons and holes will accumulate on different semiconductors thus facilitating charge separation.

Figure 2.8 Different heterostructure band alignments. (a) type I heterostructures, (b) type II heterostructures and (c) type III heterostructures. Reprinted with permission of ref. (57). Copyright (2013) Royal Society of Chemistry.

Quantum dots (QDs) were commonly used as photosensitizer to harvest visible light for wide band gap photoanode materials. Firstly, QDs usually possess narrow band gaps, and the band gaps and band positions of QDs can be tuned by particle size due to quantum confinement.^[58, 59] Secondly, Murphy^[60] reported the observation of efficient multiple exciton generation (MEG) from single photons absorbed in PbTe

QDs, which would greatly enhance the solar conversion efficiency. Last but not least, compared to chemical synthesis of organic dye molecules, QDs are easy to be synthesized with precisely control of size and morphology after decades of research.

Liu' group reported fabrication of excellent uniform CdSe QDs sensitized ZnO nanorod arrays by an all-electrochemical approach. Due to the favorable band alignment and uniform distribution of QDs, a saturated photocurrent density of 14.9 mA/cm² can be obtained at 0.8 V (vs. RHE) under AM 1.5 illumination.^[61] Similarly, CdTe QDs were used to sensitize ZnO nanoarray, incident photon to current conversion efficiency (IPCE) test shows strong photoresponse in the visible light region from 400-530nm which was consistent with the absorption of CdTe QDs, in addition to an significant increase in the UV region.^[62]

BiVO₄ possess a narrow band gap of 2.4 eV with the valence band edge located at 2.4 V vs. reference hydrogen electrode (RHE), which makes it promising sensitizer of photoanode. Su reported the fabrication of WO₃ photoanode with BiVO₄ sensitizer (Figure 2.9). WO₃ was firstly deposited on FTO by a solvothermal method, then BiVO₄ layer was deposited onto WO₃ via spin-coating. Due to the visible light absorption of BiVO₄, IPCE values of this photoanode at 420 nm was increased from 9.3% to 31% compared to planar films.^[63]

Figure 2.9 Scheme of BiVO₄ sensitized WO₃ photoanode with the structure of photoanode and band alignment. Reprint with permission from ref. (63). Copyright (2011) American Chemical Society.

Despite the enhancement of photoresponse in visible light region and the overall PEC performance including photocurrent and IPCE, photocorrosion of the QDs remain big problem which inherent the stability and durability of photoanodes.^[57]

2.3.1.4 OER co-catalysts

Semiconductors with suitable band structure may suffer from poor charge separation and intrinsic catalytic activity. Overcoming the OER kinetic limitation requires a stronger driving force (i.e. an overpotential), to drive the desired chemical reaction (OER). This overpotential reduces the usable voltage output, and hence lowers the efficiency of the PEC water oxidation. Co-catalyst loading can improve the kinetics of OER, reduce the overpotential, and facilitate charge separation as heterostructure described in 2.3.1.3, thus can be applied to enhance the overall conversion efficiency of photoanode. Thereby, the development of effective OER co-catalysts is another important topic in the PEC water oxidation research area.

FeOOH and NiOOH as OER catalysts were loaded on nanoporous BiVO₄ photoanode,^[64] Figure 2.10 shows the PEC performance of pristine and co-catalyst modified photoanodes, compared to the negligible photocurrent of pristine BiVO₄ at 0.6 V versus RHE (black solid line), photoanode with BiVO₄/FeOOH/NiOOH configuration (red line) achieves a photocurrent density of 2.73 mA/cm², shows the critical role of OER catalyst in the PEC water oxidation.

Figure 2.10 *J*-*V* curves of pristine BiVO₄ (black solid line), FeOOH, NiOOH, FeOOH/NiOOH, NiOOH/FeOOH loaded BiVO₄ (blue, green, red and pink, respectively) in a 0.5 M phosphate buffer (pH 7) under AM 1.5 G illumination. Reprint with permission from ref. (64). Copyright (2014) Science.

2.3.2 Advancement of Photocathode Research

Photocathodes are responsible for providing sufficient cathodic current to drive hydrogen evolution reaction, in which protons are reduced to H₂. As mentioned previously, the conduction band edge of the photocathode material has to be more negative than the redox potential of H⁺/H₂. The hydrogen evolution reaction is pH-dependent process: at low pH environments, the HER process mainly progresses through the reduction of protons as shown in Eq. 2-1; while in high pH environments, water will be directly reduced to generate H₂ and OH⁻ ions as shown in Eq. 2-2.

Numerous materials have been studied as photocathodes in PEC water splitting system, in this section, we will focus on those well studied p-type semiconductor.

2.3.2.1 P-type Metal Oxide Semiconductors

Among the many p-type oxide semiconductors, Cu₂O, with a direct bandgap of 2.0 eV, is the most studied metal oxide for photoelectrochemical applications. Applied

as photocathode, Cu_2O -based materials possess many advantages over other candidates, such as material abundance, low-cost, non-toxicity and favorable light-absorption properties.^[65] However, the practical potential of Cu_2O -based material is severely hindered by the poor stability in aqueous electrolyte under solar irradiation, due to its transformation to CuO and metallic copper under anodic current and cathodic current respectively.^[66, 67]

Most researches regarding Cu_2O photocathode focus on enhancing its stability. Graetzel's group applied Al-doped- ZnO/TiO_2 thin film as protection layer of Cu_2O photocathode.^[67] With favorable band alignment, n-type Al-doped- ZnO and TiO_2 not only facilitate charge separation and transfer by the formation of p-n junction, but also protect Cu_2O from corrosion by preventing the direct contacting of Cu_2O with electrolyte. After loading of RuO_x HER catalyst, 5 mA/cm^2 photocurrent density can be obtained, with 94% remaining photocurrent after 8h of chopped light irradiation at 0 V vs. RHE.^[68]

2.3.2.2 III-V Semiconductors

III-V semiconductors, with favorable band structures, are currently playing dominant roles in the research of efficient photocathodes for photoelectrochemical water splitting.

Gallium phosphide (GaP) is a typical III-V semiconductor with an indirect bandgap of 2.26 eV. By introducing different dopants, GaP can be engineered to both n-type and p-type semiconductor. The stability of n-type GaP is poor in aqueous environment, making it unsuitable for solar water splitting applications. Meanwhile, the cathodic current can protect the p-type GaP when it is used as a photocathode for hydrogen generation.^[69] Zinc dopant makes GaP p-type semiconductor, Yang's group fabricated Zn-doped GaP nanowires by a solution-liquid-solid strategy and used it as photocathode. Much smaller transient spike feature of Zn-doped GaP

nanowires compared to planar photocathode proved the enhanced reaction kinetics.^[70]

Figure 2.11 (a) J -V curves of pristine and passivated GaN photocathode. (b) Chopped illumination J -V curve of passivated GaN photocathode. (c) ABPE and (d) IPCE of pristine and passivated GaN photocathode. Reprinted with permission from ref. (71). Copyright (2017) American Chemical Society.

He's group employed a simple and low-cost surface treatment with an organic thiol compound (i.e., 1,2-ethanedithiol) to passivate GaN surface.^[71] Figure 2.11 shows the PEC performance of pristine and passivated GaN photocathode. The surface-passivated GaN photocathode showed an enhanced IPCE of 18.3% compared to 8.1% of pristine GaN photocathode at 350 nm irradiation. What's more, surface-treated

photoanode possessed good stability. 80% of initial photocurrent can be retained after 55 h continuous irradiation at -0.4 V in 1 M H₂SO₄.

Indium phosphide (InP) possess a bandgap of 1.35 eV making it an excellent light-absorbing material in PEC water splitting system. Notten's group^[72] have demonstrated the fabrication of MoS₃-decorated InP nanowire arrays as an efficient cathode for photoelectrochemical hydrogen production. Photoelectrochemical tests were carried out in 1 M HClO₄ electrolyte under chopped AM 1.5 G illumination, and the MoS₃-decorated InP nanowires demonstrated promising performance with a saturated photocurrent density of 22 mA/cm² and a maximum efficiency of 6.4%. Unfortunately, the scarcity along with the high market demand of indium limits the practical application of this material.

2.3.2.3 P-type Silicon (p-Si)

P-type silicon (p-Si), with a bandgap of 1.12 eV, has been reported as promising photocathode material by many researches. P-Si is relatively stable in acidic electrolyte, but surface oxidation may occur after long time operation.

Chorkendorff's and co-workers^[73] fabricated Si micropillars by photolithographic technique, cubane-like Mo₃S₄ catalysts were then decorated onto the p-Si surface. Small band gap, fast charge transfer and fast HER kinetics leads to a significantly enhanced electrode performance, with an impressive photocurrent density of 8 mA/cm² at 0V vs. RHE, equivalent to a IPCE of 47%, under red-light irradiation in 1 M HClO₄. What's more, this photocathode showed great stability at 0V vs. RHE under red-light irradiation.

Beside the aforementioned materials, many other p-type semiconductors can also been applied for photocathode materials, such as transition-metal chalcogenides WS₂^[74], WSe₂^[75], CuGaSe₂^[76], CuIn_{1-x}Ga_xS₂^[77] and Rh-doped SrTiO₃^[78]. Notably,

HER co-catalyst such as Pt, RuO_x, Mo_xS_y were usually applied for high conversion efficiency.

2.4 Electrochemical Water Splitting System

From the reviewed researches in 2.2 and 2.3, co-catalyst plays a critical role in high efficient solar-to-chemical conversion both in photocatalytic and PEC water splitting system. The development of effective electrocatalysts for both OER and HER is also an important topic.

The catalytic performance of electrocatalysts can be quantified by their onset potential in polarization curves, and the current density generated at certain applied overpotential using electrochemistry workstations. In solar water splitting systems, the electrocatalysts must fulfill two requirements. First, they must be able to produce large quantities of H₂ and O₂ at minimum applied overpotential. Second, they must show outstanding durability to maintain their efficiency over a time scale relevant to practical applications. To function as co-catalysts in solar water splitting systems, these electrocatalysts are generally deposited on to the photocatalysts as nanoparticles or thin layers, to prevent both excessive photon absorption and reflection, while maintaining the desire interfacial energetic status.^[39]

2.4.1 HER Catalysts

From previous description, most p-type semiconductor are coupled with HER co-catalyst to form high efficient photocathode. HER catalyst plays a critical role for improving reaction kinetics. HER is one of the most well studied processes in electrochemistry.

HER is a two-electron transfer reaction and involves two steps, namely the bonding of protons to the catalyst surface (Volmer reaction, Eq. 2-6), followed by desorption of hydrogen molecules through Heyrovsky reaction (Eq. 2-7) and/or Tafel reaction (Eq. 2-8).

where * denotes the active site on catalyst surface that capable of binding to proton.

Figure 2.12 (A) HER volcano plot for metals and MoS₂, (B) TOF plots with LSVs of various HER catalysts. (C) Chronological trend in overpotential of MoS₂-based and phosphide HER catalysts. (D) Representative microscopy images of HER catalysts. Reprinted with permission from ref. (79). copyright (2017) Science.

The hydrogen adsorption free energy ΔG_{H} determines the overall reaction rate, neither too strong nor too weak adsorption is beneficial for HER activity, $\Delta G_{\text{H}} \approx 0$ is ideal for an effective HER catalyst.^[80, 81] ΔG_{H} of a catalyst can be calculated by density functional theory, plotting exchange current densities of different catalysts against the ΔG_{H} , a volcano relationship can be obtained. Seh summarized well studied HER catalysts shown in Figure 2.12.^[79] Figure 2.12a shows a typical volcano plot for metal HER catalysts. Noble metal Pt is at the top of the plot, and experiments

have confirmed the best HER activity of Pt. Negligible overpotential is needed for driving HER on Pt surface. However, the scarcity of noble metal restrict its practical usage.

Noble-metal free HER catalysts have been intensively studied such as transition-metal sulfide, carbide and phosphide.

MoS₂ is one of most studied non-noble metal HER catalyst. DFT calculation resulted a ΔG_H of 0.08 eV at Mo edge compared to 1.92 eV at the basal plane of MoS₂, suggesting that the active sites lies on the edge of MoS₂,^[82] and experimental results later confirm the MoS₂ edge as active sites.^[83] 1T metallic MoS₂ can be obtained from chemical exfoliation of MoS₂ by lithium intercalation. Basal plane can also serve as active sites in 1T metallic MoS₂, along with the decrease of charge transfer resistance, 1T MoS₂ shows excellent HER activity.^[84-86] Co, Ni and V can be doped into the intralayer of MoS₂, by increasing the active site density or/and charge transfer, doped MoS₂ shows superior HER catalytic activities.^[87]

Transition metal carbides were promising Pt-like HER catalysts owing to their similar d-band electronic density states to Pt.^[88, 89] Molybdenum carbides possess not only high catalytic activity, but also good electrical conductivity and optimal hydrogen-adsorption properties. In addition of the low cost and high abundance, molybdenum/tungsten carbides are very promising in large scale HER application. Construction of molybdenum/tungsten carbides catalysts with fine-tuned structure at nanoscale are critical for improving the HER performance. Different morphologies such as porous MoC_x nano-octahedra^[90], Mo₂C nanorod^[91], MoC_x nanoparticles with WC nanowires^[92], porous Mo₂C nanowires^[93], Mo₂C 2D nanosheets^[94], WC_x nanocrystals^[95], and WC_x 2D nanoflakes^[96] have been studied as HER catalysts and shown good activities with proper durability.

