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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**NANOARCHITECTURAL DESIGN OF
SEMICONDUCTOR MATERIALS FOR SUSTAINABLE
ENERGY APPLICATIONS**

**MIAO JIANWEI
SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING
2016**

NANOARCHITECTURAL DESIGN OF SEMICONDUCTOR MATERIALS FOR SUSTAINABLE ENERGY APPLICATIONS

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School of Chemical and Biomedical Engineering

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Publications

† denotes equal authorship.

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List of abbreviations

Chemical names

CdCl_2	Cadmium chloride
CdS	Cadmium sulfide
CdSe	Cadmium selenide
DI water	Deionized water
H_2O_2	Hydrogen peroxide
HCl	Hydrochloric acid
L-Cys	L-cystine
MoS_2	Molybdenum disulfide
Na_2HPO_4	Sodium phosphate dibasic
NaH_2PO_4	Sodium phosphate monobasic
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	Sodium molybdate dihydrate
$\text{Na}_2\text{S}_2\text{O}_3$	Sodium thiosulfate
Na_2SO_4	Sodium sulfate
NaOH	Sodium hydroxide
NiO	Nickel oxide
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	Nickel sulfate hexahydrate
NiS_x	Nickel sulfide
Pt	Platinum
TiF_4	Titanium (VI) fluoride
TiO_2	Titanium dioxide
TTIP	Titanium isopropoxide
$\text{Zn}(\text{NO}_3)_2$	Zinc nitrate
ZnO	Zinc oxide
ZnS	Zinc sulfide

Physical terms

atm	Atmosphere
C	Capacitance
E redox	Redox potential
E _g	Bandgap
Hz	Hertz
IPCE	Incident photon-to-electron conversion efficiency
J	Current density
J _{cp}	Cathodic peak current density
J _{sc}	Short circuit current density
n	Number of electrons transferred
P	Pressure
PV	Photovoltaic
R	Reflectance
R _s	Series resistance
R _t	Charge transport resistance
STH	Solar to hydrogne efficiency
TWh	Terawatt-hour
V	Voltage
V _{oc}	Open-circuit voltage
W	Depletion width
W _s	Warburg impedance
Z	Impedance
α	Absorption coefficient
ΔG	Free energy change
η	Power conversion efficiency
λ	Wavelength

Abbreviations of commonly used terms

1D	One dimensional
2D	Two dimensional
3D	Three dimensional
Ag/AgCl	Silver chloride electrode
AM	Air mass
CB	Conduction band
CBD	Chemical bath deposition
CE	Counter electrode
CV	Cyclic voltammetry
ECD	Electrochemical deposition
EIS	Electrochemical impedance spectra
EXAFS	Extended x-ray absorption fine structure
FESEM	Field emission scanning electron microscope
FTO	Fluorine-doped tin oxide
HRTEM	High resolution transmission electron microscopy
ITO	Indium-doped tin oxide
LSV	Linear sweep voltametry
NHE	Normal hydrogen electrode
NR	Nanorod
PCE	Power conversion efficiency
PEC	Photoelectrochemical
QD	Quantum dot
RE	Reference electrode
RHE	Reversible hydrogen electrode
SCE	Saturated calomel electrode
TCO	Transparent conducting oxide
VB	Valence band
WE	Working electrode
XRD	X-ray diffraction

Abstract

The huge engine of our modern global economy is primarily powered by the fossil fuels. However, fossil fuels are exhaustible, and their combustion will lead to severe environment problems, such as global warming. Under the circumstances, it's our duty to develop alternative and sustainable energy resources that can ease the worsening crisis. Looking up into the sky, the radiation we received from the Sun has been supporting the evolution of ecological systems for more than three billions years. Artificial conversion of the solar energy into chemical fuels, mimicking what the Mother Nature does, has attracted tremendous attentions over the past few decades. Among the many systems that have been proposed, solar water splitting for hydrogen production is the most attractive one.

The overall objectives of this interdisciplinary research program are to design the architectures of semiconductor-based photocatalytic materials and electrocatalysts at nanoscale, to construct a stable photoelectrolysis cell for unassisted visible light solar water splitting and to fabricate efficient electrochemical hydrogen-evolving electrodes that can be applied in practical applications.

To first demonstrate the importance of nanoarchitectural design, anatase TiO_2 microspheres with a high percentage (90%) of exposed high-reactivity {001} facets were synthesized using hydrofluoric acid generated in situ through hydrolysis of titanium tetrafluoride (TiF_4) as a capping and stabilizing agent without introducing any additional hydrofluoric acid under hydrothermal conditions. The as-prepared TiO_2 microspheres show excellent photocatalytic activity in the degradation of toxic organic contaminants as well as production of hydrogen in water under UV light irradiation.

A facile all-electrochemical approach to fabricate well-aligned ZnO–CdSe core–shell nanorod arrays with excellent uniformity on transparent indium tin oxide (ITO) substrates. The shell thickness of the core–shell nanorods can be tuned precisely by adjusting the charge density passing through the working electrode during the deposition of CdSe quantum dots (QDs). The optimized ZnO–CdSe nanorod arrays showed excellent PEC performance with a significant saturated photocurrent density of 14.9 mA cm² at 0.8 V (vs. RHE) under AM 1.5 illumination, which is, to the best of our knowledge, the highest value ever reported for similar nanostructures, owing to the favourable band alignment and good distribution of CdSe QDs on ZnO nanorods. Our results demonstrate that the electrochemically deposited ZnO–CdSe nanorod arrays can be utilized as efficient photoanodes in PEC water splitting cells.

To achieve the ultimate goal of designing a complete water splitting system through nanoarchitectural engineering, we have designed corrosion-resistant, nanocomposite photoelectrodes for spontaneous overall solar water splitting, consisting of a CdS quantum dot (QD) modified TiO₂ photoanode and a CdSe QD modified NiO photocathode, where cadmium chalcogenide QDs are protected by a ZnS passivation layer and gas evolution cocatalysts. Our device shows spontaneous overall water splitting in a nonsacrificial environment under visible light illumination ($\lambda > 400$ nm) through mimicking nature's “Z-scheme” process. The results here also provide a conceptual layout to improve the efficiency of solar-to-fuel conversion, which is solely based on facile, scalable solution-phase techniques.

In order to bring the merits of nanoarchitectural design to a more practical stage, a unique functional electrode made of hierarchical Ni-Mo-S nanosheets with abundant exposed edges anchored on conductive and flexible carbon fiber cloth, has been developed through a facile biomolecule-assisted hydrothermal method. The

incorporation of Ni atoms in Mo-S plays a crucial role in tuning its intrinsic catalytic property by creating substantial defect sites as well as modifying the morphology of Ni-Mo-S network at atomic scale, resulting in an impressive enhancement in the catalytic activity. The Ni-Mo-S/C electrode exhibits large cathodic current and low onset potential for hydrogen evolution reaction in neutral electrolyte (pH ~7). Furthermore, the Ni-Mo-S/C electrode possesses excellent electrocatalytic stability over an extended period, much better than those of MoS₂/C and Pt plate electrode. Importantly, for the first time, the intuitive comparison test was designed to reveal the superior gas-evolving profile of Ni-Mo-S/C over that of MoS₂/C, and a lab-scale hydrogen generator was further assembled to demonstrate its potential application in practical appliances.

Chaper 1 Introduction

1.1 Background and significance

Severe environmental issues along with the forthcoming energy crisis have revived scientists' enthusiasm in developing clean and sustainable energy resources.(1-3) Over the past few decades, the scientific community has considered about an evolution from an oil-based to hydrogen-based global economy.(4, 5) Dated back to the 1970s; Bockris and Justi first came up with the concept of *hydrogen economy*, where H₂ can be used as a clean fuel, or more accurately an energy carrier, to replace the carbon-containing fossil fuels. (6) The big picture of a hydrogen economy is to deliver the energy generated from the renewable sources using H₂ over long distances, and to store them in large quantities.(7) Currently, large-scale H₂ production is mainly achieved through industrial steam reforming processes using fossil fuels, such as natural gas, as the primary source, which in turn would lead to equal immense emission of greenhouse gases. (8, 9) In terms of the sustainability, it's urgent and essential to promote alternative H₂ production technologies for the future development of hydrogen economy. Our Earth receives an energy influx of 4.3×10^{20} J from the sun in each hour, which is even comparable with the total energy consumption in one year on our planet. (10) At the same time, water covers 71% of the Earth's surface, which makes it the most abundant natural resource. Based on these facts, it is believed that efficient and economical solar energy powered water splitting systems would be the key technological components for the future hydrogen economy.(2, 5, 11, 12)

Photosynthesis is a natural energy conversion process used by plants, algae and certain bacterial species that captures solar energy in chemical compounds, such as carbohydrates and other biomass, to maintain their lives as well as to support their essential activities. Inspired by the Mother Nature, scientists are seeking ways to accomplish artificial photosynthesis, which is known as the “Holy Grail” of solar energy conversion, to produce clean and storable fuels.⁽¹³⁾ It has been more than four decades ago since Honda and Fujishima’s first report on electrochemical photolysis using TiO_2 electrode illuminated with near UV light.⁽¹⁴⁾ Since then, a wide range of materials and systems have been intensively studied and developed to fulfill the ultimate goal of efficient water splitting.

Driven by the inexhaustible irradiation from the Sun, the water splitting process can be realized through many different approaches. Semiconductor materials with favorable electronic properties can be tailored into self-supported photocatalysts and photoelectrodes to carry out photocatalytic and photoelectrochemical water splitting, respectively. In these energy conversion systems, three essential requirements have to be met to improve the overall efficiency.⁽¹⁵⁾ First, the system must be capable of absorbing solar illumination to generate sufficient excitons, namely electrons and holes. Second, those photo-induced electron-hole pairs must be separated efficiently with low energetic loss to prevent their recombination. Third, the photo-induced electrons and holes must be able to carry out the desired chemical reactions, say the decomposition of water in our systems. Under solar irradiation, the photo-induced electrons can reduce water to generate H_2 , while the holes can oxidize water to generate O_2 . Sounds more straightforward, another practical strategy is to directly link an efficient electrolyzer, which is consist of a H_2 -evolving cathode and an O_2 -

evolving anode, to a high-performance photovoltaic cell that provides sufficient driving force to split the water molecules. Alternatively, known as photobiological water splitting, solar-driven hydrogen production can also be achieved within a more complex bioreactor system that involves real photosynthesis conducted by algae or bacteria.(16-18) The H_2 generated using these systems can be collected and utilized to produce electricity in hydrogen fuel cells, or directly served as a fuel for transportation with zero pollution or greenhouse gas emitted upon combustion.(13, 19, 20)

“There’s Plenty of Room at the Bottom”, said by the distinguished theoretical physicist Dr. Feynman during the American Physical Society Meeting in 1959,(21) have inspired and encouraged scientists from different disciplines across the scientific community to explore the small world. Owing to the rapid advancement of nanotechnology over the past three decades, it’s now a well-recognized fact that there’s indeed plenty of space to be explored at the nanoscale. Nanostructured materials are now playing critical roles in the development of energy conversion/storage devices,(22-25) such as photovoltaic cells,(26-28) rechargeable lithium-ion batteries(29-31) and supercapacitors.(32, 33) Benefited from these astonishing achievements, the progress of building sustainable water splitting systems is also profoundly accelerated. (15, 34-40)

1.2 Motivations

Currently, most research efforts have been made to develop new materials and systems that can drive hydrogen evolution reaction (HER) and oxygen evolution

reaction (OER) simultaneously with an unassisted fashion.(15) Quite a number of photocatalytic systems are capable of carrying out unassisted overall water splitting have been reported. However, most of these systems require the irradiation of UV light ($\lambda < 400\text{nm}$) due to the utilization of large bandgap semiconductor materials.(8) We know that more than 40% of the solar energy incident on the Earth's surface is in the form of visible light, with the wavelength lies in between 400 nm and 750 nm as shown in Figure 1-1. As a consequence, it's essential to develop next-generation materials and systems, which can produce H_2 in large scales, by utilizing visible light. In addition, potential photocatalyst-based solar water splitting systems should also possess the capability to support rapid electron/hole transport at the interfaces as well as long term durability.(15)

Figure 1-1 The spectra of solar radiation received by the Earth. In photocatalytic and photoelectrochemical water splitting, the radiation intensity at sea level, denoted as AM 1.5 G, is usually used for experimental measurements.(41)

Many semiconductor materials, such as TiO_2 , ZnO , CdS , CdSe and NiO are promising candidates for this application because of their reasonable stability, and ability to absorb a significant fraction of solar irradiation. However, many challenges must be overcome if we wish to fully exploit the advantages of these materials. As an effective strategy, rational nanostructure design can significantly improve the physical properties of photocatalytic materials, resulting in increased specific surface area, better charge transport properties and enhanced light absorption. Meanwhile, the development of novel electrocatalysts for sustainable water splitting reactions is of equal importance.