Research on transition metal phosphides as HER catalysts were originated from DFT calculation of Ni₂P in 2005.^[97] Ni₂P as efficient HER catalyst was experimentally confirmed later by Popczun, but the synthesis is strictly air-free which inherent its application.^[98] Hu synthesized Ni₂P nanoparticles by a solid-state reaction which is simple and scalable.^[99] Amorphous and W-doped Ni₂P were synthesized, and the doped Ni₂P catalyst can achieve a current density of 20 mA/cm² at only 110 mV overpotential.^[100] Besides Ni₂P^[101], CoP^[102, 103], FeP^[104] Cu₃P^[105] have also been studied and showed excellent HER activities.

It is worth noting that Pt electrodes were sometimes used as counter electrode for HER catalyst. But recent research showed that severe dissolution of Pt occurs when serve as counter electrode, which lead to the deposition of Pt on the HER catalyst^[106], thus the results of these works are questionable.

2.4.2 OER Catalysts

OER is a four-electron transfer reaction involving multiple steps. Generally, in acidic and neutral electrolyte, two water molecules lose four electrons to form one oxygen molecule and four protons (Eq.2-9), while in alkaline electrolyte, four OH⁻ are oxidized (Eq. 2-10).^[107]

Most studied OER catalysts are metal oxide, thus volcano plots for OER catalysts have been constructed using $\Delta G_{\text{O}} - \Delta G_{\text{OH}}$ as the descriptor and shown in Figure 2.13A.^[79]

Figure 2.13 (A) OER volcano plot for metal oxides. (B) Chronological trend in overpotential of various OER catalysts in acid and alkali. Reprinted with permission from ref. (79). Copyright (2017) Science.

Effective OER catalysts studied are commonly metal oxide with four types: precious oxide including RuO_2 and IrO_2 ; transition metal oxide with spinel crystal structure including Co_3O_4 and NiCo_2O_4 ; metal oxide with perovskite crystal structure including NiLa_2O_4 and LaCoO_3 and Pyrochlores, such as $\text{Pb}_2\text{Ru}(\text{Ir})_2\text{O}_7$.

Despite intensive research over decades to develop OER catalysts in both acidic and alkaline solutions, most state-of-the-art catalysts still require far-from-ideal overpotentials of 0.25 to 0.4 V to reach current densities of interest (Figure 2.13B).

2.5 Questions to answer based on literature

As discussed in the aforementioned literature review, solar to hydrogen conversion can be realized by different systems including photocatalytic and photoelectrochemical water splitting, great progress has been made in the synthesis and structure engineering of catalysts for high conversion efficiency. Nevertheless, there are still questions remaining to be further investigated. Despite the extensive

research, the overall solar-to-hydrogen conversion efficiency is still far from satisfactory, and it depends on each part of the system.

Firstly, the low light harvesting efficiency. Despite the extensive effort on visible light harvesting, an effective photosensitizer is still needed. Band engineering, nanostructure design and sensitization is expected to provide more opportunities to enhance the visible light harvesting, thereby enhance the overall utilization of solar energy.

Secondly, the low reaction kinetics. Almost all of the solar-to-hydrogen conversion systems are coupled with co-catalysts owing to the low reaction kinetics of photocatalysts. Active and noble-metal-free catalysts towards HER and OER is still in urgent needed.

Thirdly, water splitting reaction is a strong uphill reaction with a theoretical energy input of 1.23 eV. Due to the low reaction kinetics, large overpotential (~ 0.1 - 0.3 V for HER, ~ 0.2 - 0.4 V for OER) is still required for efficient water splitting, this overpotential in turn reduced the overall solar-to-hydrogen efficiency.

2.6 PhD in context of literature

In my thesis, I focus on improving the overall solar-to-hydrogen efficiency by rational design of catalytic nanomaterials.

After thorough review of the literatures, MOFs are found to be a new kind of promising photocatalyst. The large quantity and tunable chemical property of MOFs arouse our interests in its application as photosensitizer. A series of MOFs will be coated on photoanode and studied as photosensitizer.

HER catalyst plays a critical role in solar-to-hydrogen conversion system. Noble-metal free catalyst with low overpotential is still in urgent needed. A series transition-metal carbide/graphene complex materials will be synthesized and

evaluated as HER catalysts in all pH solutions including 0.5 M H₂SO₄, 0.2 M PBS and 1 M NaOH.

A new solar-to-hydrogen conversion system will be developed to overcome the high energy requirement in water splitting by substitution of biomass-derived alcohol oxidation for OER. By reducing the external bias to drive efficient hydrogen, high overall solar-to-hydrogen efficiency is expected.

Chapter 3

Metal-Organic Frameworks (MOFs) as Promising Photosensitizers for Photoelectrochemical Water Splitting

This chapter introduces a new kind of photosensitizer: metal-organic frameworks (MOFs). A series of Ti-based MOFs are coated on TiO₂ nanowire array and used as photoanodes, solar water oxidation performance are tested. Visible light absorption of MOF is tunable by ligand modification, thus the photocurrents of photoanodes are increased according to the visible light absorption. In addition, porous structure enable MOFs to couple with plasmonic Au nanoparticles, the light absorption efficiency could be further improved due to the LSPR effect.

3.1 Introduction

Since the first discovery of photoelectrochemical (PEC) water splitting by Fujishima and Honda in 1970s,^[2] artificial photosynthesis which converts solar energy into chemical fuels, mimicking what nature does, has received great attention in the scientific community. Among the various studied materials, titanium dioxide (TiO₂) has attracted the greatest attention due to its nontoxicity, physical and chemical stability, and peculiar electronic and optical properties.^[108] However the wide band gap of TiO₂ limits its absorption of visible light, which restricts the solar energy conversion efficiency. Over the past few years, considerable efforts have been made to tune the photoresponse of TiO₂ to improve the visible light absorption, such as metallic (e.g., Fe, Zr)^[109] or non-metallic (e.g., N, F, C, S, B) doping,^[13, 14, 51, 53, 110] and dye molecule^[111, 112] or narrow band gap semiconductor (e.g., CdS, CdSe) sensitization.^[113-117] Among which, sensitization appears to be a promising strategy for harvesting solar energy by enhancing visible light absorption and improving charge separation.^[118, 119] However, dye sensitizers usually have low light absorption coefficient and are effective only when they are chemically bound onto the surface of semiconductor, with performance depending on the surface area as well as structure of the semiconductor.^[120] Furthermore, dye molecules are generally catalytically inactive, which have to be combined with molecular catalysts to realize noticeable photocatalytic activities. Alternatively, narrow band gap semiconductors with large light absorption coefficient are frequently used as photosensitizers for TiO₂ in solar energy conversion.^[112, 121] However the stability and toxicity for most of the narrow band gap semiconductors remain a serious problem.

MOFs are a new class of hybrid materials possess highly ordered framework structure and large surface area. Due to the fascinating chemical and morphological properties, MOFs are expected to be useful in a large scope of applications, including gas storage^[122, 123] and separation,^[124] chemical sensing,^[125] biomedicine^[126] and

heterogeneous catalysis.^[127, 128] More recently, MOFs are emerging as a new type of photocatalysts.^[129] Having combined metal nodes and bridging ligands, MOFs provide the possibilities of periodical arrangement of light harvesting and catalytic components in a single structure, just like the natural photosynthetic system, making them promising candidates for solar energy conversion.

Some MOFs (such as MOF-5) are recognized as semiconductors, Jorge calculated a family of isorecticular MOFs and found the band gaps are between 1.0-5.5 eV, which actually are the gaps of the HOMO and LUMO level.^[24] Due to the versatility of MOFs, band gaps of these kinds of MOFs can be tuned by simple design of the structures, in order to harvest the sunlight, such as combination of different components, structure design of the metal clusters or chemical functionalization of the linkers.^[25, 26, 126]

Among different types of MOFs, Ti-based MOFs are expected with good photocatalytic properties due to the presence of high density of Ti-oxo clusters.^[33, 130] Under light irradiation, electrons are photo-generated in organic ligands and then transferred to Ti-oxo clusters.^[33] Based on a recent study,^[131] MIL-125 (a Ti-based MOF) has a more negative LUMO level than the conduction band edge of TiO₂, making electron injection from MIL-125 to TiO₂ thermodynamically feasible.

Thus herein, we studied a series of Ti-based MOFs as photosensitizers on TiO₂ photoanode for PEC water splitting. Our results showed that the PEC water oxidation performance of TiO₂ could be significantly enhanced by applying MOFs as photosensitizers under visible light illumination.

3.2 Experimental Section

3.2.1 Chemicals and Materials

All chemicals were purchased from Sigma-Aldrich without further purification. Fluorine-doped SnO₂ (FTO) glass was purchased from Latech Scientific Supply.

3.2.2 Preparation of Photoanodes

3.2.2.1 Growth of TiO₂ nanowire arrays on FTO

Oriented rutile TiO₂ nanowire arrays were grown on FTO substrate using a hydrothermal method based on our previous report.^[45] Briefly, 0.83 mL of tetra-n-butyl orthotitanate (TBOT) was mixed with 50 mL of 6 M hydrochloric acid and stirred for 5 min. Afterwards, the growth solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, followed by placing a few pieces of pre-cleaned FTO glass. The hydrothermal reaction was conducted in an electronic oven at 150 °C for 5 h. After reaction, the TiO₂ covered FTO glass was taken out, rinsed thoroughly with deionized water and dried with flowing nitrogen. To improve the crystallinity and conductivity of TiO₂ nanowire arrays, further annealing was performed in air at 450 °C for 30 min.

3.2.2.2 Preparation of TiO₂/MOF Photoanodes

TiO₂ nanowires were firstly modified with 1, 4-benzenedicarboxylate(BDC) or BDC-NH₂, which are the ligands used for growing MIL-125 and MIL-125-NH₂ seperatively. In a particular experiment, 4 pieces of FTO covered by TiO₂ nanowire arrays were immersed in 4 mL of 20 mM BDC (DMF) or BDC-NH₂ (DMF) solution, and kept at 120 °C for 3 h. To grow TiO₂/MOFs composites, redistilled dimethylformamide (DMF) and methanol (MeOH) were used as the solvent. To 5 mL of DMF/MeOH (v/v = 9/1), 0.3 mmol of BDC and 26 µL of TBOT were firstly mixed in a 20 mL Teflon-lined autoclave, to which, four pieces of FTO covered with TiO₂ nanowires were placed against the wall of Teflon-liner with the TiO₂ side facing down. The solvothermal reaction was conducted at 150 °C for 72 h to grow TiO₂/MIL-125. TiO₂/MIL-125(NH₂) and TiO₂/MIL-125(NH₂)_{1, 2} were prepared using the same protocol with the same amount of BDC-NH₂ ligand and BDC-(NH₂)₂/BDC-(NH₂) ligand (molar ratio, 1/9), respectively.

3.2.2.3 Preparation of TiO₂/MIL-125(NH₂)/Au Photoanode

HAuCl₄ was used as gold precursor to prepare Au nanoparticles. Firstly, 2 mM HAuCl₄ (MeOH) solution was prepared and the pH was adjusted to 7. Subsequently, TiO₂/MIL-125(NH₂) samples heated at 120 °C for 10 h were soaked into the HAuCl₄ solution for 3 h, followed by washing with MeOH. After drying, gold precursors were reduced by 0.2 M NaBH₄ solution for 5 min.

3.2.3 Characterization

3.2.3.1 Materials Characterization

X-ray diffraction (XRD) patterns were collected on a Bruker AXS D8 Advance diffractometer using nickel-filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Field emission scanning electron microscope (FESEM) images were taken on a JEOL JSM-7600 with an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) images were taken on a JEOL JEM 2010F at an accelerating voltage of 200 kV. STEM-EDS elemental mapping was conducted on a JEOL JEM 2100F. UV-visible spectra were recorded using a Perkin-Elmer Lambda 900 UV-Vis-NIR spectrometer equipped with an integrating sphere. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) at 2.4×10^{-10} mbar using a monochromatic Al K α X-ray beam (1486.60 eV). Binding energies (BE) were calibrated to the carbon BE of 284.60 eV.

3.2.3.2 Photoelectrochemical Measurements

Photoelectrochemical properties of TiO₂/MOF nanocomposites were studied on CHI 660D electrochemical workstation in a standard three-electrode setup with Ag/AgCl (3M NaCl) as the reference electrode and a platinum plate as the counter electrode under simulated sunlight from a 300-Watt Xenon lamp (Newport, Oriel, 91160) equipped with an AM 1.5G filter (Newport, 81094) and a 420 nm long pass filter (Newport, FSQ-GG420). The light source was calibrated using a standard Si

photodiode. In all cases, a 0.5 M Na₂SO₄ solution (pH = 6.5) was used as the electrolyte. All potentials were converted to values relative to RHE using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + E^{\circ}_{\text{Ag/AgCl}} \quad (3-1)$$

where $E^{\circ}_{\text{Ag/AgCl}}$ is the standard potential of Ag/AgCl relative to SHE at 25 °C (0.203 V). The working area of the photoelectrode was fixed at 0.25 cm² for each experiment. The electrochemical impedance spectroscopy measurements were performed by applying a frequency ranging from 10⁻² to 10⁵ Hz with AC amplitude of 10 mV under visible light illumination (420 nm cut-off) at open-circuit voltage condition. The incident photon-to-current conversion efficiency (IPCE) was measured at a bias of 0.2 V vs. Ag/AgCl. The monochromatic light was supplied by a 300-Watt Xe lamp irradiation through a monochromator (Newport). A chopper was placed in front of the monochromator, and the signal was collected using a lock-in radiometry (Merlin) after amplification by the current preamplifier.

3.3 Results and Discussion

3.3.1 Characterization and PEC performance of MOFs sensitized TiO₂ photoanodes

Three Ti-based MOFs (MIL-125, MIL-125(NH₂), MIL-125(NH₂)_{1,2}) were studied as photosensitizers for PEC water splitting. The TiO₂/MOF hybrid nanocomposite was prepared on FTO substrate by a two-step solution phase method. In the first step, vertically oriented, single crystalline TiO₂ nanowire arrays were grown on FTO substrate based on a hydrothermal method. The as-grown ordered one-dimensional TiO₂ nanostructures possess large surface area as well as short minority carrier diffusion pathways (perpendicular to the nanowire growth direction), which could serve as excellent photoanode for PEC water splitting.^[132, 133] Figure 3.1 shows both the top view and cross-sectional view FESEM images of the TiO₂ nanowire arrays,

from which the average diameter and length of the TiO_2 nanowires were determined to be around 100 nm and 1.5 μm , respectively.

Figure 3.1 (a) Top view, and (b) cross-sectional view FESEM images of pristine TiO_2 nanowire arrays on FTO.

Subsequently, in the second step, Ti-based MOFs were grown on the surface of TiO_2 nanowires to form a core-shell hybrid nanostructure. In this step, it was found that modification of the TiO_2 surface was critical in promoting the heterogeneous nucleation and growth of MOF nanostructures. Without surface modification, the Ti-based MOF grew homogeneously in solution, resulting in phase segregated TiO_2 and MOF nanostructures (Figure 3.2). The ligand (BDC or BDC- NH_2) used to modify TiO_2 have $-\text{COOH}$ functional groups, which bind strongly with the surface Ti atom on TiO_2 and thus creates nuclei sites for the MOF growth.

Figure 3.2 TEM images of MIL-125(NH₂) grown on TiO₂ nanowires with (a) and without (b) ligand surface modification.

Figure 3.3 shows FESEM images of pristine TiO₂ nanowire arrays and TiO₂ coated with MIL-125, MIL-125(NH₂) and MIL-125(NH₂)_{1,2}, respectively. It can be observed that the surface of nanowires becomes rougher after coating with MOF nanostructures, accompanying with an increase in nanowire diameter, indicating successful coating of MOF on the surface of TiO₂ nanowires.

Figure 3.3 FESEM images of (a) TiO_2 nanowire arrays, (b) $\text{TiO}_2/\text{MIL-125}$ nanowire arrays, (c) $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$ nanowire arrays, and (d) $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)_{1.2}$ nanowire arrays. Scale bars: 200 nm.

The XRD patterns as displayed in Figure 3-4a and b also show both diffractions from TiO_2 and MOFs, which matches perfectly with the FESEM observation. Depending on the choices of ligands, the Ti-based MOFs show different light absorption properties. Figure 3.4c shows the UV-vis diffuse reflectance spectra of TiO_2 and TiO_2/MOF nanocomposites. Both TiO_2 and $\text{TiO}_2/\text{MIL-125}$ show similar light absorption onset, which is around 420 nm, suggesting the wide band gap nature for both TiO_2 and MIL-125. Based on the literature,^[25] the HOMO-LUMO gap of MIL-125 is 3.8 eV, i.e., thus MIL-125 can only absorb light in the UV spectrum.

Figure 3.4 XRD patterns of TiO₂ and TiO₂/MOF nanocomposites (a. TiO₂, b. TiO₂/MIL-125, c. TiO₂/MIL-125(NH₂), d. TiO₂/MIL-125(NH₂)_{1,2} and e. simulated MIL-125). (c) UV-Vis diffuse reflectance spectra of TiO₂ and TiO₂/MOF nanocomposites. (d) *J*-*V* curves of TiO₂ and TiO₂/MOF nanocomposites.

To reduce the HOMO-LUMO gap, the BDC ligands were modified and used for growing MIL-125 with amines. In MIL-125, the HOMO is composed of the ligand BDC C 2p orbitals, the LUMO is composed of O 2p orbitals and Ti 3d orbitals, which means the modifications of the aromatic BDC units can only change the HOMO level but unlikely to affect the LUMO level. Amines are strong electron-donating substituents, which could help to raise the HOMO level of MOFs while maintaining the LUMO level, thus reducing the HOMO-LUMO gaps.^[25] After amine

modification, monoaminated MIL-125(NH₂) shows an obvious red-shift in light absorption towards the visible light, while partially diaminated MIL-125(NH₂)_{1,2} possesses an even narrower HOMO-LUMO gap with absorption onset at around 650 nm, which correspond well with the yellow and dark brown colors of MIL-125(NH₂) and MIL-125(NH₂)_{1,2} (Figure 3.5). Clearly, ligand modification offers an effective way to tune the HOMO-LUMO gaps of MOFs, thus changing the optical properties.

Figure 3.5 FESEM images of (a) MIL-125, (b) MIL-125(NH₂), and (c) MIL-125(NH₂)_{1,2}. (d) XRD patterns of the Ti-based MOFs. Insets in a, b, c show the digital photographs of the as-prepared Ti-based MOFs respectively. Scale bars: 1 μ m.

Photocatalytic properties of as-prepared TiO₂/MOF nanocomposites were evaluated by performing PEC water splitting. Both TiO₂ and TiO₂/MOF samples with fixed sample area were used as the photoanode. Figure 3-4d displays the *J*-*V* curves for

water splitting under AM1.5 illumination with UV light cutoff ($\lambda > 420$ nm). It is clear to see that the pristine TiO_2 nanowire electrode has a very small photocurrent density of only $10 \mu\text{A}/\text{cm}^2$ at 0.75 V vs. RHE, due to the large band gap of rutile TiO_2 (3.0 eV). When sensitized with Ti-based MOFs, different PEC performances were realized. MIL-125 sensitized TiO_2 showed a comparable PEC performance as the pristine TiO_2 electrode, which is due to the fact that MIL-125 can only absorb UV light. On the contrary, significant improvements in photocurrent were observed in both MIL-125(NH_2) and MIL-125(NH_2)_{1,2} sensitized TiO_2 electrodes, resulting from much enhanced visible light absorption in these aminated MOFs. The LUMO level of MIL-125 is more negative than the conduction band edge of TiO_2 ,^[131] as a result, electron transfer from MIL-125 to TiO_2 will proceed favorably. As ligand modification merely affects the LUMO level of MOFs,^[25] it is anticipated that the electron transfer from MIL-125(NH_2) or MIL-125(NH_2)_{1,2} to TiO_2 will be unaffected. Upon visible light illumination, electrons in the HOMO level of MIL-125(NH_2) or MIL-125(NH_2)_{1,2} are photoexcited into the LUMO level, which will be quickly injected into the conduction band of TiO_2 and then be transported through TiO_2 to reach the counter electrode to reduce water. Simultaneously, the holes in the HOMO level of MOFs will drive water oxidation to evolve oxygen. Thus, the overall PEC performance will be affected by the light absorption as well as rate of chemical reactions (water reduction and oxidation).

3.3.2 Characterization and PEC performance of Au nanoparticles decorated MOFs/ TiO_2 photoanodes

Increasing the MOF layer thickness could increase the photocurrent density because of enhanced light absorption; however, if the MOF layer becomes too thick, the poor electron transport in the MOF layer could lead to significant charge recombination and thus decrease the photocurrent density. To further improve light absorption while at the same time keeping a thin MOF layer to enhance water oxidation kinetics, Au

nanoparticles were specifically selected to modify MOF sensitized TiO_2 photoelectrode. Au nanoparticles not only have strong light absorption in the visible solar spectrum due to localized surface plasmon resonance (LSPR), which can be utilized to increase the light absorption cross-section of the photosensitizer, but also have the capability to catalyze water oxidation reaction.

MIL-125(NH_2) sensitized TiO_2 was further decorated with Au nanoparticles. Figure 3.6, 3.7 show the XRD pattern, XPS spectra of Au nanoparticles modified $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$ nanocomposite. In the wide scan XPS spectra (Figure 3.7a), the newly appeared N 1s peak in $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$ and $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)/\text{Au}$ and Au 4f peak in $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)/\text{Au}$ reveal the successful decoration of MOF and Au nanoparticles onto the TiO_2 photoanode. After MOF decoration, the O 1s peak at 533 eV can be assigned to the $-\text{COO}^-$ functional groups from MOF ligand (Figure 3.7b-d). The chemical states of neither O nor N were changed after Au nanoparticles were further loaded (Figure 3.7b-f).

Figure 3.6 XRD patterns of pristine TiO_2 and sensitized TiO_2 photoanodes respectively. **Figure 3.7** XPS spectra of pristine and sensitized TiO_2 photoanodes. (a) Wide-scan spectra, (b) $\text{O}1s$ for TiO_2 , (c) $\text{O}1s$ for $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$, (d) $\text{O}1s$ for $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)/\text{Au}$, (e) $\text{N}1s$ for $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$, (f) $\text{N}1s$ for $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)/\text{Au}$, and (g) $\text{Au} 4f$ for $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)/\text{Au}$.

Figure 3.8 (a) & (b) TEM images of $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)/\text{Au}$.

Figure 3.9 (a) Dark field-STEM image, (b) to (e) corresponding EDS mapping spectra (b: Ti, c: O, d: N, e: Au, scale bars: 200 nm) of $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)/\text{Au}$, and (f) UV-vis diffuse reflectance spectra.

Figure 3.8 shows the TEM images of Au nanoparticles decorated $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$, plenty of Au nanoparticles are clearly visible. The Au nanoparticles are uniformly decorated on the $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$ nanocomposite as confirmed by the

STEM-EDS mapping measurement (Figure 3.9). After loading Au NPs, an additional light absorption peak centered at 550 nm resulting from the Au SPR excitation further confirms the successful decoration of Au NPs on $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$ (Figure 3.9f).

As electrochemical processes are interfacial, the surface area of the photoelectrode is crucial in our PEC water splitting system. The electrode surface area can be estimated by measuring the double-layer capacitance,^[134] which was done by cycling the electrode over a narrow potential window (0 - 0.1 V vs. Ag/AgCl) over which no Faradaic processes took place. The CVs were recorded over a range of scan rates between 1 - 100 mV/sec and the differences between the anodic and cathodic plateau currents were plotted as a function of the scan rate (Figure 3.10), which yielded a straight line, intercepting the origin and possessing a slope equal to the double-layer capacitance of the electrode. From Figure 3.10, the $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$ possesses the largest slope i.e., largest surface area, resulting from the highly porous structure of MOF materials. After incorporating Au nanoparticles, surface area decreased due to blocking of MOF pores by Au nanoparticles.

PEC water oxidation performance was further significantly enhanced by loading Au nanoparticles onto the $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$ photoelectrode. The stabilized photocurrent was improved by nearly 50% from $20 \mu\text{A}/\text{cm}^2$ to $30 \mu\text{A}/\text{cm}^2$ at a bias of 0.75 V vs. RHE under visible light illumination (Figure 3.11). As a control, Au nanoparticle modified TiO_2 was also fabricated by the same procedure with $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$. The enhancement of photocurrent can be attributed to two factors. Firstly, the plasmon-induced visible light absorption of Au NPs can increase the light absorption cross-section of MIL-125(NH₂), which in turn increases the light harvesting efficiency. Secondly, upon light illumination, LSPR generates a strong electromagnetic field close to the surface of Au nanoparticles. This electromagnetic field can modify the band structure at the interface between Au and other

semiconductor,^[135] which could facilitate charge separation and reduce charge recombination. Besides, the catalytic activity of Au for water oxidation should not be ignored, which also played a role to improve the water oxidation performance.

Figure 3.10 (a) Capacitive current, $\Delta i = (i_{\text{cathodic}} - i_{\text{anodic}})/2$, as a function of scan rate. The CV scans of (b) TiO₂, (c) TiO₂/Au, (d) TiO₂/MIL-125(NH₂), and (e) TiO₂/MIL-125(NH₂)/Au recorded at scan rates of 1, 2, 5, 10, 20, 50 and 100 mV/s.

Figure 3.11 PEC performance of TiO_2 and sensitized TiO_2 nanowire arrays under visible light illumination ($\lambda > 420$ nm). (a) J - V curves. (b) J - t curves upon chopped illumination at 0.75 V vs. RHE.

Figure 3.12 Stability tests of TiO_2 and sensitized TiO_2 nanowire photoanodes: J - t curves upon visible light illumination ($\lambda > 420$ nm) at 0.75 V vs. RHE.

The stability of the MOF-sensitized TiO_2 photoelectrodes was examined by recording photocurrent as a function of time during chopped and continuous visible light illumination at a bias of 0.75 V vs. RHE as shown in Figure 3.11b and Figure

3.12, respectively. All photoelectrodes displayed current spikes, which is due to the slow OER kinetics. However, the current spike became smaller after decorating Au nanoparticles, indicating improved OER kinetics. After reaching steady-state, photocurrent density for TiO_2 , TiO_2/Au , $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$ and $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)/\text{Au}$ could reach $11 \mu\text{A}/\text{cm}^2$, $14 \mu\text{A}/\text{cm}^2$, $20 \mu\text{A}/\text{cm}^2$, and $32 \mu\text{A}/\text{cm}^2$, respectively. Furthermore, these photocurrents are highly repeatable during 10 on-off circles, indicating good photostability of the MOF-sensitized electrode under strong oxidizing environment.