In this PhD program, our leading motivation is to enhance the efficiency of sustainable water splitting systems by optimizing the photo/electro-catalytic materials through rational nanoarchitectural design. 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.

1.3 Objectives

The overall objectives of this PhD program are the nanoarchitectural design of semiconductor-based photocatalytic materials and electrocatalysts, the construction of stable photoelectrolysis cell for unassisted visible light solar water splitting and the fabrication of efficient electrochemical hydrogen-evolving electrodes for practical application.

Our specific goals at different stages are:

(a) Design and preparation of semiconductor materials with controllable morphologies and nanostructures for efficient water splitting applications

In sustainable water splitting systems, it's important to tailor the morphology and nanoarchitecture of semiconductor materials to improve their overall performance. For instance, anatase TiO_2 is an important photocatalytic material, and recent studies, based on both experimental and theoretical results, suggest that the (001) surface of anatase is much more reactive than the (101) surface. An effective strategy to enhance the catalytic activities of anatase TiO_2 is to maximize the fraction of exposed (001) surface through nanoarchitectural design. In addition, the light-absorption properties of wide-bandgap semiconductors can be further improved through the formation of core-shell nanoarchitecture with an efficient light absorber, such as the nanocrystals of CdSe and CdS.

(b) Construction of stable photoelectrolysis cell using nanostructured semiconductor materials for unassisted water splitting under visible light illumination

To achieve the ultimate goal of designing a complete water splitting system, nanostructured semiconductor-based photoanode and photocathode have to be carefully designed and fabricated through a parallel approach. The optimized photoelectrodes can be integrated within a photoelectrochemical cell to perform overall water splitting. The objective of this stage is to demonstrate the prototype of a photoelectrolysis cell for unassisted visible light solar water splitting.

(c) Fabrication of hydrogen-evolving electrode that can be applied in practical applications through nanoarchitectural engineering

To further make sustainable water splitting applicable in real-life applications, it's of equal importance to develop effective electrocatalysts that can catalyze the hydrogen production efficiently in mild environment. As an example, a facile synthetic strategy has been developed to directly grow nanostructured MoS₂-based electrocatalyst on carbon fiber cloth as a high-efficiency functional electrode for hydrogen production in neutral electrolyte.

1.4 Organization of the dissertation

This dissertation contains seven chapters, which are organized as follows:

Chapter 1 provides a general introduction of the topics to be covered in this dissertation, including the background and significance of solar water splitting technologies, discusses the motivations as well as the primary objectives of this PhD research project.

Chapter 2 describes an overview of nanostructured semiconductor materials in different water photolysis technologies (photoelectrochemical/photocatalytic water splitting and photovoltaic-driven electrolysis), illustrates the historical highlights and basic principles, introduces the techniques and fundamentals, and summarizes the up-to-date research progresses.

Chapter 3 presents the design of anatase TiO₂ microspheres with high percentage of exposed high-reactivity {001} facets, which showed excellent

photocatalytic activity in the degradation of toxic organic contaminants as well as production of hydrogen in water under UV light irradiation.

Chapter 4 introduces the facile fabrication of well-aligned ZnO-CdSe core-shell nanorod arrays with excellent uniformity on transparent indium tin oxide (ITO) substrates through a facile all-electrochemical approach.

Chapter 5 presents the corrosion-resistant, nanocomposite photoelectrodes for spontaneous overall water splitting, consisting of a CdS quantum dot (QD) modified TiO₂ photoanode and a CdSe QD modified NiO photocathode, where cadmium chalcogenide QDs are protected by a ZnS passivation layer and gas evolution co-catalysts.

Chapter 6 introduces a unique functional electrode made of hierarchical Ni-Mo-S nanosheets with abundant exposed edges anchored on conductive and flexible carbon fiber cloth, developed through a facile biomolecule-assisted hydrothermal method.

Chapter 7 summarizes a general conclusion of this PhD project, and provides recommendation of directions for future research in the field of photolysis technologies.

Chaper 2 Literature review

2.1 An overview of water splitting systems

Under standard conditions, an applied potential difference of 1.23 V between the anode and cathode is required to decompose water molecules into hydrogen and oxygen, corresponding to a 237.2 kJ/mol (or 2.46 eV/molecule) change in free energy. In photocatalytic and photoelectrochemical water splitting systems, the semiconductor materials must be able to absorb photons with wavelength of 1000nm and smaller (equivalent to photon energies larger than 1.23 eV) to drive the photolysis reaction in Eq. 1

In this process, two and four electron-hole pairs must be generated for the formation of one H₂ molecule and one O₂ molecule, respectively. If a single semiconductor material has bandgap energy (E_g) large enough (>1.23 eV) to drive photolysis, with its conduction band and valence band-edges straddle the redox potentials of hydrogen (H⁺/H₂) and oxygen (O₂/H₂O), it can be utilized as a potential material for conducting overall water splitting, which means it can drive both hydrogen and oxygen evolution reaction simultaneously under illumination, as illustrated in Figure 2-1.(15)

Figure 2-1 An ideal semiconductor material, with its band-edges straddle the redox potentials of hydrogen (H^+/H_2) and oxygen ($\text{O}_2/\text{H}_2\text{O}$) for overall water splitting. Protons (H^+) are reduced into H_2 by the photo-induced electrons, while H_2O molecules are oxidized into O_2 by the photo-induced holes.(15) Reprinted with permission from (15). Copyright (2010) American Chemical Society.

In order to carry out the hydrogen and oxygen evolution reactions, the photoinduced electrons and holes have to be transferred to the liquid junction and react with H^+ , OH^- and H_2O and other solution species instantly on the surface of the semiconductor materials. During the charge-transfer processes, additional energy is required by the electrons/holes to overcome the concentration gradient as well as kinetic overpotential at the semiconductor/electrolyte interface for driving HER and OER, leading to significant energy losses in practical semiconductor-based water splitting processes. As a result, the actual energy required for generating one electron-hole pair is about 1.5 ~ 2.4 eV in most reports, although the theoretical required energy is only 1.23 eV. (42, 43)

Bolton et al. have classified solar water splitting systems into different schemes, according to the number of utilized semiconductor materials and the number of absorbed photons to generate each H_2 molecule.(42) Based on this standard, a classification of S2 indicates that the solar water splitting device is made with single

semiconductor material (single bandgap), and two photons are required for producing one H_2 molecule. Similarly, D2 (D4) systems are made with two stacking semiconductor materials, requiring two (four) absorbed photons to produce one H_2 molecule. (42) Theoretically, the conversion efficiency (η) of incident solar energy to chemical energy can be calculated using Eq.2.

$$\eta = \frac{J_g \mu_{ex} \phi_{CONV}}{S} \quad (2)$$

where J_g is photon flux absorbed by the semiconductor material, μ_{ex} is the excess chemical potential generated upon the absorption of photons, ϕ_{CONV} is the quantum yield for the chemical conversion from photons to products, and S is the total incident solar irradiation (mW/cm^2). For example, an S2 system can achieve a maximum conversion efficiency of 30% under the illumination of 1 sun intensity ($100 mW/cm^2$, AM 1.5). Similarly, a D4 system with two stacked semiconductor materials has a maximum conversion efficiency of 41% based on the same theoretical calculations. In practical photocatalyst-based solar water splitting systems, there will be energy losses due to the unused portion of absorbed photons, thus leading to a lower chemical conversion efficiency of 27% for D4 system. (42)

In photoelectrochemical (PEC) water splitting systems, applied overpotentials are generally required to drive the water splitting reactions (HER and OER). If the conduction band/valence band of a semiconductor material is not sufficiently negative/positive for proton reduction/water oxidation, very slow or negligible water splitting may be resulted.(44) To examine the efficiency of a photoelectrode in driving hydrogen evolution or water oxidation, overpotential of 50 mV at $10 mA/cm^2$

and 400 mV at 10 mA/cm² for HER and OER, respectively, are useful starting points.(44)

Figure 2-2 The band structures of some commonly used semiconductors in solar water splitting applications. The conduction band edges (left) and valence band edges (right) are referenced with respect to the NHE. The positions of the semiconductor materials on the ordinate axis indicate their highest theoretical photocurrent can be produced under the AM 1.5 illuminations. The redox potentials of water reduction and oxidation are indicated with dotted lines. (15) Reprinted with permission from (15). Copyright (2010) American Chemical Society.

Figure 2-2 shows the band structures of some frequently used p-type and n-type semiconductor materials in solar water splitting applications. The conduction band edges are on the left hand side, and the valence band edges are on the right hand side. The ordinate axis indicates the maximum theoretical photocurrent that can be generated by each semiconductor material under Air Mass 1.5 (AM 1.5) illumination. Some large bandgap n-type semiconductor materials, such as TiO₂ and ZnO, cannot generate large photocurrent under AM 1.5 illumination, although their band edges straddle the redox potentials of H⁺/H₂ and O₂/H₂O. In comparison, several p-type

semiconductors with smaller bandgap are capable of producing larger photocurrent densities. In photoelectrochemical water splitting systems, higher conversion efficiencies can be obtained by utilizing multiple semiconductor materials with different bandgaps. As an example, a dual bandgap solar water splitting cell (D4), which connects an n-type semiconductor material that can drive OER with a smaller bandgap p-type semiconductor material that possesses sufficiently negative conduction band for HER, can achieve better performance. By combining semiconductors with complementary bandgap energy in such system, a more significant portion of the incident solar irradiation can be absorbed effectively. (45)

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. (46)

In photoelectrochemical water splitting systems that require an external bias to drive the electrolysis, the conversion efficiency η can be calculated using Eq.3:

$$\eta = \frac{J_{mp}(1.23 - V_{app})}{P_{in}} \quad (3)$$

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. In order to make sure that the measured efficiency is

accurate, the photoelectrochemical measurements should be taken within a two-electrode configuration. And also, the water splitting products, namely hydrogen and oxygen must be separated to suppress the reverse reactions; otherwise errors may be resulted during the measurements. The true solar to hydrogen efficiency (STH), where no bias is applied, can be estimated by measuring the photocurrent generated under the short-circuit conditions ($V_{app} = 0$), where the only energy input is light. For integrated PEC devices (back-to-back cell configuration) or photocatalytic water splitting systems (slurry system), the efficiency must be calculated by collecting the actually evolved oxygen and hydrogen, and then analyzed with gas chromatography (GC).

Osterloh et al. have summarized more than 130 inorganic catalytic materials for water splitting systems in 2008.⁽⁴⁷⁾ More recently, computational methods have been developed to choose the best material combinations among so many candidates, as well as to design and synthesize new potential materials.

2.2 Photocatalytic water splitting systems

The purpose for developing photocatalytic water splitting systems is to efficiently and economically convert solar energy into storable chemical compounds, namely H_2 and O_2 . In photocatalytic water splitting systems, self-supported photocatalysts are directly suspended in aqueous solution instead of using photoelectrodes and electrolytic systems.

Compared to photoelectrochemical water splitting cells, photocatalytic water splitting possess several advantages as photolysis can be achieved in the

homogeneous phase without using those expensive transparent oxide (TCO) thin film-coated substrates, and directional illumination is generally not required in such systems. (48) However, the explosive mixtures of H_2 and O_2 generated in these systems have to be separated, and additional energy will be consumed for the separation process, thus leading to a lower overall efficiency.

Figure 2-3 The energy scheme for the two different strategies used in photocatalytic water splitting systems, namely single absorber and z-scheme systems(48) Reprinted with permission from (48). Copyright (2011) Cambridge University Press.