To get a deeper understanding on the improved PEC water oxidation performance, electrochemical impedance spectroscopy was carried out to study the charge transfer processes across the electrode/electrolyte interface. Figure 3.13a shows the electrochemical impedance Nyquist plots. The semicircles in the Nyquist plot provide information on the charge transfer processes.^[117] From Figure 3.13a, it is clear that $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$ has a much larger charge transfer resistance at the electrode/electrolyte interface than TiO_2 . This observation should not be surprising as MOFs usually have poor electrocatalytic activities. By decorating Au nanoparticles on $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$, a reduction in diameter of the semicircle was noticed in the Nyquist plot, indicating improved charge transfer, which could be attributed to improved charge separation induced by LSPR of Au nanoparticles as well as enhanced water oxidation kinetics.

Figure 3.13 PEC performance of TiO_2 and sensitized TiO_2 nanowire arrays under visible light illumination ($\lambda > 420$ nm). (a) Nyquist plots. (b) IPCE curves.

Incident photon-to-current conversion efficiency (IPCE) test was further carried out to examine the current contributions. Figure 3.13b shows the IPCE spectra of TiO_2 and MOF-sensitized TiO_2 photoelectrodes, which match well with the results of UV-vis absorption (Figure 3.9f). In the wavelength region between 420 nm and 500 nm, $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$ shows an obvious enhancement of IPCE as compared to the pristine TiO_2 , due to improved visible light absorption of MIL-125(NH_2), resulting in enhanced overall PEC performance. Loading Au nanoparticles on $\text{TiO}_2/\text{MIL-125}(\text{NH}_2)$ creates an addition IPCE peak centered at 550 nm, arising from the LSPR absorption of Au. It is clear that modification of MIL-125(NH_2) and Au nanoparticles on TiO_2 nanowires significantly improves the visible light absorption and thus enhances the PEC water oxidation performance.

3.4 Conclusion

In summary, Ti-based MOFs have been demonstrated as promising photosensitizers for PEC water splitting. When applied as the photoanode for solar water oxidation, the photocurrent of TiO_2 nanowire photoelectrode could be improved by nearly 100% under visible light through sensitization with aminated Ti-based MOFs. By

coupling with plasmonic nanoparticles, the light absorption efficiency could be further improved due to the LSPR effect.

The advantages of using MOFs as photosensitizers are as following: first, the great chemical tailorability enables tuning of the optical and catalytic properties of MOFs at the molecular scale, which can benefit both the light absorption as well as catalytic reactions, second, the highly porous structure of MOFs can also be utilized to incorporate other functional molecules such as photosensitizers or molecular catalysts to work synergistically to improve the photocatalytic efficiency. Considering the diversity of MOFs, a large number of MOFs are expected to work as promising photosensitizers or photocatalysts for solar-driven energy conversion and/or environmental remediation.

Chapter 4

Ultra-Small Transition Metal Carbide Nanoclusters Encapsulated in N, S Co-doped Graphene for All-pH Hydrogen Evolution

Noble metal free catalysts with high catalytic activity and good durability have long been pursued as alternatives of noble metal catalysts for renewable energy technologies. This chapter introduce a facile one-step method to prepare ultra-small transition metal carbide nanoclusters encapsulated in N, S co-doped graphene as noble-metal-free electrocatalysts for all-pH hydrogen evolution. In which, high density MoC_{1-x} (2.8 nm) or WC_{1-x} (2.0 nm) nanoclusters are encapsulated in nanoporous N, S co-doped graphene matrix. Both catalysts exhibited excellent hydrogen evolution reaction (HER) catalytic activity and durability in a wide range of pH from 0 to 14.

4.1 Introduction

Hydrogen has been widely used in chemical industry for hydrogenation and ammonia production, and now is becoming one of the most promising alternative energy carriers to replace carbon-based fuels.^[136] Annual world demand of hydrogen keeps increasing, and approximately 500 billion cubic meters of hydrogen are produced every year.^[4] However, more than 90% of the hydrogen is still made from fossil fuels, such as natural gas or coal through steam reforming,^[5] which unavoidably generates CO₂ as a byproduct and is obviously not sustainable in a long term. As a result, alternative processes for hydrogen production have to be developed to meet the sustainable future for human beings.^[137]

Splitting of water provides a green and sustainable technique to generate molecular hydrogen in large scale, in which the hydrogen evolution reaction (HER) catalyst plays a crucial role in lowering the reaction activation barrier. Noble metals (e.g., Pt) show excellent catalytic activity for HER, but their practical application is greatly restricted due to their scarceness. Transition-metal carbides, especially molybdenum and tungsten carbides were found to possess similar d-band electronic density-of-states to that of noble metals^[88, 89] which were thus considered as promising noble-metal-free HER catalysts. In 2012, commercial molybdenum carbide micro particles were tested for HER, which showed unexpected high catalytic activity and durability.^[138] Since then, molybdenum/tungsten carbides have been widely studied as noble-metal-like HER catalysts for water splitting.

Traditional synthetic method for molybdenum/tungsten carbides involves pyrolysis and carburization at high temperatures (800-1100°C), which usually causes uncontrollable particle sintering and produces large particles with wide size distributions. Construction of nanostructured molybdenum/tungsten carbides with well-defined structures is critical for achieving good HER performance. Over the past few years, different morphologies such as porous MoC_x nano-octahedra^[90],

Mo₂C nanorod^[91], MoC_x nanoparticles with WC nanowires^[92], porous Mo₂C nanowires^[93], Mo₂C 2D nanosheets^[94], WC_x nanocrystals^[95], and WC_x 2D nanoflakes^[96] have been studied as HER catalysts and shown good activities with proper durability. But these strategies often require tedious and complicated synthesis steps.^[139]

To improve electrical conductivity, carbon nanomaterials such as graphitic C₃N₄^[140], graphene^[95, 141-144], 16 carbon nanotubes^[145, 146] and carbon nanofibers^[147] were used for the synthesis of XC_{1-x} (X = Mo or W) electrocatalysts. In which, carbon nanomaterials not only serve as the carbon source, but also act as the conductive support for XC_{1-x} nanoparticles, which provide both large surface area and high electrical conductivity that greatly enhance the HER performance. However, the XC_{1-x} nanoparticles on the carbon support often show large particle sizes and wide size distributions and the aggregation of XC_{1-x} nanoparticles during synthesis is unavoidable.

Herein, we report a facile one-step method to prepare ultra-small MoC_{1-x} (2.8 nm) and WC_{1-x} (2.0 nm) nanoclusters encapsulated in nanoporous N, S co-doped graphene. Both transition metal carbide catalysts show excellent HER activity and stability across a wide pH range from 0 to 14, which is attributed to the ultra-small size of the MoC_{1-x} and WC_{1-x} nanoclusters as well as the intimate interaction between the nanoclusters and the graphene support.

4.2 Experimental Section

4.2.1 Chemicals and Materials

All chemicals were purchased from Sigma-Aldrich and Alfa Aesar without further purification. Milli-Q water (resistivity over 18 MΩ·cm) from a Millipore Q water purification system was used to prepare the electrolyte and reaction solutions.

Commercial Pt/C (20 wt% Pt on Vulcan XC-72) was purchased from Premetek. Commercial molybdenum carbide (Mo_2C , 99%) was obtained from Sigma-Aldrich.

4.2.2 Preparation of Catalysts

4.2.2.1 Preparation of $\text{MoC}_{1-x}/\text{C}$ Catalyst

In a typical procedure, a mixture of melamine, L-cysteine and ammonium molybdate tetrahydrate with a mass ratio of 60: 1: 3 was first ball-milled into a homogeneous precursor. Subsequently, the well-mixed precursor was pyrolyzed in a tubular furnace under argon atmosphere. The calcination temperature was first increased from room temperature to 600 °C at a ramp rate of 5 °C/min, maintained at 600 °C for 2 h, and then slowly increased to 1000 °C at 2 °C/min and maintained at 1000 °C for another hour. After cooling down to room temperature under argon atmosphere, the final product was collected for subsequent characterization.

4.2.2.2 Preparation of WC_{1-x}/C Catalyst

For the preparation of WC_{1-x}/C catalyst, a mixture of melamine, L-cysteine and ammonium metatungstate hydrate with a mass ratio of 12: 1: 1 was first ball-milled into a homogeneous precursor. Following, the well-mixed precursor was pyrolyzed in a tubular furnace under argon atmosphere using the same ramping procedure as that used for preparation of $\text{MoC}_{1-x}/\text{C}$. To further tune the size of WC_{1-x} , an additional calcination step at 300, 350 or 400 °C for 30 min was conducted before increasing the temperature to 600 °C.

4.2.2.3 Preparation of N, S Co-doped Porous Graphene

Homogenously mixed melamine and L-cysteine were undergone a pyrolysis and carbonization process described before. After cooling down to room temperature under argon atmosphere, the final product was collected as N, S co-doped porous graphene.

4.2.3 Characterization

4.2.3.1 Materials Characterization

Transmission electron microscopy (TEM), dark-field scanning TEM (DF-STEM), elemental mapping measurements, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) characterization parameters are described in section 3.2.3.1. Size distribution was estimated using Nano Measurer 1.2 software. N₂-sorption isotherms were collected on a Quantachrome Instruments Autosorb AS-6B adsorption analyzer at -196 °C. Brunauer–Emmett–Teller (BET) surface area was calculated from adsorption data. Raman spectroscopy was performed in backscattering mode on a Renishaw inVia Raman microscope using a 514.5 nm laser. The laser power at the exit was 5 mW and the beam was focused on the sample using a 50X objective lens.

4.2.3.2 Electrochemical Measurements

Electrochemical measurements were carried out on an electrochemical workstation CHI 660E (CHI Instruments). Hydrogen evolution reaction (HER) activities were evaluated in a three-electrode configuration, using glassy carbon rotating disk electrode (5 mm in diameter) as the working electrode, a graphite rod and saturated calomel electrode (SCE, Hg/Hg₂Cl₂, CHI 150) as the counter and reference electrode, respectively. All potentials were normalized to reversible hydrogen electrode (RHE) scale using the following Nernst equation:

$$E_{RHE} = E_{Hg/Hg_2Cl_2} + 0.0591 \times pH + E^o_{Hg/Hg_2Cl_2} \quad (4-1)$$

where E^o_{Hg/Hg_2Cl_2} is the standard potential of saturated calomel electrode at 25 °C (0.241 V vs. RHE). Three electrolytes were prepared to evaluate the catalytic activities of the as-prepared catalysts, including 0.5 M H₂SO₄ (pH = 0.4), 0.2 M PBS (pH = 7), and 1 M NaOH (pH = 13.5).

To prepare the working electrode: 10 mg of catalyst was first dispersed in 1 mL of pre-mixed solvent (isopropanol/ethanol = 1/1, volume ratio), followed by adding 10 μL of 5 wt% Nafion solution. The mixture was then ultrasonicated for at least 1 h to form a homogeneous dispersion. Afterwards, 3 to 12 μL of the catalyst ink was drop-casted onto a glassy carbon electrode (GCE) with a diameter of 5 mm, and left to dry in air, which gave a catalyst loading of 0.15 to 0.6 mg/cm^2 on GCE.

Linear sweep voltammograms (LSVs) were conducted at a scan rate of 2 mV/s. Tafel slope was calculated using the following Tafel equation:

$$\eta = a + b \log j \quad (4-2)$$

where η is the overpotential, b is the Tafel slope, and j is the current density. The onset potential was determined based on the starting point of the linear region in the Tafel plot. All data were corrected for an Ohmic drop ($\sim 4 \Omega$ for 0.5 M H_2SO_4 and 1 M NaOH electrolyte, $\sim 40 \Omega$ for 0.2 M PBS solution). To avoid possible cross contamination, newly prepared electrolyte was always used for each electrochemical measurement.

Faradaic efficiency was estimated using volumetric method. The actual-evolved hydrogen gas on electrode was collected in a 15 ml graduated tube, which was filled with the electrolyte. Potential controlled electrolysis was carried out at 10 mA for 200 min under standard conditions (25 $^\circ\text{C}$ and 1 atm). The gas volume at each 20 min was recorded. Meanwhile, the accumulated charges passing through the working electrode were recorded using electrochemical workstation. To determine the composition and purity of evolved gas, the collected gas was sampled with a Hamilton syringe and then analyzed using gas chromatograph (GC, Agilent GC490). From the GC spectra, hydrogen was the only detectable gaseous product.

To evaluate the durability of the catalyst, $\text{MoC}_{1-x}/\text{C}$ and WC_{1-x}/C inks were prepared and loaded on a carbon cloth with a catalyst loading of 0.3 mg/cm^2 .

Chronoamperometric curves were recorded at constant overpotentials in different electrolytes.

4.3 Results and Discussion

Molybdenum carbide nanoclusters encapsulated in N, S co-doped graphene ($\text{MoC}_{1-x}/\text{C}$) were synthesized by a one-step calcination of premixed molybdenum precursor with melamine and L-cysteine in an inert atmosphere (Scheme 4.1). At the first stage (from 200 to 600 °C), the molybdenum precursor, ammonium molybdate, decomposed to form MoO_x , meanwhile, melamine was polymerized to form C_3N_4 with S doping from L-cysteine. The newly formed S-doped C_3N_4 served as the soft template, which prevents aggregation of the MoO_x nanoparticles and thereby enables their uniform distribution. Further increase in calcination temperature led to carbonization of S-doped C_3N_4 to form N, S co-doped graphene, and meanwhile the S-doped C_3N_4 provided the carbon source for carbonization of MoO_x to form MoC_{1-x} nanoclusters.

Scheme 4.1 A schematic illustration showing the synthesis process of $\text{MoC}_{1-x}/\text{C}$ catalyst.