Two main strategies have been developed to achieve overall photocatalytic water splitting, as shown in Figure 2-3. (48) The first strategy is to decompose water molecules into H_2 and O_2 utilizing single semiconductor absorber, or known as a one-step system. To accomplish solar water splitting with this strategy, the photocatalyst must be stable under intensive photon irradiation. Besides, they should possess preferable bandgap energy as well as suitable conduction and valence band edges for driving H_2 and O_2 generation simultaneously. Limited by these stringent requirements, reports on efficient photocatalysts for one-step water splitting are still rare to date. Domen's group has demonstrated that one-step photocatalytic water

splitting can be achieved using GaN:ZnO solid solution, $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, prepared through high temperature treatment of the physical mixture of Ga_2O_3 and ZnO under ammonia flow. (49) With RuO_2 as co-catalyst, the GaN:ZnO photocatalyst can simultaneously produce H_2 and O_2 with a stoichiometric ratio of 2:1. The bandgap of the GaN:ZnO photocatalyst is about 2.4 eV, smaller than both GaN (3.4 eV) and ZnO (3.2 eV). With a similar method, the solid solution of ZnO and Ge_3N_4 , $(\text{Zn}_{1+x}\text{Ge})(\text{N}_2\text{O}_x)$, can be prepared using the mixture of GeO_2 and ZnO at high temperature under ammonia flow, however, the efficiency of this system is much lower. (50) Liu et al. showed that the oxide solid solution of BiYWO_6 (BYW), with a bandgap of 2.71 eV, could function as a photocatalyst to drive overall water splitting upon visible light illumination when loaded with efficient co-catalysts, such as RuO_2 (Figure 2-4). (51) These results suggest that the properties of visible-light-active photocatalysts can be controlled through the formation of feasible solid solutions, thus resulting in tunable conduction and valence bands that benefit the design of effective photocatalysts for solar water splitting.

Figure 2-4 Photocatalytic water splitting over the solid solution of BiYWO_6 decorated with RuO_2 . (a) Schematic illustration of the system. (b) Stoichiometric splitting of water using BiYWO_6 under full spectrum light irradiation. (51) Reprinted with permission from(51). Copyright (2008) American Chemical society

For the second strategy of photocatalytic water splitting, a two-step photoexcitation mechanism is adopted using two different photocatalysts, where the complete water decomposition process is broken up into two separate stages: hydrogen evolution and oxygen evolution. These two-step systems are inspired by the z-scheme in natural photosynthesis in green plants, so they are also called z-scheme systems. Shuttling redox couples (Red/Ox) are usually employed in these systems to combine the separated half-reactions. Upon illumination, the reductant (Red) can be oxidized into oxidant by the holes generated from H₂-evolving photocatalysts, while the oxidant (Ox) can be reduced to reductant by the electrons generated from O₂-evolving photocatalysts at the same time. Consequently, a wide range of semiconductor materials can be utilized in Z-scheme systems, although most of them are not applicable for one-step systems. However, this system possesses a significant disadvantage, as the amount of photons required to drive the two-step photoexcitation is two times the amount required in a one-step system. Since Bard et al. first proposed the working principle of two-step photocatalytic water splitting systems in 1979, (52) a large number of semiconductors and various redox couples have been developed and applied in this application.

Figure 2-5 Freestanding z-scheme direct solar water splitting constructed using the nanowires of Rh-SrTiO₃ and BiVO₄. (a) Cross-sectional SEM image of the bi-layered nanowire mesh. (b) Schematic illustration of photocatalytic water splitting based on Ru/Rh-SrTiO₃ and BiVO₄ nanowire system. (c) Cycling measurements of the overall water splitting using mixed Ru/Rh-SrTiO₃ and BiVO₄ nanowire mesh film. (d) Overall water splitting using bi-layered film.(53) Reprinted with permission from (53). Copyright (2014) American Chemical Society

As shown in Figure 2-5, Liu's group further demonstrated a modified freestanding z-scheme water splitting system, assembled using inorganic semiconductor nanowire meshes.(53) The nanowires of Rh-SrTiO₃ and BiVO₄ can be synthesized in large scales using a two-step self-templated ion exchange strategy. Then, the paper-like freestanding mixed or bi-layered nanowire meshes can be easily fabricated using one or two step vacuum filtration. Figure 2-5(a) shows the cross-sectional view of the bi-layered Rh-SrTiO₃-BiVO₄ mesh, from which the interface between the two components can be clearly observed. The working principle of this z-

scheme water splitting system is illustrated in Figure 2-5 (b). Evidenced from Figure 2-5 (c) and (d), both mixed and bi-layered nanowire mesh can perform unassisted stoichiometric water splitting under visible-light illumination.

2.3 Photoelectrochemical water splitting systems

As discussed in previous section, a photoelectrochemical water splitting cell is consisted of one photocathode and one photoanode for driving hydrogen evolution and water oxidation, respectively. The photoelectrode materials must possess optimal band structures for absorbing solar irradiation and driving desired reactions. The valence band of the photoanode materials should be sufficiently positive for the oxygen evolution reaction, and the conduction band of the photocathode should be negative enough for the hydrogen evolution reaction. Another essential requirement is that, the photoelectrode materials must exhibit outstanding durability within aqueous electrolyte environment. Figure 2-6 illustrates several commonly used semiconductor materials for solar water splitting applications. (54)

Figure 2-6 Semiconductor materials that used in solar water splitting application. Their band edges are plotted vs. the redox potentials of hydrogen evolution and water oxidation. (54) Reprinted with permission from (54). Copyright (2009) The Royal Society of Chemistry.

In the practical studies of photoelectrochemical solar water splitting, the performance of photocathodes and photoanodes can be tested and analyzed separately. The polarization curve (current-voltage data) of each photoelectrode can be obtained using electrochemistry workstations within a three-electrode set-up independently, and this is important for choosing and optimizing candidate materials.

2.3.1 Photocathode materials

Photocathodes are responsible for providing sufficient cathodic current to drive hydrogen evolution reaction, in which protons are reduced to H_2 . As mentioned previously, the conduction band edge of the photocathode material has to be more negative than the redox potential of H^+/H_2 . 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.4; while in high pH environments, water will be directly reduced to generate H_2 and OH^- ions as shown in Eq.5. (55)

Under solar illumination, the photo-generated electrons are transferred to the interface between the photocathode and electrolyte, while the holes are brought back into the bulk of the semiconductor materials. Cathodic current can be generated due to the injection of the photo-generated electrons from the semiconductors into the electrolytes during this process. The cathodic current protects the photocathode from oxidation at certain extent. This explains the reason why p-type photocathodes are more stable than the n-type photoanodes in photoelectrochemical cells. (15) Quite a number of p-type semiconductor materials have been investigated as photocathodes in

photoelectrochemical water splitting cells or photoelectrochemical systems that decompose other compounds, such as HBr and HI. (56) In this section, we are going to review some of the most thoroughly studied photocathode materials.

2.3.1.1 P-type silicon

P-type silicon (p-Si), with a bandgap of 1.12 eV, has been reported as promising photocathode material by many groups. It was demonstrated that the required overpotential for driving photoelectrochemical hydrogen evolution could be significantly lowered by modifying the planar p-Si photocathodes with various metal catalysts. (57, 58) Dominey et al. have reported that the surface-modified p-Si can achieve a photon to hydrogen efficiency of 6% under the monochromatic 633 nm illumination. (57) Generally speaking, p-Si photocathode is stable under low pH environments, but surface oxidation may take place during long-term tests. In this case, the stability of p-Si electrodes can be enhanced with passivation process, through the covalent attachment of methyl groups. (59, 60)

Boettcher and colleagues have studied photoelectrochemical hydrogen evolution using the microwire arrays of B-doped p-Si, however their results suggest that the performance of the microwire electrode, with yielded efficiencies < 0.2%, was not as good as the planar electrode, mainly due to its low photovoltage.(61) At almost the same time, Chorkendorff's and co-workers have bonded bio-inspired molybdenum sulfide co-catalysts on to the surface of p-Si pillar.(62) Their design of the tandem "chemical solar cell" for complete water splitting can be found in Figure 2-7 (a), where the cubane-like Mo₃S₄ decorated p-Si micropillars function as high-efficiency hydrogen-evolving photocathodes. As illustrated in Figure 2-7 (b), the well-oriented

Si micropillars, with average diameter and length of 3 and 50 μm , respectively, were obtained using a photolithographic technique. The favorable electrode architectural design (1D) and the incorporation of effective co-catalysts synergistically leads to a significantly enhanced electrode performance, with an impressive photocurrent density of 8 mA/cm^2 at 0V vs. RHE, equivalent to a IPCE of 47%, under red-light irradiation in 1 M HClO_4 (Figure 2-7(c)). Besides, evidenced from Figure 2-7(d), the photocathode also showed excellent stability with unity Faraday efficiency.

Figure 2-7 Mo₃S₄ modified p-Si pillar as H₂ evolving photocathode. (a) Schematic of the architectural design for the complete water splitting based on micropillars. (b) Cross-sectional SEM image of the p-Si pillars. (c) Polarization curves of different photocathodes measured in 1.0 M HClO_4 solution under red-light irradiation ($\lambda > 620$ nm). (d) Stability test of Mo₃S₄/Si pillars as hydrogen-evolving photocathode at 0V vs. RHE under red-light irradiation. (62) Reprinted with permission of (62). Copyright 2011 Nature Publishing Group.

Recent developments of p-Si-based photocathode reveal that the optimum electrode configuration is also a crucial factor that determines the overall electrode

performance. Esposito et al. employed a metal-insulator-semiconductor architecture during the design of their photocathode, which showed substantially improved efficiency.⁽⁶³⁾ Earlier this year (2015), Vesborg's group, for the first time, demonstrated a back-illuminated H₂-evolving photocathode with a bifacial light absorbing electrode structure.⁽⁶⁴⁾

2.3.1.2 III-V semiconductor

The binary, ternary and quaternary combination of Group III elements (Al, Ga and In) and Group V elements (N, P, As and Sb) bring us the family of III-V semiconductors. The prominent physical properties of these compounds have significantly advanced the development of modern semiconductor industry, including the manufacturing of transistors, optoelectronics and solar cells.^(65, 66) Some III-V semiconductors, with favorable band structures, are currently playing central roles in the fabrication 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 (with sulfur or tellurium as dopant) and p-type (with zinc as dopant) 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. Memming and Schwandt for the first time demonstrated the capability of GaP for generate hydrogen gas under illumination.⁽⁶⁷⁾ However, the minority carrier diffusion length of GaP, compared to its absorption depth of visible light, is quite

small for driving efficient solar water splitting.(68) It was proved that structuring of n-GaP, by etching macropore, could enhance its photocurrent in photoelectrochemical regenerative cells as shown in Figure 2-8, and it's believed that similar modification would also improve the performance of p-GaP. (69)

Figure 2-8 The charge separation process within a GaP can be enhanced with structured macroporous junction (69) Reprinted with permission from (69). Copyright (2009) American Chemical Society.

Yang and co-workers further proved that the nanowires of p-GaP are potential photocathode materials that can be scaled up for practical applications.(70, 71) Figure 2-9 (a) shows the GaP nanowires synthesized using a solution-liquid-solid (SLS) strategy without the introduction of surfactants. As a dopant, Zn was incorporated into the GaP nanowires during the synthesis, and the p-type conductivity of Zn-doped p-GaP was affirmed with different approaches. The photoelectrochemical performances of the GaP electrodes were tested in near-neutral electrolyte under chopped simulated solar irradiation. Both planar and nanowire electrodes showed similar onset potential of 0.5 V vs. RHE, and their relatively anodic onset may benefit the design of complete water splitting systems. The transient spike feature from the J - V curve of the nanowire

electrode is much smaller compared to the planar electrode, suggesting its improved reaction kinetics owe to the large surface area. Figure 2-9 (c) compares the absorbed photon-to-current efficiency (APCE) spectra of the nanowire and planar electrodes, and affirmed the much better charge separation efficiency of the GaP nanowires. An up-to-date research published by Standing et al. showed that the arrayed p-GaP nanowires could further boost efficiency of photoelectrochemical hydrogen production.(72)

Figure 2-9 Zinc-doped p-GaP nanowires as photocathode materials for photoelectrochemical water reduction. (a) SEM image of Zn-doped GaP nanowires. (b) Photoelectrochemical performance (J - V scans under chopped 100 mW/cm² AM 1.5 G illumination) of p-GaP planar (yellow) and nanowire (blue) electrodes. (c) The absorbed photon-to-current efficiency (APCE) spectra of GaP planar (yellow) and nanowire (blue, 64 μg/cm²) electrodes.(71) Reprinted with permission from . Copyright (2012) American Chemical Society.

The bandgap of indium phosphide (InP), another well-studied III-V semiconductor, is about 1.35 eV, making it an excellent light-absorbing material in photoelectrochemical cells. Unfortunately, the scarcity along with the high market demand of indium limits the practical application of this material. (73) Heller et al. have modified the surface of oxidized InP with Ru co-catalysts, and achieved a solar

to hydrogen efficiency of 12%.⁽⁷⁴⁾ Later, they further modified p-InP electrodes with Rh and Re using electrochemical deposition, and achieved efficiencies of 13.3% and 11.4%, respectively. In their work, the chemical conversion efficiencies were estimated as the ratio of the energy generated from the photo-decomposed hydrogen in an ideal hydrogen fuel cell to the energy of total input photon flux (light source).

⁽⁷⁵⁾ Parkinson and his co-workers have decorated InP photocathode using noble metal catalysts, with MoSe₂ and WSe₂ as photoanode to split HBr, and achieved a conversion efficiency of 7.8% (calculation based on stored free energy).⁽⁴⁵⁾ More recently, Notten's group have demonstrated the fabrication of MoS₃-decorated InP nanowire arrays as an efficient cathode for photoelectrochemical hydrogen production.⁽⁷⁶⁾ The InP nanowire arrays in their work were prepared through the vapor-liquid-solid (VLS) growth mechanism, using a metalorganic vapor phase epitaxy (MOVPE) system in the presence of gold catalysts. Figure 2-10 (a) and (b) show the 30° tilted and cross-sectional SEM images, respectively, of the as grown InP nanowires on the substrate. As a noble-metal-free co-catalyst, MoS₃ nanoparticles were deposited onto the surface of InP nanowires using a photochemical deposition approach with (NH₄)₂MoS₄ precursor. Confirmed by TEM and EDX mapping, it was found that the catalyst nanoparticles were randomly attached onto the InP nanowires as shown in Figure 2-10 (c). 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 (I_{ph}) of 22 mA/cm² and a maximum efficiency of 6.4%

Figure 2-10 MoS₃-decorated InP nanowire arrays as an efficient photocathode for photoelectrochemical hydrogen production. (a) 30°-tilted and (b) cross-sectional SEM images of InP nanowire arrays. (c) TEM image and elemental mapping of a single MoS₃-decorated InP nanowire. (d) *J-V* curve (black) and conversion efficiency InP nanowire arrays decorated with MoS₃ in 1 M HClO₄ under chopped illumination. (76) Reprinted with permission from (76). Copyright (2014) American Chemical Society.

The application potentials of other III-V semiconductors have also been discussed. Turner and co-workers have reported the syntheses of GaPN and GaAsPN epilayers, and both showed apparently enhanced stability towards photocrossion compared to pristine GaP.(77) Wu et al. have reported the fabrication of GaAsP core-shell nanowire arrays on Si substrates at wafer scale as an efficient photocathode.(78)

2.3.1.3 Transition-metal chalcogenides

Researchers from different groups have shown that tungsten chalcogenides, such as WS₂ and WSe₂ are also promising candidates in photoelectrochemical applications. In 1982, Baglio and co-workers demonstrated that p-WS₂ modified with Pt or Pd co-catalysts can be applied as an efficient hydrogen-evolving photocathode in acidic medium under visible light illumination. (79) Razzini's group have demonstrated the capability of WSe₂ in splitting HI, evolved H₂ bubbles were formed at the crystal steps while I₂ were generated on the flat surface of WSe₂ crystal.(80)

Figure 2-11 P-WSe₂ photocathodes. (a) The *J-V* behavior of noble metal catalyst modified p-WSe₂ photocathode in different electrolytes under 100 mW/cm² illumination. (b) Photostability of the p-WSe₂ electrode in electrolytes with different pH values (81) Reprinted with permission from (81). Copyright (2013) American Chemical Society.

McKone and co-workers have reported the application of noble metal-decorated p-WSe₂ as a photocathode in photoelectrochemical water splitting cell.(81) Their WSe₂ crystals were synthesized using a chemical vapor transport technique, and the noble metal catalysts were deposited onto the WSe₂ crystals through the photoelectrochemical deposition approach. The typical *photocurrent-voltage*

behaviors of the modified p-WSe₂ photocathode under 100 mW/cm² illuminations at different pH values are illustrated in Figure 2-11(a). Promising photocurrent densities of ~14 mA/cm² and ~18 mA/cm² can be yielded at 0V vs. RHE in 0.5 M H₂SO₄ and KHP buffer, respectively. Besides, the advanced photocathode also demonstrated remarkable stability in both acidic and basic media (Figure 2-11(b)).

2.3.1.4 P-type oxide semiconductors

Among the many p-type oxide semiconductors, Cu₂O, with a direct bandgap of ~2 eV, is absolutely the most studied material for photoelectrochemical applications. The p-type conductive behavior of Cu₂O is a result of the presence copper vacancies.(82, 83) When applied as the photocathodes, Cu₂O-based materials possess quite a number of advantages over other candidates, such as material abundance, low-cost, non-toxicity and favorable light-absorption properties.(84) However, the application potential of Cu₂O-based materials is severely hindered by their notoriously poor stability in aqueous electrolyte under solar irradiation: anodic current may lead to its oxidization into CuO, while cathodic current may cause its reduction into metallic copper. (85, 86)

Figure 2-12 The schematic illustration (up) and SEM image (down) of surface-protected Cu_2O photocathode. (87) Reprinted with permission from (87). Copyright (2011) Nature Publishing Group.

Most of the recent reported progresses toward the development of Cu_2O photocathodes are focus on enhancing their photoelectrochemical stability. Parachino et al. proposed an effective strategy to protect the electro-deposited Cu_2O film against photocathodic decomposition through the atomic layer deposition (ALD) of a protective nanolayer, which is composed of Al-doped ZnO and TiO_2 as shown in Figure 2-12. (87) Owe to the favorable band alignments (type-II band offset) established among the different components, the photocorrosion used to take place on the interface was significantly minimized. The optimal photoelectrode in their case study could generate a large cathodic photocurrent of 7.6 mA/cm^2 , and also demonstrated remarkable stability and a close-to-unity faraday efficiency. Zhang et al. came up with another approach to improve the stability of Cu_2O nanowires using a thin carbon protective layer. (88)

Figure 2-13 Amorphous molybdenum sulfide-coated Cu₂O photocathode. (a) Schematic illustration and (b) digital photograph of the MoS_{2+x}-coated Cu₂O photocathode. (c) Cross-sectional SEM image. (d) *J*-*V* curves of MoS_{2+x}-Cu₂O obtained at different pH values. (89) Reprinted with permission from (89). Copyright (2014) Nature Publishing Group.

Carlos and his teammates took one step further, and demonstrated that amorphous molybdenum sulfide (MoS_{2+x})-coated Cu₂O can be used as an efficient photocathode even under slightly basic environment. (89) They first coated the surface of Cu₂O with n-type oxide (Al-doped ZnO and TiO₂) nanolayers through ALD. MoS_{2+x} catalytic layer was then deposited onto the electrode surface using either electrochemical deposition (ECD, applying consecutive cyclic voltammetry) or anodic photoelectrodeposition approach. Figure 2-13 (a) and (b) show the schematic illustration and the digital photograph of the amorphous molybdenum sulfide coated Cu₂O photocathode. The cross-sectional structure of the photocathode is illustrated in Figure 2-13 (c), in which distinct functional layers can be clearly observed.

Interestingly, they found that the architecturally engineered photocathode can generate substantial photocurrents within a wide pH range, and showed surprisingly good stability and a ~100% Faradaic yield.

Figure 2-14 Dye-sensitized NiO photocathode for water reduction (a) schematic and the energy diagram of dye-sensitized NiO photocathode. (b) The effect of CodmgBF₂ co-catalyst in determining the performance of NiO-based photocathodes.(90) Reprinted with permission from (90). Copyright (2013) American Chemical Society.

Another important p-type oxide semiconductor is nickel oxide (NiO), which has been widely used as the photocathode material in p-type dye-sensitized solar cells. (91-94) Similar to Cu_2O , the p-type conductivity of NiO is mainly attributed to the Ni vacancies in the crystal lattice. (95, 96) Wu's group has successfully extended the application of Dye-sensitized p-type NiO photocathode in solar water splitting application as shown in Figure 2-14 (a). (90) The NiO film on FTO was first fabricated through the doctor-blade method, using $\text{Ni}(\text{OH})_2$ sol prepared by mixing NiCl_2 and copolymer F108 in the ethanol-water mixture. An Al_xO_y layer, which can significantly inhibit the charge recombination, was then deposited onto the surface of NiO using the ALD technique. The bi-functional cyclometalated Ru(II) compound, labeled as O22, was then firmly anchored onto the film, forming a favorable spatial arrangement that can effectively facilitate the hole injection to NiO. To further

improve the catalytic activity of this photocathode, the group has investigated the effects of a well-studied water reduction catalyst, namely $\text{Co}(\text{dmgBF}_2)_2$. As shown in Figure 2-14 (b), the incorporation of $\text{Co}(\text{dmgBF}_2)_2$ cocatalysts can apparently improve the saturated photocurrent of the photocathode as well as shift the onset potential towards anodic direction by ~ 40 mV compared to the electrode without catalyst.

2.3.1.5 Other photocathode materials

Many other candidate photocathode materials have also been proposed and demonstrated. Fernández and his teammates have fabricated $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ thin film that can decompose water at moderate pH (5~7) environment. (97) Marsen's group has reported the fabrication of a CuGaSe_2 thin film photocathode using a vacuum deposition approach. With a bandgap of 1.65 eV, the hydrogen-evolving photocathode can produce a photocurrent of 13 mA/cm^2 under outdoor 1 sun illumination. (98) Iwashina and Kudo have showcased a photocathode prepared using powdered Rh-doped SrTiO_3 , which exhibited p-type conductive and showed photoresponse towards visible light irradiation with a wavelength up to 540 nm. (99) Recently, Bourgeteau and her teammates have designed a high-performance H_2 -evolving photocathode based on organic semiconductor. (100)

2.3.2 Photoanode materials

In photoelectrochemical cells, photoanode is the electrode on which oxygen evolution reactions or other oxidation reactions take place. (15) In most cases, the

photoanodes should be n-type semiconducting materials, as the band bending at the interface between the electrode and electrolyte may lead to the formation of energetically favorable electric fields, which can push the photogenerated holes towards the surface of electrodes to react with the solution species. The bandgap and band edge positions of the photoanode materials have to fulfill the requirements of single- or multiple-bandgap photoelectrochemical water splitting systems. In addition, these materials should possess excellent stability under oxidizing conditions in aqueous environment. The efficiencies of the water oxidation are sometimes limited by the interfacial kinetics of the OER. In this case, catalysts that can enhance OER need to be utilized to modify the photoanodes, and some of the commonly used OER catalysts will be discussed in the following sections.

As mentioned previously, 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 (VB) is made up with O $2p$ orbitals, while the conduction band (CB) 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, while the conduction band edge of these 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. (101) 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. (102) 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.