4.3.1 Characterization of $\text{MoC}_{1-x}/\text{C}$ catalyst

Figure 4.1a displays a typical high-resolution transmission electron microscope (HRTEM) image of as-prepared $\text{MoC}_{1-x}/\text{C}$, from which high density MoC_{1-x} nanoclusters with ultra-small size uniformly encapsulated in graphene can be clearly observed. The measured lattice fringes with lattice spacings of 0.25 and 0.19 nm can

be assigned to the (100) and (101) planes of hexagonal γ -MoC, while lattice distances of 0.22 and 0.23 nm are originated from the (231) and (103) facets of β -Mo₂C and η -MoC, respectively. MoC_{1-x} nanoclusters are uniformly embedded in lamellar graphene (as indicated by the black arrows in Figure 4.1a), and the porous structure of the graphene support is clearly observable (Figure 4.1b). The average diameter of MoC_{1-x} nanoclusters was calculated to be around 2.8 nm with a narrow size distribution (Figure 4.1c). Figure 4.1d-h show the dark-field scanning transmission electron microscope (DF-STEM) image as well as the corresponding EDX elemental mapping of the as-prepared MoC_{1-x}/C, which reveals uniform distribution of the Mo, C, N, and S elements, suggesting the uniform distribution of MoC_{1-x} nanoclusters on graphene as well as N, S co-doped graphene support.

Porous structure of graphene can be clearly observed from Figure 4.1b, which was attributed to the sulfur doping in C₃N₄ formation. During the first pyrolysis step, the thiol groups on L-cysteine covalently bonded with the newly formed C₃N₄ plane via the formation of -C-S-C- bonds, probably through a radical mechanism, because the thiol groups on L-cysteine are highly reactive and susceptible to hydrogen extraction by free radicals.^[148] This insertion of L-cysteine moieties provide steric hindrances, which impeding the extension of the 2D C₃N₄ plane, thus form the porous C₃N₄ nanostructure, and finally results in the porous graphene after carbonization. This was further confirmed by the TEM images and N₂-sorption isotherms of samples prepared with and without L-cysteine (Figure 4.2). Graphene tend to growing into continuous sheet without pores when the L-cysteine precursor was absence (Figure 4.2b). Sample prepared with L-cysteine precursor exhibited N₂ isotherm close to type IV with hysteresis loops (Figure 4.2c), suggesting its porous structure. While a narrow pore-size distribution between 3-5 nm and wide pore size distribution between 10-100 nm is observed from Figure 4.2d, which suggesting the coexistence of meso and macropores, confirming the porous structure of MoC_{1-x}/C

catalyst prepared with L-cysteine precursor. In the contrary, without L-cysteine precursor, no clear peaks with significant pore volume were observed, revealing its non-porous structure.

Figure 4.1 HRTEM and TEM image (a & b), size distribution (c), DF-STEM image (d), and the corresponding EDX-mapping (e, red, purple, green and yellow for C, Mo, N and S element, respectively) of MoC_{1-x}/C.

Figure 4.2 TEM images of $\text{MoC}_{1-x}/\text{C}$ catalysts prepared with (a) or without (b) L-cysteine precursors. N_2 -sorption isotherms (c) and pore distribution (d) of $\text{MoC}_{1-x}/\text{C}$ catalysts prepared with or without L-cysteine precursors.

The structure and composition of $\text{MoC}_{1-x}/\text{C}$ were further examined by powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). XRD pattern (Figure 4.3a) indicates that the MoC_{1-x} nanoclusters compose of a mixture of γ -MoC (JCPDS #04-007-4120), η -MoC (JCPDS #04-002-6881) and β -Mo₂C (JCPDS #00-045-1013). γ -MoC, η -MoC and β -Mo₂C have very similar hexagonal crystal structures with different stacking sequences.^[149] The large full width at half maximum (FWHM) of the XRD peak indicates very small sizes of the MoC_{1-x}

nanoclusters, consistent with the TEM measurement (Figure 4.1a and b). XPS survey spectra (Figure 4.3b) show peaks from Mo 3d, Mo 3p, Mo 4p, C 1s, S 2p, while the N 1s peak overlaps with the Mo 3p peak. To reveal the chemical status of MoC_{1-x} , high-resolution Mo 3d and C 1s spectra were collected. As displayed in Figure 4.3c, Mo 3d spectrum splits into $3d_{5/2}$ and $3d_{3/2}$ peaks resulting from the spin-orbital coupling feature. The oxidation state of Mo varies from 0 to +6 with both Mo-Mo and Mo-C bonds present in the molybdenum carbide structure, which gives complicated chemical states of Mo in MoC_{1-x} . According to literature^[4, 149], 0, +3, +4, +6 are the most common oxidation states of molybdenum in molybdenum carbide. High-resolution XPS spectrum of Mo 3d was thus de-convoluted into four Mo 3d doublets, corresponding to different oxidation states of Mo, in which, metallic Mo^0 is dominant, which should originate from the Mo-Mo bond in molybdenum carbide. Both presences of the Mo-Mo and Mo-C bonds in molybdenum carbide explain the low oxidation states of Mo^{3+} and Mo^{4+} . A small portion of Mo^{6+} was also observed, which could be due to the slight surface oxidation of MoC_{1-x} .^[4, 150] The XPS spectrum of C 1s can be deconvoluted into carbidic C from molybdenum carbide and C-C, C-N, C=N and C-O from the graphene support.

Figure 4.3 Characterization of as-prepared $\text{MoC}_{1-x}/\text{C}$ catalyst. (a) XRD spectra, (b) XPS spectra, (c, d) high-resolution XPS scan of Mo 3d (c), C 1s (d) core level.

N 1s and S 2p high-resolution XPS spectra were also collected to reveal the chemical status of dopants in graphene (Figure 4.4). As shown in Figure 4.4a, N doping mainly originates from pyridinic-N and pyrrolic-N. The S 2p spectrum could be deconvoluted into two peaks of C-SO₂ and C-SO₃ (Figure 4.4b). No signal appeared at 160 to 164 eV, which is usually assigned to the C-S-C or Mo-S peak, suggesting that sulfur atoms were doped in graphene with high oxidation states, which is consistent with our previous study.^[148]

Figure 4.4 N 1s core level (a) and S 2p core level (b) XPS spectrum of MoC_{1-x}/C catalyst.

4.3.2 HER Catalytic Activity of MoC_{1-x}/C Catalyst

The electrocatalytic activity of the as-prepared MoC_{1-x}/C was evaluated on glassy carbon electrode by linear sweep voltammetry (LSV). For comparison, commercial 20 wt% Pt/C, commercial Mo₂C and N, S co-doped graphene were also tested. Catalyst loading on glassy carbon electrode was optimized to 0.45 mg/cm² (Figure 4.5a).

To optimize the catalyst performance, MoC_{1-x}/C samples were prepared with different ratio of Mo, melamine precursors with fixed L-cysteine amount. LSV curves of these catalysts for HER is shown in Figure 4.5b. Onset of HER decrease along with the Mo: melamine precursor ratio until 1: 20, then increase again. This is reasonable because the Mo precursor amount lead to different MoC_{1-x} nanoparticles ratio in the final product, while too much MoC_{1-x} nanoparticles with less graphene support would decrease the charge transfer within the materials thus suppress the catalytic activity. Mo: melamine precursor ratio of 1:20 was selected to synthesis following MoC_{1-x}/C catalyst.

Figure 4.5 LSV curves of $\text{MoC}_{1-x}/\text{C}$ catalyst in 0.5 M H_2SO_4 with different catalyst loading amount (a), 0.45mg/cm² loading showed the best performance thus used for all catalyst evaluation on glassy carbon. . LSV curves of $\text{MoC}_{1-x}/\text{C}$ catalyst prepared with different precursor ratio in 0.5 M H_2SO_4 (b). Scan rate: 2mV/s.

Figure 4.6 show the LSV curves (a) and the corresponding Tafel plots (b) for various catalysts in 0.5 M H_2SO_4 . Among which, $\text{MoC}_{1-x}/\text{C}$ exhibits a very low onset potential at 60 mV vs. RHE with cathodic current density increasing rapidly at more negative potentials, reaching a current density of 10 mA/cm² at only 135 mV vs. RHE in acidic electrolyte, while N, S co-doped graphene and commercial Mo_2C show very large onset potential and slow current density rise. The $\text{MoC}_{1-x}/\text{C}$ catalyst gives a Tafel slope of 62 mV/decade in acidic electrolyte, suggesting that HER on molybdenum carbide catalyst is rate limited at the proton desorption step.

Figure 4.6 HER performance of as-prepared $\text{MoC}_{1-x}/\text{C}$ catalyst in 0.5M H_2SO_4 solution. (a) LSV curves of $\text{MoC}_{1-x}/\text{C}$ and commercial 20 wt% Pt/C, commercial Mo_2C and N, S co-doped graphene, scan rate is 2 mV/s. (b) relative Tafel plots of $\text{MoC}_{1-x}/\text{C}$ and controls. (c) Measured hydrogen production versus theoretical value on $\text{MoC}_{1-x}/\text{C}$ electrode at 10 mA/cm^2 current density for 200min. (d) chronoamperometric curves of $\text{MoC}_{1-x}/\text{C}$ catalyst recorded at a constant overpotential of 130 mV in 0.5M H_2SO_4 solution up to 33h.

Faradaic efficiency of $\text{MoC}_{1-x}/\text{C}$ was examined in 0.5 M H_2SO_4 by volumetric method. The actual volume of hydrogen product was plotted against the theoretical value as shown in Figure 4.6c, which gives a nearly 100% Faradaic efficiency for the $\text{MoC}_{1-x}/\text{C}$ catalyst. Besides, stability is a very important consideration to evaluate a catalyst. Figure 4.6d shows a chronoamperometric curve of $\text{MoC}_{1-x}/\text{C}$ recorded at a constant overpotential of 130 mV in 0.5 M H_2SO_4 . The current density maintains

94% of the initial value after 33 hours of continuous operation, indicating outstanding durability of the $\text{MoC}_{1-x}/\text{C}$ catalyst.

Figure 4.7 HER performance of as-prepared $\text{MoC}_{1-x}/\text{C}$ catalyst in neutral and alkaline solution. LSV curves (a) and relative Tafel plots (b) of $\text{MoC}_{1-x}/\text{C}$ and controls (commercial 20 wt% Pt/C, commercial Mo_2C , and N, S co-doped graphene) in 0.2M PBS solution, pH value is 7, scan rate is 2mV/s. LSV curves (c) and relative Tafel plots (d) of $\text{MoC}_{1-x}/\text{C}$ and controls in 1M NaOH solution, pH value is 13.5, scan rate is 2mV/s.

For overall water splitting, oxygen evolution reaction (OER) as the other half reaction typically requires lower overpotential with more choices of catalysts in alkaline medium, thus it becomes essential to develop high-performance noble-metal-free HER catalysts that can be operated across a wide range of pH. Towards this goal, we further examined the HER performance of the as-prepared $\text{MoC}_{1-x}/\text{C}$ catalyst in neutral 0.2 M PBS (pH = 7) and alkaline 1 M NaOH (pH = 13.5)

electrolyte. The $\text{MoC}_{1-x}/\text{C}$ catalyst displays decent HER catalytic activity (Figure 4.7) with nearly 100% faradaic efficiency (Figure 4.8) and good stability (Figure 4.9) in both neutral and alkaline environment, rendering it an excellent noble-metal-free HER catalyst across all pH.

Figure 4.8 Measured hydrogen production versus theoretical value on $\text{MoC}_{1-x}/\text{C}$ electrode at $10\text{mA}/\text{cm}^2$ current density for 200min in 0.2M PBS solution (a, pH=7) and 1M NaOH solution (b, pH=13.5).

Figure 4.9 Chronoamperometric curves of $\text{MoC}_{1-x}/\text{C}$ catalyst recorded at a constant overpotential of 150 mV in 0.2M PBS solution and 140 mV in 1M NaOH solution up to 25h.

The outstanding HER performance of the $\text{MoC}_{1-x}/\text{C}$ catalyst can be attributed to the following three factors. Firstly, the ultra-small size of the MoC_{1-x} nanoclusters allows

exposing much more catalytically active sites for $\text{MoC}_{1-x}/\text{C}$ as compared to commercial Mo_2C microparticles. Secondly, the intimate interaction between the MoC_{1-x} nanoclusters and the N, S co-doped graphene matrix permits extraction of electrons from MoC_{1-x} to N, S co-doped graphene because of the strong electron-withdrawing capability of N and S dopants (Figure 4.10), rendering a positive charged surface of MoC_{1-x} , which down-shifts the d-band center of MoC_{1-x} ^[151,4] and thus decreases the Mo–H binding strength and enhances the HER activity of $\text{MoC}_{1-x}/\text{C}$. Finally, the excellent conductivity of porous graphene matrix not only enables fast electron transport in the electrode, but also provides a three-dimensional diffusion channel, which collectively benefit the HER.

Figure 4.10 Comparison of Raman spectrum before and after encapsulating MoC_{1-x} nanoclusters in N, S co-doped graphene.

4.3.3 Characterization and HER Catalytic Activity of WC_{1-x}/C Catalyst

The method developed in this work is very general in preparing transition-metal carbide/graphene composite. For example, by replacing the molybdenum precursor with the tungsten precursor, WC_{1-x} nanoclusters encapsulated in N, S co-doped graphene (WC_{1-x}/C) could be synthesized.

Figure 4.11 (a & b) HRTEM and TEM image of WC_{1-x}/C. Inset in (b) shows the size distribution of WC_{1-x} nanoclusters. (c) XRD pattern. (d) Comparison of LSV curves of WC_{1-x}/C (solid line), N, S co-doped graphene (dashed line) and commercial Pt/C (dotted line) in 0.5 M H₂SO₄ (black), 0.2 M PBS (red) and 1M NaOH (blue). Scan rate: 2mV/s.

Figure 4.11a-b showed the TEM images of as-prepared WC_{1-x}/C sample. From the HRTEM image (Figure 4.11a), WC_{1-x} nanoparticles uniformly distributed in lamellar graphene can be observed. The lattice distance of 0.24nm and 0.25nm can be assigned to (002) facet of α -W₂C and (100) facet of α -WC respectively. Low magnification TEM image (Figure 4.11b) shows the porous graphene structure which were formed due to heteroatom doping. Ultra-small WC_{1-x} nanoparticles were found embedded in the porous graphene with very high density. The average

diameter of WC_{1-x} nanoparticles was calculated to be 2 nm with narrow size distribution (1.2 to 2.8 nm). XRD pattern (Figure 4.11c) of as-prepared WC_{1-x}/C sample revealed the largely widening peaks which consistent with the ultra-small size of nanoparticles. α -WC (JCPDS #01-077-8462) and α - W_2C (JCPDS #00-002-1134) with hexagonal crystalline structure were found to be the products in the as-prepared composite.

Figure 4.12 DF-STEM image (a) and relative EDX-mapping (e, red, purple, green and yellow for C, W, N and S elements respectively) of WC_{1-x}/C catalyst.

DF-STEM image and EDX elemental mapping of as-prepared WC_{1-x}/C sample are shown in Figure 4.12, which revealed uniformly distributed W, C, N, S atoms,

suggesting the uniform dispersion of WC_{1-x} nanoparticles in N, S co-doped porous graphene.

Figure 4.13 (a) Tafel plots of WC_{1-x}/C catalyst in 0.5 M H_2SO_4 (black), 0.2 M PBS (red) and 1 M NaOH solution (blue). (b) Chronoamperometric curves of WC_{1-x}/C catalyst recorded at a constant overpotential of 150 mV in 0.5 M H_2SO_4 , 200 mV in 0.2 M PBS solution and 250 mV in 1 M NaOH solution up to 25h.

HER catalytic activity of WC_{1-x}/C sample was also evaluated. The as-prepared samples were tested in 0.5M H_2SO_4 (pH 0.4), 0.2M PBS (pH 7), 1M NaOH (pH13.5) respectively, results are shown in Figure 4.11d and Figure 4.13. The as-prepared WC_{1-x}/C catalyst showed great catalytic activity in acidic electrolyte with 70 mV onset potential, and 154mV overpotential for 10mA/cm^2 current density, a Tafel slop of 65 mV/decade revealing the fast reaction kinetics (Figure 4.13a). In neutral and alkaline electrolyte, the onset potential for HER on WC_{1-x}/C catalysts were 86 mV, 132 mV respectively. To obtain a current density of 10mA/cm^2 , 220 mV and 262 mV overpotential were needed in neutral and alkaline electrolyte respectively. Tafel slops of 110 mV/decade and 115 mV/decade respectively suggested proton desorption as the rate-determining step.

To evaluate the stability of WC_{1-x}/C , chronoamperometric curves were recorded at constant overpotentials in solutions with different pH (Figure 4.13b), results showed stable current densities and 84%, 78%, 80% of current were maintained after 25h in acidic, neutral and alkaline electrolytes respectively.

Interestingly, the size of nanoparticles embedded in graphene can be tuned by modifying the typical pyrolysis protocol. A series of WC_{1-x}/C samples was synthesized and characterized. The final particle size of WC_{1-x} in the composite is decided by the size of intermediate WO_3 nanoparticle. In an inert atmosphere, ammonia metatungstate decomposed to WO_3 at 250-380°C^[152, 153], thus an additional calcination step at 300°C, 350°C or 400°C for 30min was conducted before ramp up to 600°C, and then follow the typical calcination protocol. The samples are denoted as WC_{1-x}/C -300, WC_{1-x}/C -350 and WC_{1-x}/C -400 respectively.

Figure 4.14 shows the TEM images of pre-described WC_{1-x}/C samples with three additional samples. The average sizes of WC_{1-x} nanoparticles were calculated to be 2nm, 6nm, 20nm, 40nm respectively.

Figure 4.14 TEM images and the size distribution (inset) of WC_{1-x}/C catalyst with different particle size, (a) WC_{1-x}/C , (b) $WC_{1-x}/C-300$, (c) $WC_{1-x}/C-350$, (d) $WC_{1-x}/C-400$.

Catalytic activities of these samples have also been evaluated and shown in Figure 4.15. Results showed that along with the increasing of nanoparticle size, onset potential increased from 70 to 200mV, and current density decreased dramatically. This activity varying from nanoparticle size is reasonable since the size of catalyst decide the surface catalytic active sites.

Figure 4.15 HER performance of WC_{1-x}/C catalyst with different particle size, LSV curves of as-prepared WC_{1-x}/C (a), $WC_{1-x}/C-300$ (b), $WC_{1-x}/C-350$ (c), $WC_{1-x}/C-400$ (d) and N, S co-doped graphene control in 0.5M H_2SO_4 , scan rate is 2mV/s.

Figure 4.16 shows the photograph of as-synthesized catalysts, with the great catalytic activities in a wide pH range, the catalysts are of great promising in various applications.

Figure 4.16 Digital photograph of N, S co-doped graphene, MoC_{1-x}/C and WC_{1-x}/C catalysts.

4.4 Conclusion

In summary, we have developed a general one step method to prepare ultra-small transition-metal carbide nanoclusters encapsulated in N, S co-doped graphene as noble-metal-free electrocatalysts for all pH hydrogen evolution. The ultra-small size of transition-metal carbide nanoclusters provides lots of catalytically active sites. The intimate interaction between transition-metal carbide nanoclusters and N, S co-doped graphene modifies the binding strength of H on transition-metal carbides. The porous graphene supports enable quick charge transport and fast reactant/product diffusion. All of which contribute simultaneously, giving rise to the excellent HER performance of the transition-metal carbide/graphene composite catalysts.

Chapter 5

Sustainable Hydrogen and Chemicals Production via Photoelectrochemical Reforming of Biomass-Derived Alcohols

Simultaneous hydrogen and chemicals production without emitting CO₂ at room temperature via photoelectrochemical reforming of biomass-derived alcohols has been developed in this chapter. Hydrogen quantum efficiencies reach around 80% across the entire visible solar spectrum from 450 to 850 nm, achieving an ultrahigh hydrogen production rate of 7.91 $\mu\text{mol min}^{-1} \text{cm}^{-2}$ illumination area under AM 1.5G illumination.

5.1 Introduction

Hydrogen is not only widely used in the chemical industry for ammonia production and hydrogenation, but also projected as one of the most promising long-term sustainable clean energy carrier.^[136] Based on Freedonia's study in 2014, the annual world demand of hydrogen is increasing by 3.5%, and projected to be more than 300 billion m³ in 2018. However, till now, more than 90% of hydrogen is still produced from fossil fuels, such as natural gas or coal through steam reforming^[5], which unavoidably produces CO₂ as a byproduct. As a result, alternative processes for hydrogen production have to be developed to meet the sustainable future for human beings.^[137] Hydrogen production from renewable biomass is highly promising because of the abundant natural resources.^[154-157] However, the production of hydrogen directly from biomass such as sugar, starch, or crop waste is challenging.^[158] The production of hydrogen from sugar through catalytic reaction has been demonstrated, but only 50% selectivity towards H₂ could be achieved.^[159, 160] Alternatively, bio-alcohol, the main product from biomass fermentation, provides a more promising resource for hydrogen production.^[161-165]

Both steam reforming and autothermal reforming of bio-alcohols have been studied for hydrogen production,^[162, 166, 167] but these processes generally require complex equipment and high temperature (from 573 K to 1073 K).^[163] Additionally, CO₂ emission could not be avoided. The presence of CO in produced hydrogen further limits the applications of alcohol reforming in areas that need pure hydrogen, for instance, the proton exchange membrane (PEM) fuel cells.^[159]

Herein, we present a new strategy for solar-to-hydrogen conversion via photoelectrochemical reforming of biomass derived alcohols. Bio-ethanol obtained from fermentation of biomass contains a mixture of ethanol and water with a low ethanol concentration ranging from 5 to 97 g/L (or 0.11 to 2.1 mol/L)^[168], which requires multi-step purification to reach the concentration for practical usage such as

in steam reforming of ethanol. But, it is sufficient to produce pure hydrogen in our system.

Ethanol (the main product of biomass fermentation) is oxidized to acetate with a 4-electron reaction on anode, while water is reduced to produce hydrogen on cathode, Eq. 5-1 to 5-3 describe the anode, cathode and overall reactions respectively. Since ethanol oxidation requires very low potential (< 1 V),^[169] high solar-to-hydrogen efficiency is expected to obtain.

5.2 Experimental Section

5.2.1 Chemicals and Materials

All chemicals were purchased from Sigma-Aldrich without further purification. Milli-Q water (resistivity over 18 MΩ cm) from a Millipore Q water purification system was used to prepare the electrolyte and reaction solutions. Ni foam (10 × 10 cm²) was purchased from Latech Scientific Supply, Singapore. The ion-exchange membrane (Selemion, AMV 160 mm × 280 mm) was purchased from AGC engineering, Japan. Single-junction GaAs thin-film solar cell was supplied by Alta device, USA. Band-pass filters (± 5 nm) centered at 400, 500, 600, 694, 800 and 855 nm were purchased from Edmund Optics, Singapore.

5.2.2 Preparation of Catalysts

5.2.2.1 Preparation of NiP_x/Ni foam cathode

NiP_x/Ni foam cathode was prepared by cathodic electrodeposition in a three-electrode electrochemical cell at room temperature. The electrolyte contained 0.1 M

NiSO₄, 0.3 M NaH₂PO₂, 0.15 M H₃BO₃ and 0.1 M NH₄Cl. Constant current density electrodeposition was carried out at 10 mA/cm² for 300 s. After deposition, the NiP_x/Ni foam electrode was rinsed with ethanol and deionized water and then dried under vacuum.

5.2.2.2 Preparation of Pd/Ni foam anode

Pd/Ni foam anode was prepared by galvanic replacement reaction. Firstly, Ni foam was washed in a mixed solution of deionized water: ethanol: acetone (1: 1: 1) three times, followed by immersing in 1 wt% HCl solution for 5 min under sonication. After further washed in deionized water, the cleaned Ni foam was dried by N₂. 4 pieces of Ni foam were then immediately immersed into 2 mL of PdCl₂ solution with 1 wt% HCl for 1 min; different concentrations of PdCl₂ solution (0.05 mg/mL, 0.1 mg/mL, 0.15 mg/mL, 0.2 mg/mL, and 0.3 mg/mL) were used to prepare Pd/Ni foam-1 to 5 samples, respectively.

5.2.3 Characterization.

5.2.3.1 Materials Characterization

X-ray diffraction (XRD), Field emission scanning electron microscope (FESEM) Energy dispersive X-ray spectroscopy (EDS), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) characterization were described in section 3.2.3.1.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was conducted on a Prodigy ICP Spectrometer with argon as the carrier gas. Pd/Ni foam sample (1×1 cm²) was heated in a vial containing 1 mL of concentrated HCl on a hotplate. After complete dissolution of Ni foam, concentrated HNO₃ (60 μL) was added to dissolve Pd particles. The solution was then diluted and undergone for ICP-OES test.

5.2.3.2 Determination of Ethanol Oxidation Products

The products after ethanol oxidation on Pd/Ni foam anode were analyzed by high-performance liquid chromatography (HPLC, Agilent 1260) with Hi-Plex H (300×d-7 mm, 8 μm) column from Agilent. The temperature of the column was maintained at 35 °C with diluted sulfuric acid (50 mM) used as the eluent. 2 μL of sample solution was injected into the column and the separated compounds were detected with a refractive index detector. A three-electrode configuration was used for the ethanol oxidation production test. Electrolyte contained 2 M NaOH and 2 M ethanol. A Pt plate and saturated calomel electrode (SCE, Hg/Hg₂Cl₂) were used as the counter and reference electrode, respectively. Oxidation of ethanol was conducted at -0.3 V vs. SCE. Each run of test lasted 3 h and 4 mL of solution was taken out after each run and then sent for HPLC measurement. Faradaic efficiency (FE) was calculated based on the following equation:

$$FE = \frac{4 \cdot n \cdot e \cdot N_A}{Q} \quad (5-4)$$

where 4 is the number of electrons transferred during ethanol oxidation to acetate, n is moles of product, e represents the elementary charge, N_A is Avogadro's constant, Q is the charge transferred via external circuit.

5.2.3.3 Electrochemical characterization.

Electrochemical measurements were carried out on an electrochemical workstation CHI 660E (CHI Instruments). Hydrogen evolution reaction (HER) activities were evaluated in a three-electrode configuration, using as-prepared electrode ($1 \times 1 \text{ cm}^2$) as the working electrode with a graphite rod as the counter electrode and a saturated calomel electrode (SCE, CHI 150) as the reference electrode. 50 mL of 2 M NaOH aqueous solution was used as the electrolyte. The potential was normalized to RHE as described before. The gas product was analyzed by a gas chromatography (Agilent GC 490).

Alcohol oxidation activities of Pd/Ni foam electrodes were also tested in a three electrode configuration. The electrolyte containing 2 M NaOH and 2 M alcohol was purged with N₂ for at least half an hour before being used. Working electrodes were scanned for 10 cycles at a scan rate of 100 mV/s before recording the CV data in the potential range of -0.8 to 0.3 V (vs. SCE) at a scan rate of 10 mV/s.