Under solar irradiations, the holes in the valence band of n-type photoanodes will diffuse to the electrode-electrolyte interface to oxidize water. The conduction band edges of those commonly used photoanode materials are ~ 3.0 V vs. NHE, much higher than the redox potential of oxygen evolution reaction (1.23 V vs. NHE). In this case, it's a tough challenge to design efficient oxygen-evolving photoanodes, since a significant portion of absorbed photon energy would be wasted through thermal relaxation. (15) As a consequence, most of the photoanode materials found in literatures are functioning at low efficiencies to perform oxygen evolution reactions. In this section, several state-of-the-art photoanode materials will be discussed, particularly the transitional metal oxides, which have been extensively studied in the past four decades, since the first report made by Honda and Fujishima using TiO_2 as the photoanode for driving photolysis under UV illumination. (14)

2.3.2.1 Titanium dioxide

TiO_2 -based materials are now playing central roles in photoelectrochemical applications, especially in the area of dye-sensitized solar cells. (103) But the unfavorable visible-light absorption capability of phase-pure TiO_2 -based photoelectrodes, due to the relatively large bandgap energy, severely limits their conversion efficiency. (104) To overcome the challenge, two major strategies have

been developed, namely doping TiO_2 with transition metals (105-107) and creating reduced form of TiO_x . (108, 109) However, these strategies sometimes bring us new problems, for examples, the attenuated thermal stability and reduced charge mobility. In 2001, as a significant breakthrough to the field, Asahi's research group introduced N-doped TiO_2 , which was stable and active towards visible irradiation ($\lambda < 500 \text{ nm}$). (110) One year later, Khan's group reported another strategy to enhance the properties of TiO_2 using flame pyrolysis, and the chemically modified photoanode showed a maximum photo-conversion efficiency of 8.35% at an applied bias of 0.3V. (111)

Over the past ten years, rapid advancement in nanotechnology brought us the dramatic structural evolution of TiO_2 -based materials at micro- and nano-scales. (28, 112-114) Bard's group has reported the fabrication of C-doped TiO_2 nanotube arrays as a revolutionary photoanode (Figure 2-15(a)). (115) In their work, the high-aspect-ratio TiO_2 nanotubes were fabricated through the anodization of Ti substrate in an electrolyte containing 1 M monoammonium phosphate (MAP) and 0.5 wt% ammonium fluoride. The morphology of the resulting TiO_2 film is voltage-dependent, and well-structured TiO_2 nanotubes can be obtained with an applied voltage of $\sim 15 \text{ V}$. Carbon, as a dopant, was introduced into the TiO_2 films through high-temperature ($500 \sim 800 \text{ }^\circ\text{C}$) annealing in the presence of CO gas flow. Figure 2-15 (b) shows the cross-sectional SEM image of the as-fabricated C-doped TiO_2 nanotube arrays obtained at $600 \text{ }^\circ\text{C}$, in which the tubular nanostructures were well retained after the thermal treatment. The photoelectrochemical activities of the C-doped TiO_2 nanotube arrays were evaluated in 1 M KOH. Illustrated in Figure 2-15 (c) are the J - V behaviors of C-doped TiO_2 nanotubes under different lighting conditions. The authors found that the optimum temperature used during the treatment should be $\sim 600^\circ\text{C}$ (Figure 2-15(d)), as further increment in temperature may results in a decreased

photocatalytic sites. Compared to the pristine TiO_2 photoanode, the modified nanotube arrays exhibited apparently improved photoresponses towards visible-light irradiation. These results suggest that both doping and nanostructuring are important and effective strategies that can be employed to modify the catalytic properties of photocatalysts.

Figure 2-15 C-doped TiO_2 nanotube arrays. (a) Schematic of TiO_2 nanotube-based anode in photoelectrochemical cell. (b) Cross-sectional SEM image of C-doped TiO_2 nanotubes. (c) The J - V behaviors of C-doped TiO_2 nanotubes prepared at 600°C under different lighting conditions. (d) The maximum photocurrent density as a function of the temperature used during the heat treatment. (115) Reprinted with permission from (115). Copyright (2006) American Chemical Society.

By using TiO_2 as the photoanode, another important progress was achieved by Wang et al., who improved the performance of TiO_2 nanowires through a facile hydrogen treatment. (116) Shown in Figure 2-16 (a), oriented rutile TiO_2 nanowires were first grown onto the surface of FTO-coated glass substrate using the

hydrothermal method developed by Liu and Aydil. To modify the pristine electrodes, the as-synthesized TiO_2 samples were first subjected to a 3-hour high-temperature (550°C) treatment in air, followed by annealing under H_2 atmosphere at varied temperatures ($200\sim 500^\circ\text{C}$) for half an hour. The hydrogen treatment could change the color of pristine TiO_2 to different extents, depending on the temperature, as illustrated in Figure 2-16(b). The darker colors (yellowish green) signify the improved visible light absorption of the H-doped TiO_2 after the treatments at $300\sim 450^\circ\text{C}$. However, temperatures exceeding 450°C may lead to the reduction of SnO_2 to metallic Sn within the FTO substrate, thus resulting in the damage of the electrode. The photoelectrochemical performance of the samples treated at 350 , 400 and 450°C were compared in 1 M NaOH electrolyte under 100 mW/cm^2 illumination as shown in Figure 2-16 (c). The photoanode prepared at 350°C showed the best performance among the three electrodes, with a maximum photocurrent of $\sim 2.5\text{ mA/cm}^2$. The poorer performance of the other two electrodes may cause by the increased sheet-resistance of the FTO substrates during high-temperature treatments. The consistent trend was observed using the IPCE measurements (Figure 2-16(d)). The authors attribute the enhancement of H-doped TiO_2 nanowires to the increased donor density, as a result of formation of numerous oxygen vacancies after the treatment.

Figure 2-16 Hydrogen-doped TiO₂ nanowire arrays. (a) Top-view SEM image of the TiO₂ nanowire arrays. (b) Digital photograph of the pristine and H-doped TiO₂ nanowire arrays treated at different temperatures. (c) *J-V* behavior of H-doped TiO₂ prepared at different temperature. (d) IPCE spectra of pristine TiO₂ and H-doped TiO₂ prepared at different temperatures collected at -0.6 V vs. Ag/AgCl.(116) Reprinted with permission from (116). Copyright (2006) American Chemical Society.

To date, continuous efforts have been devoted to the further improvements of TiO₂-based photoanodes. Cho and his teammates have designed branched TiO₂ nanoarrays, which can provide much larger surface area for more efficient hydrogen production. (117) Lin's group has sensitized the TiO₂ nanotube arrays using palladium QDs with uniform size, which surprisingly boosted the photon-to-current efficiency to almost 100% at $\lambda = 330$ nm.(118) Li's group has decorated the TiO₂ nanowires using gold nanoparticles, and has investigated their structural effects in depth. (119) Hwang and co-workers explored the effects of the length of nanowire as well as the thickness of ALD coating in determining the performance of TiO₂ photoanodes. (120)

2.3.2.2 Zinc oxide

Similar to TiO_2 , Zinc oxide (ZnO) is also a wide bandgap semiconductor that has been extensively studied in solar water splitting applications. (121) Due to the presence of oxygen vacancies or Zn interstitials, ZnO usually exhibits n-type conductivity. ZnO is an amphoteric oxide, which can react with both acids and bases, making it a less stable material in solar water splitting applications. However, many comparative studies suggest that the electron mobility in ZnO is much better than that in TiO_2 films.(122, 123) To date, numerous practical strategies, such as nanostructuring, doping and sensitization, allow us to fully utilize the merits of ZnO as a photoanode.

Yang et al. have reported the application of N-doped ZnO nanowire arrays in solar water splitting cell. (124) As shown in Figure 2-17(a), the dense and homogeneous ZnO nanowires were first grown on ITO-coated glass substrate using a hydrothermal method. Nitrogen dopants were successfully introduced into the lattice of ZnO crystals through a two-step thermal annealing approach. The samples were first treated at 530°C under ammonia environment, followed by annealing at the same temperature under N_2 environment for 30 min. The doping process can change the white color of pristine ZnO to yellowish gray. At first, extending the duration of ammonia treatment can increase the dopant concentration, but will eventually reach a plateau of $\sim 4\%$, as shown in Figure 2-17(b). From the results of photoelectrochemical tests, N-doped ZnO exhibits an order of magnitude improvement in photocurrent compared to the pristine (Figure 2-17(c)). Besides, the

photoanode also demonstrated a reasonable stability in the amperometric test (Figure 2-17(d)).

Figure 2-17 N-doped ZnO nanowire arrays-based photoanode. (a) SEM image of the ZnO nanowire arrays prepared using hydrothermal method. (b) The concentration of N dopant as a function of annealing time under ammonia environment. (c) J - V behaviors of pristine and N-doped ZnO nanowires in buffered NaClO_4 electrolyte (pH= 7) under 100 mW/cm^2 illuminated and dark conditions. (d) Photocurrent responses under constant applied voltage of 0.5 V vs. Ag/AgCl. (124) Reprinted with permission from (124). Copyright (2009) American Chemical Society.

Figure 2-18 ZnOS solid solution nanowire arrays. (a) Schematic illustration of the preparation of ZnOS nanowire arrays. (b) J - V behaviors of different ZnO nanowire-based photoanodes. (c) Hydrogen production of different samples at 0.5 V vs. Ag/AgCl in 0.5 M Na₂S and K₂SO₃ electrolyte (pH= 11).⁽¹²⁵⁾ Reprinted with permission from ⁽¹²⁵⁾. Copyright (2011) John Wiley and Sons.

An alternative approach to strengthen the photoresponses of ZnO, developed by Chen and co-workers, is to form the solid solution with ZnS.⁽¹²⁵⁾ The procedures for fabricating of ZnO-ZnS solid solution-based photoanode are illustrated in Figure 2-18 (a). Well-aligned ZnO nanowires were first synthesized using hydrothermal method, followed by the deposition of ZnS QDs. The ZnO-ZnS composites were then converted to the solid the random solution after the thermal treatment carried out at 450°C. Compositional studies suggest that the distribution of sulfur elements was asymmetric, most probably due to the random allocation of ZnS QDs during the deposition process. Photoelectrochemical tests were performed in 0.5 M Na₂S and K₂SO₃ electrolyte (pH =11) to compare the three different photoanodes (Figure 2-18(b)). At an applied potential of 0 V vs. Ag/AgCl, The ZnO-ZnS solid solution photoanode exhibited a pronounced photocurrent of 0.88 mA/cm², which is two times larger than that of pristine ZnO nanowires (0.45 mA/cm²). The amount of evolved H₂ was further measured using a gas chromatograph (GC) under simulated solar

irradiation as shown in Figure 2-18(c), which shows a consistent trend with the J - V behaviors. The authors attribute the enhancement to the increased density of $O_{2p} + S_{3p}$ and Zn_{4p} unoccupied states within the solid solution of ZnO-ZnS, which effectively altered the band structure of the composite.

Many other research groups across the world have reported the milestones achieved for improving the performance of ZnO-based photoelectrodes. Wang et al. have reported the double-sided CdS and CdSe QD-sensitized ZnO nanoarrays, which could maximize the utilization of visible light.(126) Yang's group has designed branched N-doped ZnO nanotetrapods to boost the roughness factor of the photoanode, hence maximizing its light-harvesting capacity on unit geometric surface area.(127) More recently, Guo et al. have reported the fabrication of graphene QDs-sensitized ZnO nanowires as a green photoanode for enhanced water splitting. (128)

2.3.2.3 Perovskites

Titanates, such as $BaTiO_3$ and $SrTiO_3$, are promising candidate materials in solar water splitting applications, since the incorporation of Ba^{2+} or Sr^{2+} can lead to the formation of perovskite structure. Besides, the addition of these cations may also results in the shift of the conduction band edge of titanates to a level that is more negative than NHE. With the decoration of Pt or other appropriate HER co-catalysts; these titanate materials can achieve complete water splitting under near-UV illumination, simultaneously producing hydrogen and oxygen. (15) The perovskite structures can be also found in $NaTaO_3$, which is an isoelectronic compound to $SrTiO_3$ and possess a tunable bandgap of (~ 4.0 eV). Kudo et al. have enhanced the

performance of NaTaO_3 with a 2% doping of La. They found that the surface area of the crystal was increased by 8 times, and the La-doped Na-doped NaTaO_3 exhibited improved activity in decomposing water with an breakthrough O_2 evolution rate of 9.7 mmol/hr under the illumination of 400 W-Hg light source in pure water. Figure 2-19 shows the morphology and reaction mechanisms of 2% La-doped NaTaO_3 . (129)

Figure 2-19 The surface morphology (left) and reaction mechanisms (right) of $\text{NaTaO}_3\text{:La}$ (129) Reprinted with permission from (129). Copyright (2003) American Chemical Society.

The perovskite structures in titanates, niobates and tantalates can be further modified with the addition of highly charged metal counterion species. This type of materials, such as $\text{Ba}_5\text{Ta}_4\text{O}_{15}$, (130-132) $\text{Sr}_2\text{Ta}_2\text{O}_7$, (133, 134) $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ (135) and $\text{La}_2\text{Ti}_2\text{O}_7$, (136-138) has been reported as promising photocatalysts for water splitting applications, and some of them can be modified into photoanodes. In these materials, the non-bridging oxygen atoms can form terminal $\text{Metal}=\text{O}$ (oxo) groups, which are generally recognized as catalytic centers for oxygen evolution reaction. (139)

2.3.2.4 Other photoanode materials

Owing to its abundance in Earth's crust, excellent light absorption properties and outstanding chemical stability, hematite ($\alpha\text{-Fe}_2\text{O}_3$) is another important and well-studied photoanode material. In 1976, Hardee and Bard, for the first time, reported the use of $\alpha\text{-Fe}_2\text{O}_3$ in solar water splitting application.⁽¹⁴⁰⁾ They fabricated the polycrystalline Fe_2O_3 films on Ti substrate through the chemical vapor deposition (CVD) approach, and studied their photoelectrochemical behaviors in electrolytes with different pH values. Later, Kennedy's group doped $\alpha\text{-Fe}_2\text{O}_3$ with different Group IVA elements, and concluded that Si^{4+} , Sn^{4+} and Ge^{4+} -doped $\alpha\text{-Fe}_2\text{O}_3$ have better photoelectrochemical performance compared to the Ti^{4+} doped one.⁽¹⁴¹⁾ Cesar and co-workers have reported the fabrication of translucent $\alpha\text{-Fe}_2\text{O}_3$ film as the photoanode for photoelectrochemical water splitting, and have studied the nanostructure-directing effect of Si dopants.⁽¹⁴²⁾ Gamelin's team have coated an amorphous cobalt/phosphate (Co-Pi) composite co-catalyst onto the surface of $\alpha\text{-Fe}_2\text{O}_3$ film, and the composite photoanode have achieved a significant cathodic shift (>350 mV) in the onset overpotential (Figure 2-20).⁽¹⁴³⁾ Sivula et al. have summarized the most important progresses that have been made in developing $\alpha\text{-Fe}_2\text{O}_3$ -based photoelectrodes over the past four decades.⁽¹⁴⁴⁾

Figure 2-20 Cobalt/phosphate (Co-Pi) composite modified $\alpha\text{-Fe}_2\text{O}_3$ photoanode. (a) SEM image of the Co-Pi/ $\alpha\text{-Fe}_2\text{O}_3$ photoanode. (b) J - V behaviors of the Co-Pi modified- and pristine $\alpha\text{-Fe}_2\text{O}_3$ photoanodes under dark and illuminated conditions (AM 1.5, back illumination) (c) Working principles of CoPi/ $\alpha\text{-Fe}_2\text{O}_3$ photoanode. (143) Reprinted with permission from (143). Copyright (2009) American Chemical Society.

Covalent M-O-M networks can be easily formed in the oxides of metal with high nuclear charge, such as Mo^{6+} and W^{6+} . With a bandgap of 2.7 eV, WO_3 can function as a photoanode that oxidize water to oxygen, even without the additional OER co-catalysts. (145) Relevant computational simulations indicate that the surface of WO_3 crystal is fully covered by oxygen atoms, which can ease the water oxidation by forming hydroxyl and hydroperoxide intermediates. (146)

Many colored oxide compounds that consist of soft metal ions, such as Pb^{2+} and Bi^{3+} , have been synthesized and tested in solar water splitting systems. Monoclinic BiVO_4 (BVO) has a bandgap of 2.4 eV, and is capable of driving oxygen evolution reaction under visible light illumination. However the poor charge carrier separation in BiVO_4 severely limits its solar energy conversion efficiency. Kim and Choi have modified nanoporous BiVO_4 photoanodes using double-layered OER co-catalysts, namely FeOOH and NiOOH , and showed greatly enhanced charge separation. (147) Luo et al. have reported the development of a porous Mo-doped BiVO_4 electrode that can carry out photoelectrochemical water oxidation in seawater. (148)

2.4 Electrocatalysts

The development of effective electrocatalysts is another important topic in the field of solar water splitting, for both photoelectrochemical and photocatalytic systems. The utilization of appropriate co-catalysts may lower the electrochemical overpotentials that required in hydrogen and oxygen evolution reactions. In addition, these co-catalysts provide interfaces to improve the efficiency of electron-hole separation processes, thus leading to a higher overall efficiency. (48)

The catalytic performance of these 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. (15) In the following sections, some outstanding electrocatalysts for hydrogen and oxygen evolution reactions will be briefly discussed.

2.4.1 Electrocatalysts for hydrogen evolution reaction (HER)

The hydrogen evolution reaction (HER), which was first discovered in the 18th century, is one of the most well studied processes in electrochemistry. It is frequently used as a model for the investigating the kinetics of other electrochemical reaction systems. It's generally accepted that HER process involve two steps, namely the bonding of protons to the catalyst surface $H^+ + e^- + * \rightarrow H^*$ (Volmer reaction), where * denotes the active site that capable of binding to proton, followed by desorption of hydrogen molecules through Heyrovsky reaction ($H^+ + e^- + H^* \rightarrow H_2 + *$) and Tafel reaction ($2H^* \rightarrow H_2 + *$). (149)

Platinum (Pt) and other noble metals are considered as the most effective electrocatalysts towards hydrogen evolution reaction, but their scarcity and expensiveness limit their practical applications for large-scale hydrogen generation. Nickel (Ni) is the most active pure metal catalyst for HER among non-precious metals. Consequently, most mixed-metal HER catalysts found in literature are binary or ternary systems that contain Ni, such as Ni-Co, Ni-Mo, Ni-Mo-Cd and Ni-Mo-Fe. (15) Many research groups found that, the performance of these materials are comparable to those expensive noble metals, as the high current density can be generated with a small Tafel slope. Other than pure metals and mixed-metal catalysts, many chemical compounds that are consisted of metal and non-metal elements also show excellent activities in HER. Various oxide materials have been tested, and Goodenough et al. showed that $\text{Sr}_x\text{NbO}_{3-\delta}$ is a promising HER catalyst in acidic medium, due to its low cost and outstanding stability.(150)

Sulfides, such as NiS and MoS_2 , also exhibit great catalytic performance in HER. (151, 152) Hinnemann and coworkers have discussed about the important criteria in choosing the suitable catalysts for HER at room temperature, based on density functional theory (DFT) calculations.(153) Metals that form firm bonds with H atoms are excluded from the list of ideal HER catalysts, since the H_2 desorption process can be severely limited by the strong interaction. On the other hand, metals that do not form bonds with H atoms, such as gold, are also excluded from the list, due to the unfavorably slow proton/electron transfer step. Therefore, for an ideal HER catalyst, the free energy of adsorbed H should be similar to that of the reactant or production. This theory explains why hydrogenase and nitrogenase can catalyze H_2 evolution reaction the most efficiently (Figure 2-21a).

Figure 2-21 (a) Free energy diagram for hydrogen evolution on different catalysts and metals at a potential $U = 0$ (RHE), (b) molecular model of the Mo edge with sulfur monomers on MoS_2 , (c) the polarization curves obtained using Pt and MoS_2 , (d) scanning tunneling microscopy (STM) images for the MoS_2 nanoparticles supported on graphite. (153) Reprinted with permission from (153). Copyright (2005) American Chemical Society.

Interestingly, it was found that the edge of MoS_2 closely resembles the structure of the nitrogenase active site, as the sulfur atom that binds to hydrogen is two-fold coordinated in both case (Figure 2-21b). They further prepared nano-sized MoS_2 on graphite substrate to study the catalytic behaviors under acidic condition, and revealed their ideal HER performance with a reasonable onset overpotential of 0.1 – 0.2 V.

Figure 2-22 STM images of MoS₂ nanocrystals with different size and coverage: (a) annealed at 400°C, (b) annealed at 550°C. (c) Polarization curves of different MoS₂ samples. (d) Plot of exchange current density against the length of MoS₂ edges. (154) Reprinted with permission from (154) with permission. Copyright (2007) American Association for the Advancement of Science.

In 2007, Jaramillo et al. further identified the active sites that are responsible for driving electrochemical hydrogen evolution on MoS₂. (154) The ratio between edge sites and basal plane sites of MoS₂ nanocrystals can be tuned by changing the annealing temperatures (Figure 2-22a & b), and the sintering process will not change the nature of the sulfide Mo edges. As shown in Figure 2-22c, the polarization curves of MoS₂ nanocrystals with different area coverage and edge length were recorded and compared. All the samples showed similar Tafel slope (55 – 60 mV/dec) regardless of sintering temperature and area coverage. The exchange current densities that extracted from the Tafel plots of different samples were plotted against their corresponding edge length as illustrated in Figure 2-22d. The result reveals the linear correlation between the catalytic activities and exposed edge sites for MoS₂ nanocrystals. This

discovery is a remarkable milestone as it provides important guidelines for the design of MoS₂-based HER catalysts.

Figure 2-23 (a) SEM image of the MoS₂/RGO composite. (b) polarization curves and (c) Tafel plots of MoS₂/RGO, MoS₂ nanoparticles and Pt. (d) Stability test of MoS₂/RGO. (155) Reprinted with permission from (155). Copyright (2011) American Chemical Society.

Owing to the rapid advancement in nanomaterial design, the development of MoS₂-based HER catalyst has been accelerated over the past few years. Li and coworkers have reported the syntheses of graphene-supported MoS₂ nanoparticles through a facile one-step solvothermal approach.⁽¹⁵⁵⁾ Functioning as a novel support, the graphene oxide can mediate the uniform growth of MoS₂ nanoparticles (Figure 2-23a). In sharp contrast, the absence of graphene oxide will lead to the formation of random-sized MoS₂ aggregates. The authors attributed the homogeneous distribution of MoS₂ to the favorable interactions between the Mo precursors and the surface functional groups of GO. Compared to the coalesced MoS₂ particles, the MoS₂/RGO demonstrated drastically improved catalytic activity towards HER (Figure 2-23b). As

shown in Figure 2-23c, the 41 mV/dec Tafel slope of MoS₂/RGO indicates that the Heyrovsky reaction (electrochemical H₂ desorption) is the rate-limiting step. Apart from the excellent catalytic activities, the composite also showed outstanding stability, as the cathodic current can be well retained after 1000 consecutive testing cycles.

Figure 2-24 (a) Schematic illustration of defect-rich MoS₂ nanosheets with additional exposed edge sites. (b) Comparison of the HER polarization curves obtained using different MoS₂ samples, blank glassy carbon electrode and Pt electrode.(156) Reprinted with permission from (156). Copyright (2013) John Wiley and Sons.

More recent findings suggest that defect engineering is an effective approach to further boost the catalytic performance of MoS₂-based HER catalysts. Xie's group has reported a scalable pathway to fabricate defect-rich MoS₂ ultrathin nanosheets, and they found that the concentration of precursor plays critical roles in determining the final morphology of MoS₂ nanosheets.(156) During the syntheses, excessive amount of thiourea can be adsorbed onto the primary nuclei of MoS₂, thus hindering the epitaxial-oriented expansion of MoS₂ nanosheet and resulting in the formation of substantial defects across the basal plane (Figure 2-24a). Compared to the bulk MoS₂ and defect-free MoS₂ nanosheets, the defect-rich sample exhibited greatly improved catalytic behavior (Figure 2-24b).

2.4.2 Electrocatalysts for oxygen evolution reaction (OER)

RuO_2 is the most well studied catalyst material for electrochemical oxygen evolution reaction. Due to the more complex intermediate structure and reaction kinetics of an oxidized phase in water oxygen reactions, the exchange current densities of OER catalysts are usually 100~1000 times smaller than that reported for HER catalysts (Pt and Pd), which can reach the $\sim 10^{-3} \text{ A/cm}^2$ scale. As a consequence, the electrodes for water oxidation are usually operated at higher overpotentials. Tafel plots, which describe the overpotential-current density behavior (η - J) of these materials, are usually employed to compare their intrinsic catalytic performance towards OER.⁽¹⁵⁾ Tafel slope of these materials are laid in the range between 30 and 120 mV/decade, and most of them possess a Tafel slope of $\sim 40 \text{ mV/decade}$. The development of effective OER catalysts has been focused on four different classes of conductive metal oxides. The first class is metal dioxides, which include the most extensively studied OER catalysts RuO_2 and other precious metal dioxides. The second class consists of those oxides with spinel crystal structure, such as Co_3O_4 and NiCo_2O_4 . The members of the third class include many oxides with perovskite crystal structures, like NiLa_2O_4 and LaCoO_3 , while Pyrochlores, such as $\text{Pb}_2\text{Ru}(\text{Ir})_2\text{O}_7$, belong to the last class.