Electrochemical alcohol reforming activities were evaluated in a two-electrode configuration, applying the Pd/Ni foam electrode as the anode and NiP_x/Ni foam electrode as the cathode in a home-made H-cell filled with 2 M NaOH in the cathode compartment and 2 M NaOH + 2 M alcohol in the anode compartment. Anion-exchange membrane (AGC engineering) was used to separate the anode from the cathode. For ethanol oxidation, 1 × 1 cm² Pd/Ni foam and 1 × 1 cm² NiP_x/Ni foam electrodes were used. For the rest of alcohols, 2 × 2 cm² Pd/Ni foam and 1 × 1 cm² NiP_x/Ni foam were adopted.

A single junction GaAs solar cell purchased from Alta device, USA was connected to the NiP_x/Ni foam cathode and Pd/Ni foam anode to power the alcohol reforming device without applying external bias. Solar cell was illuminated with AM 1.5G illumination (100 mW cm⁻²) using a non-reflective aperture of 0.226 cm² to define the active area. The geometric catalyst electrode area for Pd/Ni foam and NiP_x/Ni foam are 1 × 1 cm². The current was recorded by chronoamperometry for different time periods under chopped or continuous illumination. Incident photon to current conversion efficiency (IPCE) of the GaAs solar cell was measured using a photovoltaic spectral response system (PVE300, Bentham) illuminated with dual Xenon/quartz halogen light source. For measuring the incident photon to hydrogen conversion efficiency (IPHE), band-pass filters (Edmund Optics, Singapore) were added in the light path between light source and solar cell. Current of the solar cell with and without connecting to the catalyst electrodes were recorded. Taking the HER Faradaic efficiency into account, IPHE could thus be estimated based on:

$$IPCE(\lambda) = \left(\frac{h \cdot c}{\lambda \cdot e} \right) \times \frac{J(\lambda)}{P(\lambda)} \times 100\% \quad (5-5)$$

$$IPHE(\lambda) = IPCE(\lambda) \times \frac{J_{H_2}(\lambda)}{J(\lambda)} \times FE \times 100\% \quad (5-6)$$

where h is the Planck's constant; c is the speed of light; e is the elementary charge; $J(\lambda)$ and $J_{H_2}(\lambda)$ are the current density of solar cell under illumination without and with connecting to the catalyst electrodes; $P(\lambda)$ is the power density of incident light and FE is the Faradaic efficiency for hydrogen evolution reaction, which was tested using the volumetric method as described before.

5.3 Results and Discussion

5.3.1 Characterization and Electrochemical Activity of Electrodes

The hydrogen evolution cathode was prepared by electrochemical deposition of amorphous NiP_x on Ni foam. Nickel (Ni) foam was used as the electrode to support the catalysts, which ensures porous three-dimensional structure for high catalyst loading as well as easy diffusion of reactants and products. FESEM image (Figure 5.1a) shows the uniform deposition of NiP_x on Ni foam. XRD patterns (Figure 5.1b) show no obvious peaks except pristine Ni foam which confirm the amorphous nature of NiP_x on Ni foam. XPS spectra of Ni (Figure 5.1c) shows the Ni²⁺ of nickel phosphide and Ni⁰ from Ni foam. Phosphide was confirmed from the XPS spectra of P shown in Figure 5.1d.

Faradaic efficiency of hydrogen evolution is measured to be 97% (Figure 5.1e). The stability of NiP_x/ Ni foam cathode was tested with commercial Pt/C as control (Figure 5.1f) shows much better stability of NiP_x/ Ni foam.

Figure 5.1 Characterization of Ni_xP/Ni foam cathode. (a) FESEM images, (b) XRD spectra, (c) Ni 2p and (d) P 2p XPS spectra of Ni_xP/Ni foam electrode. (e) Faradaic efficiency of hydrogen evolution measured at constant current in a two-electrode configuration with the anion-exchange membrane separating the anode and the cathode. (f) Stability test for Ni_xP/Ni foam cathode in 2 M NaOH, inset: stability test for commercial Pt/C loaded on Ni foam in 2 M NaOH.

Figure 5.2 Characterization of Pd/Ni foam anode. FESEM images of (a) Ni foam, (b) Pd/Ni foam-1, (c) Pd/Ni foam-2, (d) Pd/Ni foam-3, (e) Pd/Ni foam-4, and (f) Pd/Ni foam-5. EDS mapping of Pd/Ni foam-4 (g & h), g for Ni and h for Pd.

Figure 5.3 XRD patterns of different Pd/Ni foam samples.

Alcohol oxidation anode was prepared by a galvanic replacement reaction on Ni foam. The reason for selecting Pd as the catalyst instead of Pt is that Pd favors the partial oxidation of alcohol ^[170], which can convert alcohols into useful chemicals instead of CO₂. The loading amount of Pd on Ni foam was optimized by changing the concentration of PdCl₂ precursor solution.

FESEM images (Figure 5.2a-f) show the uniform deposition of Pd nanoparticles on Ni foam after galvanic replacement reaction, and XRD patterns (Figure 5.3) confirm the cubic Pd on Ni foam. Based on the inductively coupled plasma optical emission spectrometry (ICP-OES) measurements, the Pd loading amount on Pd/Ni foam-1 to 5 samples were determined to be 0.15, 0.3, 0.45, 0.6 and 0.9 mg/cm², respectively.

Figure 5.4 Performance of Pd/Ni foam anode. (a) CV curves of ethanol oxidation in 2 M NaOH with different ethanol concentrations obtained at a scan rate of 10 mV/cm². (b) CV curves of ethanol oxidation in 2 M ethanol with different NaOH concentrations obtained at a scan rate of 10 mV/cm².

The reaction mechanism for ethanol electrocatalytic oxidation is rather complex involving several adsorbed intermediates and yet remained unclear.^[170] Typical CV curve of ethanol oxidation on Pd electrode (Figure 5.4) shows an oxidation peak in the forward scan, after reaching the peak potential, current density decreased due to loss of active sites, which can be attributed to the oxidation of Pd and/or the strong

attachment of reaction intermediates (known as catalyst poisoning), while in the reverse scan, another oxidation peak appears along with the reduction of PdO_x and/or the detachment of reaction intermediates. The onset potential of ethanol oxidation in alkaline electrolyte is about -0.5V vs SCE (0.5V vs RHE), which is far less than the water oxidation potential (larger than 1.23V vs RHE), showing the great thermodynamic advantage compared to water oxidation. As reaction substrates, increasing concentrations of ethanol and NaOH leads to increased current density (Figure 5.4a-b). The optimal concentrations were found to be 2 M for both ethanol and NaOH.

5.3.2 Photoelectrochemical Reforming of Biomass-Derived Alcohols

Our new solar-to-hydrogen system by photoelectrochemical reforming of biomass-derived alcohols was constructed by a cathode for HER, an anode for alcohol oxidation, connected with a single-junction GaAs solar cell, and an anion-exchange membrane to separate the cathode and the anode. Figure 5.5 shows the photographs of the as-prepared electrodes. Using our prepared NiP_x and Pd/Ni foam electrodes, a PEC reforming device is constructed and shown in figure 5.6a.

Figure 5.5 Photographs of the as-prepared electrodes.

HER characteristic of our NiP_x cathode in 2 M NaOH is shown in Figure 5.6b, with pristine Ni foam and state-of-the-art Pt/C as controls. Ethanol electrooxidation activity of Pd/Ni foam anodes were also tested in 2 M ethanol, 2 M NaOH solution (Figure 5.6c). The onset potential for ethanol oxidation is $\sim$ -0.5 V vs. SCE (0.5 V vs. RHE), indicating very low thermodynamic resistance. Along with increasing Pd

loading amount, the ethanol oxidation current density increases together with a shift of the peak potential toward the positive bias. The cyclic voltammetry (CV) peak disappears when Pd loading reaches 0.6 mg/cm² (Pd/Ni foam-4), after which, further increase in Pd loading does not change the electrocatalytic performance. Thus Pd/Ni foam-4 was used in the following experiment. Simultaneous hydrogen and chemical production in a two-electrode configuration including a NiP_x/Ni foam cathode and a Pd/Ni foam anode was investigated (Figure 5.6d). Our system reaches a hydrogen production current density of 10 mA/cm² by applying just 0.70 V across the electrodes.

Figure 5.6 Electrochemical performances of different electrodes for HER and ethanol oxidation. (a) Schematic diagram of the ethanol photoelectrochemical reforming device. (b) HER characteristics of different electrodes in a three-electrode configuration in 2 M NaOH

aqueous solution. (c) CV curves of ethanol oxidation on Pd/Ni foam electrodes with different Pd loading in 2 M ethanol + 2 M NaOH aqueous solution. (d) Ethanol reforming characteristics of Pd/Ni foam anode with different cathode in a two-electrode configuration in 2 M ethanol + 2 M NaOH aqueous solution.

Figure 5.7 (a) HPLC spectra of the solution after different runs of ethanol oxidation. (b) Acetate amount and Faradaic efficiency of ethanol oxidation.

Useful chemicals instead of CO₂ were obtained by ethanol oxidation and was confirmed by HPLC, acetate was identified as the only product. HPLC spectra showed the acetate peak at retention time of 15.9 min together with the reactant ethanol peak at 22.1 min without any other peaks. Figure 5.7a shows the increasing of acetate production as well as the decreasing of ethanol along with reaction time. The Faradaic efficiency of ethanol oxidation to acetate is nearly 100% (Figure 5.7b).

Figure 5.8 Photoelectrochemical reforming of ethanol to produce hydrogen and acetate. (a) *J-V* curve of a single-junction GaAs solar cell under AM 1.5G illumination, and polarization curve of NiP_x/Ni foam and Pd/Ni foam electrodes in a two-electrode configuration in 2 M ethanol + 2 M NaOH aqueous solution. (b) Current density–time curve of the electrodes in a standalone, unbiased light-driven configuration in 2 M ethanol + 2 M NaOH aqueous solution under chopped AM 1.5G illumination. (c) Current density–time curve of electrodes in a standalone, unbiased light-driven configuration in 2 M ethanol + 2 M NaOH aqueous solution under continuous AM 1.5G illumination. Inset shows the first 3 cycles of current density–time curve under short-time chopped AM 1.5G illumination. (d) IPCE spectrum of a single-junction GaAs solar cell and IPHE spectrum of our device operated in 2 M ethanol + 2 M NaOH aqueous solution.

The low energy requirement of our system enables the usage of a single solar cell to power our device. We connected a single-junction GaAs solar cell with wires to the immersed catalyst electrodes. The predicted operating current density (normalized to the illumination area of the solar cell) reaches $\sim 26.2 \text{ mA/cm}^2$ (Figure 5.8a). Then, we tested our device in a standalone, unbiased light-driven configuration. Figure 5.8b and inset of Figure 5.8c show the current density-time (J - t) curves under chopped AM 1.5G illumination, which confirm the operating current density of 26.2 mA/cm^2 as predicted. Furthermore, both chopping curves reveal rapid responses in our system toward light illumination. The hydrogen production rate reached $7.91 \text{ } \mu\text{mol min}^{-1} \text{ cm}^{-2}$ illumination area. During operation, only hydrogen bubbles were observed on the cathode, which should be beneficial for the subsequent H₂ collection.

Aside from high activity, excellent durability is of equal importance for practical applications. To probe the stability of the electrodes, continuous photolysis was performed over 10 h, which showed very little decay in current density (Figure 5.8c), indicating outstanding durability of our system. The evolved hydrogen gas was quantified as a function of incident photon energy (Figure 5.8d). The measured incident-photon-to-hydrogen conversion efficiencies (IPHE) are around 80% across nearly the entire visible region of the solar spectrum from 450 to 850 nm, which well resemble the incident-photon-to-current conversion efficiency (IPCE) of the GaAs solar cell.

Figure 5.9 Photoelectrochemical reforming of different biomass-derived alcohols. (a) CV curves of alcohol (2 M) oxidation in 2 M NaOH aqueous solution. (b) *J*-*V* curve of a single-junction GaAs solar cell under AM 1.5G illumination, and polarization curves of different alcohols oxidation in a two-electrode configuration in 2 M alcohol + 2 M NaOH aqueous solution. (c, d) Current density–time curves of the electrodes in a standalone, unbiased light-driven configuration in 2 M alcohol + 2 M NaOH aqueous solution under chopped (c) and continuous (d) AM 1.5G illumination.

Besides ethanol, a few other alcohols including methanol, ethylene glycol, glycerin, and isopropanol appear as the byproducts of biomass fermentation. To ensure the generality, we also investigated the oxidation of these alcohols in our system for the production of hydrogen. Figure 5.9a shows the CV curves of different alcohol

oxidation on Pd/Ni foam anode, confirming that Pd catalyst is active for all these alcohols oxidation. The onset potential follows the order of isopropanol < methanol < glycerin < ethylene glycol. Pd catalyst showed the best activity for isopropanol oxidation at low potentials, but higher current densities for oxidizing other alcohols at high potentials. In a two-electrode configuration, current density-voltage (*J*-*V*) curves of the catalyst electrodes showed the same trend of activity (Figure 5.9b). The *J*-*V* curves of the catalyst electrodes intersect that of GaAs solar cell at 0.68 V, 0.75 V, 0.76 V, 0.81 V for isopropanol, methanol, glycerin, ethylene glycol, respectively, predicting the operating current densities of 26.2 mA/cm² for all examined alcohols. Chopped and continuous *J*-*t* curves in a standalone, unbiased light-driven configuration with each alcohol confirmed the operating current density of about 26.2 mA/cm² with great system stability (Figure 5.9c, d).