Chaper 3 Anatase TiO₂ microspheres with reactive {001} facets for improved photocatalytic activity¹

3.1 Introduction

Anatase titanium dioxide (TiO₂) is one of the most important semiconductors, which finds applications in many different fields including photovoltaics, photo/electrochromics, photocatalysis, photonics, sensors, and smart surface coatings. (157-164) The activity of anatase TiO₂ strongly depends on its crystallinity, size and surface states. Both theoretical and experimental studies show that the (001) surface of anatase TiO₂ is much more reactive than the thermodynamically more stable (101) surface. (165-168) The surface energy of the {001} facet of anatase is twice more than that of the {101} facet ($\gamma_{\{001\}}=0.9\text{J/m}^2 > \gamma_{\{100\}}=0.53\text{J/m}^2 > \gamma_{\{101\}}=0.44\text{J/m}^2$). (169, 170) As a result, the (001) surface of anatase TiO₂ would diminish quickly during the crystal growth stage in order to minimize the total surface energy, resulting in most synthetic anatase crystals, as well as those naturally appearing, dominated by the less-reactive (101) surface.

Important progress was made recently by Yang et al., who reported the synthesis of anatase TiO₂ microcrystals with 47 percent of reactive {001} facets. (171) Thereafter, a large number of studies have been conducted towards the preparation of different shaped anatase TiO₂ micro- or nanocrystals with exposed {001} facets. (28, 166, 168, 172-184) For example, Murray et al., synthesized small and thin anatase TiO₂ nanocrystals using a standard air-free Schlenk line technique under nitrogen atmosphere. (178) Kang et al., compared the morphological differences between

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anatase microcrystals synthesized from TiF_4 and TiCl_3 .⁽¹⁷⁹⁾ Zhao et al. studied the evolution of anatase TiO_2 microspheres on titanium substrate in a one-pot hydrothermal reaction. With increase in hydrothermal reaction time, they observed the surface crystal facet transformation from $\{001\}$ to $\{101\}$, which they attributed to the etching effect caused by the added hydrofluoric acid during the reaction.⁽¹⁸⁰⁾ Yang et al., investigated the stability of $\{001\}$ faceted anatase TiO_2 nanosheets under hydrothermal conditions.⁽¹⁸¹⁾ However, most of the synthesis reported so far was carried out in the hydrofluoric acid, which is highly toxic and corrosive. In addition, the synthesized anatase TiO_2 micro- or nanocrystals are exposed with both high-energy $\{001\}$ facets and thermodynamically stable $\{101\}$ facets.

In this chapter, we will discuss about the development of a facile hydrothermal method for preparing anatase TiO_2 microspheres with $> 90\%$ exposed reactive $\{001\}$ facets without introducing any additional hydrofluoric acid. The as-prepared anatase TiO_2 microspheres exhibit excellent photocatalytic activity in degrading toxic organic contaminants and producing hydrogen from water under UV light irradiation.

3.2 Experimental

3.2.1 Synthesis of anatase TiO_2 microspheres and referenced TiO_2 microsheets

The formation of anatase TiO_2 microspheres is based on hydrolysis and condensation of titanium tetrafluoride (TiF_4). In a typical synthesis, 60 ml of 0.04 M TiF_4 aqueous solution, which was prepared by adding 0.297g of TiF_4 in 60 ml of 0.01 M HCl solution, was added into a Teflon-lined stainless steel autoclave (125 ml volume, Parr Instrument Co.). To examine the effect of Cl^- on the formation of TiO_2 microsphere, 0.01 M HNO_3 solutions or 0.005 M H_2SO_4 solution was used instead of the HCl solution to prepare the TiF_4 precursor solution. NaCl was also used to change

the concentration of Cl^- in the starting TiF_4 solution. The autoclave was kept inside an electric oven at 200°C for 0 – 5 hours, After synthesis, the autoclave was cooled naturally to room temperature and the products were washed with 0.1 M NaOH aqueous solution and deionized water for several times and collected by centrifugation. For comparison of the photocatalytic activity, referenced TiO_2 microspheres were synthesized according to the literature method. In a typical synthesis, 27 ml of deionized water, 3 ml of 0.04 M TiF_4 aqueous solution and 0.4 ml of hydrofluoric acid (10 wt%) were added to a Teflon-lined stainless steel autoclave and the autoclave was kept inside an electric oven at 180°C for 4 hours.

3.2.2 Material characterization

The crystal structure of the TiO_2 microspheres was examined using powder X-ray diffraction (XRD). The XRD patterns were recorded in a Bruker-AXS Microdiffractometer (model D5005) with Cu $\text{K}\alpha$ radiation ($\lambda=1.5406\text{\AA}$) from 20° to 70° at a scanning speed of $2.4^\circ/\text{min}$. The X-ray tube voltage and current were set at 45 KV and 40 mA, respectively. Morphology and composition of the microspheres were studied using field emission scanning electron microscopy, energy-dispersive X-ray spectroscopy (FESEM/EDX, JSM-6700F), transmission electron microscopy (TEM/HRTEM, FEI Tecnai G2 30, 300kV). The fraction of {001} facets was estimated by measuring the dimensions of the crystallites from FESEM images and calculating the respective areas of the {101} and {001} facets. The fraction of {001} facets were calculated by assuming that these two planes make up nearly 100% of all the surfaces and using the following equation:

$$\text{Fraction of 001 facets} = \sum A_{(001)} / (\sum A_{(001)} + \sum A_{(101)}) \quad (6)$$

Chemical composition of the microspheres was also examined with X-ray photoelectron spectroscopy (XPS, Surface Science SSX-100). All binding energies were referenced to the C1s peak (284.6 eV) arising from adventitious hydrocarbons.

3.2.3 Photocatalytic degradation of methyl orange (MO)

In the photodegradation test, 20 mg of as-prepared anatase TiO₂ microspheres was added to 45ml of deionized water in a 100 ml beaker. The mixture was then ultrasonicated for 30 minutes over a water bath to ensure good catalyst dispersion, following by adding 5ml of 100mg/l methyl orange (MO) solution, which had been bubbled with purified air for 1 hour prior to use. The mixture was then stirred in the dark at room temperature for 30 minutes and later illuminated with UV lamp (Mineralight Lamp, Model UVGL-25) at a distance set to give a surface light intensity of 400 μ W/cm² for 60 minutes. During the illumination, 5 ml of solution together with the catalyst was drawn out every 10 minutes to determine the concentration of the remaining MO using UV-vis spectrophotometry; the solution was separated the catalyst through syringe filtration.

3.2.4 Photocatalytic hydrogen evolution test

Photocatalytic reaction for hydrogen evolution was carried out in a gas-closed circulation system. 5 mg of photocatalyst particles were dispersed in 3ml of water methanol solution in a 14ml quartz cell. Argon (~1300 Torr) was introduced into the reaction system after deaeration. The reaction system was irradiated using a 450 W Xe lamp at a distance set to give a surface light intensity of ~ 400mW/cm². The amounts of evolved hydrogen gas were determined every 1 hour using an inline gas chromatograph (Agilent 3000A micro GC).

3.3 Results and discussion

3.3.1 Characterization of the anatase TiO₂ microspheres

Anatase TiO₂ microspheres with >90% exposed reactive {001} facets were synthesized using hydrofluoric acid generated in-situ through hydrolysis of TiF₄ as a capping and stabilizing agent under hydrothermal reactions. As shown in Figure 3-1, the as-synthesized TiO₂ microspheres have an average size of around 2.5 μm with relatively narrow size distribution. The mean size and size distribution was consistent with the dynamic light scattering (DLS) data (Figure 3-2).

Figure 3-1 (a-c) FESEM images of anatase TiO₂ microspheres synthesized after 4 hours of hydrothermal reaction. (d) is the corresponding XRD pattern.

Figure 3-2 Dynamic light scattering size distributions for TiO₂ microspheres

Some microspheres joined together during the crystal growth stage to form TiO₂ multimers. The surfaces of the microspheres are covered with interconnected square nanoflakes to develop a mosaic structure. From the symmetries of the well-faceted nanoflake structure, the flat squares visible in the FESEMs are the {001} facets of the anatase TiO₂. The individual square nanoflake is connected closely with its neighbors, resulting in the complete exposure and surface coverage of the high-energy {001} facets. The crystallinity of the microspheres was characterized using X-ray diffraction (XRD). As shown in Figure 1d, several sharp diffraction peaks were clearly observed and could be well assigned to the tetragonal anatase phase (space group: *I*4₁/amd; tetragonal symmetry, $a_o = 3.7852 \text{ \AA}$ and $c_o = 9.5139 \text{ \AA}$, JCPDS file no. 21-1272),(185) which shows that the as-prepared TiO₂ microspheres are of high crystalline quality. No spurious diffractions due to crystallographic impurities such as rutile or brookite were identified. The relative intensity of the (004) diffraction peak is enhanced as compared with that of the powder diffraction pattern, suggesting that the anatase TiO₂ microspheres are bounded by the {001} facets.

The chemical stoichiometry of the microspheres was examined with energy-dispersive X-ray spectroscopy (EDX) and the atomic ratio of Ti to O was found to be ~1:2, as shown in Figure 3-3.

Figure 3-3 Energy dispersive X-ray spectroscopy (EDX) spectrum of anatase TiO₂ microspheres synthesized after 4 hours of hydrothermal reaction prior to NaOH washing. Note: Silicon signal comes from the silicon wafer used for FESEM characterization.

Detailed morphological and structural information about as-synthesized TiO₂ microspheres was further studied by transmission electron microscopy (TEM). As shown in Figure 3-4, many flat regions can be easily identified on the external edge of the anatase TiO₂ microspheres, which are the projection of the anatase {001} facets.

Figure 3-4 TEM images of anatase TiO₂ microspheres synthesized after 4 hours of hydrothermal reaction

3.3.2 Investigation of the formation mechanism of TiO₂ microspheres

Experiments with varying reaction time were carried out to study the formation process of the anatase TiO₂ microspheres. When the reaction time was less than 30 minutes, no product was formed and the reaction solution remained clear. After 30 minutes of reaction, anatase TiO₂ started to form through the hydrolysis and condensation of TiF₄. The TiO₂ microspheres after 1 hour of hydrothermal reaction have sizes around 1 μm. The external surface of the microsphere was covered by many dome-like round surfaces (Figure 3-5a). Each round surface belongs to a single piece of crystal, which grows from a central point along the radial direction. The individual crystal branch grows along the [001] direction, which was confirmed with HRTEM (Figure 3-6). (186, 187)

Figure 3-5 FESEM images of anatase TiO₂ microspheres synthesized after different amount of reaction times, showing the surface morphology transformation. Reaction time: (a) 1hour, (b) 1.25 hours, (c) 1.5 hours, (d) 1.75 hours, (e) 2 hours, (f) 3 hours, (g) 4 hours, and (h) 4.5 hours.

Figure 3-6 TEM and HRTEM images of anatase TiO₂ microspheres synthesized after 1 hour of hydrothermal reaction.

Figure 3-7 XRD patterns of anatase TiO₂ microspheres synthesized after different amount of reaction times (1hr, 2hrs and 4hrs).

Figure 3-8 XPS spectrum of the anatase TiO₂ microspheres with and without NaOH washing, showing the characteristic peak from F.