5.4 Conclusion

In summary, we have developed a new solar-to-hydrogen system by photoelectrochemical reforming of biomass-derived alcohols to simultaneously produce pure hydrogen and chemicals at room temperature. The hydrogen quantum efficiencies reach 80% across the entire visible region of the solar spectrum, leading to an ultrahigh hydrogen production rate of 7.91 $\mu\text{mol min}^{-1} \text{cm}^{-2}$ illumination area of a single-junction GaAs solar cell under AM 1.5G illumination. Moreover, by properly choosing the anodic catalyst, the alcohols can be selectively converted to useful liquid chemicals with nearly 100% selectivity.

Our system should offer a general approach for biomass photoreforming for simultaneous hydrogen and chemicals production (e.g., oxidize biomass derived 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid).

Chapter 6

Conclusions and Recommendations for Future Research Directions

This chapter gives a general discussion to conclude the whole thesis and discusses the originality of the research works in this thesis. Based on the current research status, the work that can be focused on in the near future is also discussed.

6.1 General Conclusion

In this dissertation, I focus on improving the overall solar-to-hydrogen efficiency by rational design of catalytic nanomaterials. The working principles, materials selections and up-to-date development of different sustainable water splitting systems have been discussed in detail. New nanomaterials were designed in developing effective and efficient photo(electrodes). Throughout this four-year program, unique nanostructured functional materials, with high catalytic property have been successfully designed, synthesized and applied in different solar-to-hydrogen system, including photoelectrochemical, electrochemical water splitting and photoelectrochemical reforming of biomass-derived alcohols.

In Chapter 3, we reported the promising application of metal-organic frameworks (MOFs) materials as photosensitizers for photoelectrochemical (PEC) water splitting. Three Ti-based MOFs have been synthesized, and decorated on the single-crystalline rutile nanowire arrays. Through ligands modification, the optical properties of MOFs can be tuned. Water oxidation performance of TiO_2 has been significantly improved by these MOF sensitizers, particularly in the visible light region of the solar spectrum. Au nanoparticles have been incorporated into MOF layer to further increase the light absorption cross-section due to the surface plasmonic resonance (SPR). We believe that MOF materials are very promising photosensitizers, and our work may stimulate intensive research in MOF based photosensitizers for solar energy conversion.

(1) MOFs as a new kind of microporous materials, are highly promising in a large scope of applications, including gas storage and separation, chemical sensing, biomedicine and heterogeneous catalysis. Recently, research of MOF materials as photocatalysts has received great interest. Lots of papers have reported the synthesis of novel photocatalytic MOFs, especially in the visible light region. MOFs with suitable band gaps and electronic chemical potentials are very promising for the photosensitizing application. However researches regarding this area are rarely

reported. We report the usage of a series of Ti-based MOFs as photosensitizers for PEC water splitting, which will help to expand the research scope of MOFs.

(2) Dye molecules and narrow band-gap semiconductors are common used photosensitizers. However, the low light absorption coefficient of dye molecules and the stability and toxicity of most semiconductor sensitizers restrict their application. In this manuscript, Ti-based MOF materials have been successfully used as photosensitizers. And moreover, due to the tailorability of the organic ligands, light responsive behaviors for our MOF sensitizers can be easily tuned by a simple ligand modification. Here, the ligands of Ti-based MOFs are modified by amino groups, along with the increasing of amino group ratio, light absorption of MOFs shift from UV light to visible light region, which directly increase the utilization of solar energy in our PEC water splitting system.

(3) Increasing the amount of photosensitizers is an effective way to enhance the light absorption according to previous researches. However, this brings another problem which is the elongation of transportation path, thus the recombination rate of photo-generated electron-hole pairs will increase. As a result, there will be an optimum layer thickness. Due to the highly porous structure, MOF layer provides a different strategy by incorporating other functional components (such as photosensitizers or molecular catalysts) into MOF layer to work synergistically and improve the photocatalytic efficiency. As a proof of concept, here we incorporated Au nanoparticles inside the MOF layer, due to the SPR effect, light absorption efficiency could be further improved, and the overall PEC performance has been enhanced.

In Chapter 4, we reported a facile one-step method to prepare ultra-small transition metal carbide nanoclusters encapsulated in N, S co-doped graphene as noble-metal-free electrocatalysts for all-pH hydrogen evolution, in which, high density MoC_{1-x} or

WC_{1-x} nanoclusters are encapsulated in nanoporous N, S co-doped graphene matrix. Both catalysts exhibited excellent hydrogen evolution reaction (HER) catalytic activity and durability in a wide range of pH from 0 to 14.

(1) Noble metal such as Pt possess high catalytic activity for HER, but restricted in industrial application for its excessive price and lack of abundance. Transition-metal carbides, especially molybdenum and tungsten carbides were found to have similar d-band electronic density-of-state to that of Pt, which were considered as promising non-noble metal HER catalyst. High temperature synthesis routes usually cause uncontrollable particle sintering and produce large molybdenum carbides particles with wide size distributions. Construction of nanostructured molybdenum carbides with well-defined structures is critical for achieving great HER performance. The as-prepared MoC_{1-x}/C materials possess ultra-small particle size (2.8 nm) with narrow size distribution (1.8 to 3.2 nm). This controllable morphology enable the maximum exposing of active sites and contribute to the outstanding HER performance.

(2) This one-pot synthesis strategy provide MoC_{1-x} nanoparticle with N, S co-doped graphene as substrate materials. The lammer graphene Porous graphene serves as soft template which prevents the aggregation of Mo precursor (MoO_x) and results in the ultra-small size of MoC_{1-x} nanoparticles. In addition, the excellent conductivity of porous graphene matrix not only enables fast electron transport in the electrode, but also provides a three-dimensional diffusion channel, which collectively benefit the HER.

(3) The intimate interaction between the MoC_{1-x} nanoclusters and the N, S co-doped graphene matrix permits extraction of electrons from MoC_{1-x} to N, S co-doped graphene owing to the strong electron-withdrawing capability of N and S dopants, rendering a positive charged surface of MoC_{1-x}, which down-shifts the d-band center

of MoC_{1-x} and thus decreases the Mo–H binding strength and enhances the HER activity of $\text{MoC}_{1-x}/\text{C}$.

(4) This work is very general in preparing transition-metal carbide/graphene composite. For example, by replacing the molybdenum precursor with the tungsten precursor, WC_{1-x} nanoclusters encapsulated in N, S co-doped graphene (WC_{1-x}/C) could be synthesized. Similar to $\text{MoC}_{1-x}/\text{C}$, ultra-small WC_{1-x} nanoparticles (2.0nm) can be obtained, the as-prepared WC_{1-x}/C composite catalyst also exhibits good HER performance across a wide range of pH from 0 to 14.

In Chapter 5, I have developed a new solar-to-hydrogen system by PEC reforming of biomass-derived alcohols to simultaneously produce pure hydrogen and chemicals at room temperature.

Mimicking what the Mother Nature does, converting sunlight directly into chemical fuels offers a promising solution to address the global energy and environmental crisis. Water splitting provides an attractive strategy for high-purity hydrogen production with near zero carbon emission. However, the energetic convenience of water splitting is severely limited by the oxygen evolution half reaction. To reduce the energy consumption, we investigate the possibility of replacing water oxidation in a water electrolysis cell with the oxidation of biomass-derived alcohols (alcohol can be produced in large scale from biomass through fermentation). The device demonstrates unprecedented performances of simultaneous hydrogen and chemicals production with extremely high efficiency, selectivity and stability. Powered by a commercial single junction GaAs solar cell, the hydrogen quantum efficiencies of the reforming device are well maintained around 80% across the entire visible solar spectrum from 450 nm to 850 nm, reaching an ultrahigh hydrogen production rate of $7.91 \mu\text{mol min}^{-1} \text{cm}^{-2}$ illumination area under AM 1.5G illumination (100 mW/cm^2). By carefully choosing the proper anodic catalyst, the biomass-derived

alcohols can be selectively converted to useful chemicals with near 100% selectivity. This system should offer a general approach for biomass photoreforming for simultaneous hydrogen and chemicals production.

(1) It is the first time to demonstrate the direct conversion of solar energy and biomass to hydrogen and chemicals with extremely high efficiency, outstanding selectivity and stability. Oxidation of alcohol produced from biomass fermentation allows electrolysis at potentials less than 1 V, as such it is sufficient for hydrogen production powered by only one commercial solar cell.

(2) Power by a single commercial GaAs solar cell, the hydrogen evolution current density of our reforming device reaches as high as $\sim 26.2 \text{ mA/cm}^2$, which is about 2.5 times that of the value obtained from a water photolysis cell driven by two solar cells reported recently^{171, 172}. The measured hydrogen quantum efficiencies are around 80% across the entire visible solar spectrum from 450 to 850 nm, reaching an ultrahigh hydrogen production rate of $7.91 \text{ } \mu\text{mol min}^{-1} \text{ cm}^{-2}$ illumination area under AM 1.5G illumination.

(3) The photoreforming device showed excellent durability over 10 h of continuous operation under AM 1.5G illumination. Only hydrogen bubbles were evolved from the cathode, which should be beneficial for hydrogen collection. Alcohol aqueous solution directly obtained from biomass fermentation can be used in this system to produce high-purity hydrogen with nearly 100% conversion of alcohol towards useful chemicals.

6.2 Recommendations for Future Research Directions

In viewing of current research achievements, there are many promising research directions waiting to be explored. Based on the current progress discussed in this thesis, some suggestions on the potential works which can be conducted in the future will be given in this section.

First, regarding solar driven water splitting system, we have put our efforts on the light absorption and HER catalyst development. Outstanding performance have been obtained, but still far from satisfactory. We believe that there is still great potential to further improve the overall solar-to-hydrogen efficiency from rational design of advanced nanomaterials.

I have proved that MOF materials are very promising for visible light harvesting in Chapter 3. Considering the diversity of MOFs, a large number of MOFs are expected to work as promising photosensitizers for solar-to-hydrogen conversion. For example, porphyrin-based MOFs. Porphyrin as the functional group of chlorophylls which harvest sunlight in nature photosynthesis process, and widely used in dye-sensitized solar cell (DSSC), is a very promising component which can be used as the linkers. Ho-Jin Son and co-workers fabricated two MOFs with modified porphyrin as linkers,^[29] they found that these MOFs may exhibit the antenna-like light-harvesting properties just like the nature photosynthesis system. Based on their study, the photo-generated exciton can migrate along a specific direction over up to 45 porphyrin struts in the MOF, which makes this MOF very promising in the applications of solar energy conversion. Furthermore, the porphyrin ring in the MOFs structure can be used as a platform which allows metalation. Along with the porous structure, porphyrin-based MOFs can be easily modified to achieve even better light harvesting and catalytic activity.

HER catalyst is critical for the overall solar-to-hydrogen efficiency. We have discussed a noble-metal-free HER catalyst based on carbide/graphene complex materials. Further reduce the overpotential of HER catalysts is important and achievable. A recent paper^[146] reported a new carburization method and successfully prepared ultrasmall and phase-pure W_2C nanoparticles. Pre-oxidized multi-walled carbon nanotubes (MWNT) are used to load WO_x precursor, then carbon atoms from

MWNT would be activated and diffused into WO_x at simultaneously high temperature and low pressure, thus obtain selectively reduced W_2C product. This new synthesis method provide coking-free carbide catalyst, thus possess outstanding HER catalytic activity. Besides synthesis method development for carbide nanoparticles, morphology engineering also provide effective way to enhance the HER performance. Carbides with morphologies of nano-octahedra, nanorods, nanowires, nanosheets, 2D nanoflakes have been reported, and more interesting morphology are expected with the development of nanotechnology.

Compared to HER, the mechanisms of oxygen evolution is more complicated and poorly understood. At current stage, it's of equal importance to obtain efficient OER electrocatalyst based on earth-abundant materials. Despite intensive research over decades to develop OER catalysts in both acidic and alkaline solutions, most state-of-the-art catalysts still require far-from-ideal overpotentials to reach current densities of interest. Considering the abundance of oxygen in air, we replace OER with bio-mass derived alcohol oxidation reaction (AOR), which greatly decrease the required bias as well as produce hydrogen with valuable chemicals simultaneously. A problem in this system lies on the development of AOR catalysts, most efficient catalysts are still based on noble metal such as Pt, Pd.^[173-176] Current studies focus on the noble metal catalysts including structure engineering, noble metal alloy, and noble-metal-based complex materials to enhance the activity and durability. Earth-abundant-materials-based catalysts for AOR is in highly demands, however AOR catalysts comprised of non-noble metal materials has rarely been reported. Recently, ultrathin Co_3O_4 nanosheets were found to be active for AOR, and the oxidation product is solely ethyl acetate.^[177] However the large onset potential (at 1.4 V vs. RHE) would limit the overall conversion efficiency. Efficient catalysts based on earth-abundant-materials should be a promising research direction for improving the solar-to-hydrogen efficiency.

Compared to water splitting, we have proved that PEC reforming of biomass-derived alcohols is a more efficient solar-to-hydrogen system. Actually, besides of biomass-derived alcohols, many other chemicals which are readily oxidative can be used to replace OER in hydrogen production system. The selection criterion is based on two facts, the first one is the low oxidation potential, which means the low energy input to drive efficient current density and hydrogen production. The second criterion is to produce value-added chemicals after oxidation reaction. Considering these two criteria, chemicals such as benzyl alcohol, furfural, furfuryl alcohol, and 5-hydroxymethylfurfural (HMF) are promising in this application.^[178] Research regarding efficient catalysts for these reactions should benefit the development of this new solar-to-hydrogen system.

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