Increased reaction time not only increase the size of TiO₂ microspheres, but also modifies the crystal terminating surface from round to square faceted. This surface transformation could be rationalized as the following: initially, as the TiF₄ begins to hydrolyze, the concentration of F⁻ in the solution is low and most of the fluoride exists as complexes with titanium (e.g., TiF₃(OH), TiF₂(OH)₂, and TiF(OH)₃)(188) The amount of ionized F⁻ is not enough to stabilize the anatase (001) surface. Because of the high surface energy, the (001) surface diminishes quickly during the crystal growth stage and the reactive {001} facets are not observed. As the HF and F⁻ concentration rises, more F⁻ can adsorb on the TiO₂ (001) surfaces and lower the surface energy of the (001) planes. This passivation slows the growth of the (001) surface with respect to the other planes, which grow faster and eventually grow themselves out of existence. Since hydrochloric acid was used for preparing TiF₄

precursor solution, Cl^- may also play a role in controlling the morphology of TiO_2 .(28, 189) To understand this effect, we carried out the following control experiments. We used nitric acid and sulfuric acid to replace the hydrochloric acid for preparing the TiF_4 precursor solution. Exactly the same TiO_2 microspheres could still be synthesized using TiF_4 precursor solution prepared from nitric acid and sulfuric acid. Even if we increased the concentration of Cl^- in the starting precursor solution by adding NaCl , no obvious morphological change was observed for the prepared TiO_2 microspheres. Furthermore, no chlorine was identified in both the EDX and XPS measurements, which strongly suggests that the stabilizing effect of Cl^- is weak. After 4 hours of hydrothermal reaction, some eroded holes started to appear on the outer nanoflake surfaces (Figure 3-5h). This corrosion on the surface is launched by the in-situ generated HF through hydrolysis of TiF_4 .(180)

3.3.3 Photodegradation and photocatalytic hydrogen evolution tests using TiO_2 microspheres

We tested the TiO_2 microspheres as solid-state photocatalysts and investigated their photocatalytic activity under UV light irradiation. Photocatalytic degradation of methyl orange in aqueous solution was used as a model system and anatase TiO_2 microspheres with both exposed $\{001\}$ and $\{101\}$ facets synthesized according to the literature method was used as a reference for comparison.(171) It is clearly demonstrated that the anatase TiO_2 microspheres optimized in our work with the exposed $\{001\}$ facets show the best performance. Considering that the anatase TiO_2 microspheres ($\sim 1.1 \text{ m}^2/\text{g}$) had a similar external surface area with that of the anatase TiO_2 microspheres ($\sim 1.3 \text{ m}^2/\text{g}$), the improved photocatalytic activity of TiO_2 microspheres should come from the higher photoactivity of the $\{001\}$ facets.

Figure 3-9 Photocatalytic degradation of methyl orange (MO) using different photocatalysts under UV irradiation. C_0 and C are initial concentration and concentration at time t of MO. ($\blacktriangle$) TiO_2 Microspheres synthesized after 4 hours of hydrothermal reaction, ($\blacksquare$) referenced TiO_2 microsheets, and ($\blacktriangledown$) TiO_2 microspheres synthesized after 1 hour of hydrothermal reaction.

The TiO_2 microspheres also exhibit stable photocatalytic activity to produce hydrogen from water under UV light irradiation. Hydrogen gas evolution as a function of time during a 4-hour testing period is shown in Figure 3-10. The hydrogen production rate is $\sim 2\mu\text{mol}/\text{hour}$ for TiO_2 microspheres synthesized after 4 hours of hydrothermal reaction and loaded with 1wt% Pt, which is about 20% more efficient than the referenced TiO_2 microsheets.

Figure 3-10 Hydrogen evolution from photocatalytic water splitting under UV irradiation. (▲) TiO₂ Microspheres synthesized after 4 hours of hydrothermal reaction, (■) referenced TiO₂ microspheres, and (▼) TiO₂ microspheres synthesized after 1 hour of hydrothermal reaction.

Our results are consistent with previous reports that {001} facets of anatase have higher reactivity than the others.(166, 171) However, a recent study found that the reactivity of the facets of anatase TiO₂ for hydrogen evolution followed the order {001} < {101} < {010} when the TiO₂ surfaces were not fluorinated.(190) Our photocatalyst particles were used after desorbing fluorine from the surface by NaOH treatment and the percentage of 001 facets in our photocatalysts is much higher (90%) than that in ref. 76 (40%). These differences may be responsible for the differences in the observed reactivity.

3.4 Summary

In summary, we developed a facile hydrothermal method for synthesizing anatase TiO₂ microspheres with > 90% exposed {001} facets using hydrofluoric acid generated in-situ through hydrolysis of TiF₄ as a capping and stabilizing agent

without introducing any additional hydrofluoric acid. The high exposure of reactive {001} facets makes the anatase TiO_2 microspheres an efficient photocatalyst in degrading toxic organic contaminants and producing hydrogen from water under UV light irradiation. Because of the large exposure of reactive {001} facets, the TiO_2 microspheres can also serve as an ideal model system in studying the surface related properties.

Chaper 4 Electrochemical fabrication of ZnO-CdSe core-shell nanorod arrays for efficient photoelectrochemical water splitting²

4.1 Introduction

Severe environmental issues along with the forthcoming energy crisis have revived scientists' enthusiasm for developing clean and sustainable energy resources. As a promising renewable energy technology, photoelectrochemical (PEC) hydrogen generation has attracted extensive attention since the pioneering work by Fujishima and Honda.(13-15, 103) More recently, one-dimensional (1D) nanostructures (e.g., nanorods, nanowires and nanotubes) of wide bandgap semiconductors, such as ZnO and TiO₂, have been successfully developed and applied in various emerging PEC applications.(28, 116, 120, 128, 191-196) Compared to their bulk counterparts, these single-crystalline nanostructures can orthogonalize the directions of light absorption and minority carrier transport and provide direct electrical pathways, which enhance the utilization of minority carriers and improve the overall performance of photoelectrochemical devices. However, the power conversion efficiency of pure ZnO and TiO₂ nanostructures is limited by their poor absorption of visible-light, due to their relatively large bandgap (>3.2 eV). Quantum dot (QD) sensitization is an effective way to extend the photo-response of ZnO or TiO₂ to visible light. Many narrow bandgap semiconductor QDs, such as CdS, CdSe and CdTe, have been used to sensitize ZnO and TiO₂ nanofilms.(126, 197-208) These modifications have significantly improved the overall energy conversion efficiency in photovoltaic and PEC devices, owing to the favorable visible-light response and tunable band

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structures of QDs. In general, the QD sensitization can be accomplished by adopting two different strategies. The first strategy involves direct growth of QDs on the surface of metal oxide electrodes, through chemical bath deposition,(209, 210) successive ionic layer adsorption and reaction (206, 211, 212) or electrochemical deposition.(197) Alternatively, pre-synthesized colloidal QDs can be attached to the metal oxide matrix with direct adsorption or linker-assisted adsorption. Among these methods, electrochemical deposition is most preferable, as it is simple, efficient, scalable and cost effective for producing semiconductor QDs with controllable density and excellent uniformity.

In the present study, we demonstrate a facile and efficient method for the fabrication of ZnO–CdSe QD core–shell nanorod arrays through an all-electrochemical approach, in which both ZnO nanorods and CdSe QDs were electrochemically deposited onto the ITO electrode. The CdSe QDs form a type II band alignment with ZnO,(213) resulting in efficient injection of photogenerated electrons from CdSe to ZnO. The structural and optical properties of the as-fabricated electrodes were characterized using various techniques including scanning and transmission electron microscopy, X-ray diffraction, and UV-vis spectroscopy. The optimized ZnO–CdSe nanorod arrays can generate a significant photocurrent density of 14.9 mA cm^{-2} at 0.8 V (vs. RHE) in 0.2 M Na₂S, which is, to the best of our knowledge, the highest value ever reported for similar nanostructures. These ZnO–CdSe photoanodes exhibited excellent stability and apparently enhanced incident photon-to-current conversion efficiency (IPCE). All these results showed their application potential for efficient PEC water splitting to produce hydrogen.

4.2 Experimental section

4.2.1 Materials

All chemical reagents were purchased from Sigma-Aldrich and were used directly without further purification. Deionized (DI) water (resistivity over 18 M Ω cm) from a Millipore Q water purification system was used in all experiments.

4.2.2 Electrochemical deposition of ZnO nanorods

Prior to the deposition of ZnO nanorods, the ITO coated glass substrates (Shenzhen JMT Glass Co., Ltd, 12 Ω /sq) were cleaned with detergent under sonication for 90 min, followed by washing with deionized water. Then, ZnO nanorods were deposited onto the pre-cleaned ITO-coated glass substrates using an electrochemical approach. The deposition of ZnO nanorods was carried out in a 50 ml three-chambered electrochemical cell. 40 ml of aqueous solution containing 5 mM Zn(NO₃)₂ and 50 mM NaNO₃ (pH = 9) was used as the electrolyte, and the temperature was kept at 85 °C in a hot water bath. Pre-cleaned ITO-coated glass, platinum (Pt) foil and saturated calomel electrode (SCE) were used as the working, counter and reference electrodes, respectively. The ZnO nanorod arrays were deposited onto ITO-coated glass substrates using a multi-potential step technique. A ZnO seed-layer was first deposited on ITO with a potential of -1.3 V vs. SCE for 10 seconds. Thereafter, a constant potential of -1.0 V vs. SCE was applied for 2000 seconds. After the deposition, the as-prepared films were rinsed with DI water, dried with compressed N₂ flow and then annealed at 350 °C in air.

4.2.3 Electrochemical deposition of CdSe quantum dots

The CdSe quantum dots were electrochemically deposited onto ZnO nanorod arrays from a solution of 10 mM CdCl₂ and 5 mM elemental Se in 30 ml of DMF

inside a 50 ml two-neck round bottom flask. The electrodeposition was conducted at 125 °C using a two-electrode set-up, with ITO–ZnO or bare ITO as the working electrode and a Pt plate as the counter electrode. During deposition, a constant current density of -0.55 mA cm^{-2} was applied to the ITO–ZnO working electrode. The deposition time was varied from 50 seconds to 400 seconds to optimize the coverage of CdSe QDs on ZnO nanorod arrays.

Figure 4-1 Fabrication of the ZnO–CdSe core-shell nanorod arrays through a solution based all-electrochemical approach, and their application as photoanodes in photoelectrochemical water splitting cells.

4.2.4 Material characterization

The crystal structure, morphology and chemical composition of the core-shell nanorod arrays were analyzed by X-ray diffraction (XRD, Bruker AXS D8 Advance), scanning electron microscopy (SEM, JEOL JSM-6700F), transmission electron microscopy (TEM, FEI Tecnai G2 30) and energy dispersive X-ray spectroscopy

(EDS, JEOL JED-2300 Analysis Station), respectively. The light absorption properties were measured using a Perkin-Elmer Lambda 900 UV-vis-NIR spectrometer equipped with an integrating sphere.

4.2.5 Photoelectrochemical measurements

The photoelectrochemical tests were performed using an electrochemical workstation (CHI 760D). A three-electrode set-up, with a platinum plate (1 cm x 2 cm) and a SCE (in 3 M KCl) as the counter and reference electrodes, respectively, was used to study the illuminated open circuit potential and photocurrent–voltage (J – V) behaviors of the samples. Meanwhile, the zero-bias photocurrent and stability tests were carried out using a two-electrode set-up, in which the working electrode (ZnO, CdSe and ZnO–CdSe) and the counter electrode (Pt) were short circuited. 0.2 M Na₂S (pH = 13) was preferentially used as the electrolyte in photoelectrochemical measurements, while 0.5 M Na₂SO₄ (pH = 6.9) was also used for scavenger-free tests. Prior to each measurement, the electrolyte was deaerated by purging it with nitrogen continuously for 30 minutes. A 300 W xenon lamp (Newport) coupled to an AM 1.5G filter was used as the standard light source throughout the tests. The illumination intensity on the surface of electrodes was $\sim 100 \text{ mW cm}^{-2}$, calibrated using a standard silicon photodiode. All potentials in photocurrent–voltage (J – V) curves were converted to the RHE scale.

4.2.6 IPCE measurements

The incident photon-to-current conversion efficiency (IPCE) was measured under zero-bias (two-electrode, short-circuit) condition. The monochromatic light was supplied by a xenon lamp illuminating 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.

4.3 Results and discussion

4.3.1 Material characterization

In our present work, all photoelectrodes (ZnO nanorod arrays, CdSe thin film and ZnO–CdSe nanorod arrays) were prepared through an electrochemical deposition technique. The fabrication of ZnO–CdSe core–shell nanorod arrays is shown schematically in Figure 4-1.

Figure 4-2 (a) Top and (b) cross-sectional view FESEM images of oriented ZnO nanorod arrays. (c) Top and (d) cross-sectional view FESEM images of ZnO–CdSe nanorod arrays.

Figure 4-2a and b show typical field emission scanning electron microscopy (FESEM) images of the ZnO nanorod arrays prepared using electrochemical deposition. From these FESEM images, it is observed that the entire surface of the ITO substrate is evenly covered with ZnO nanorods. The ZnO nanorods exhibit a regular hexagonal cross-section with flat top surfaces. The average diameter and

length of the ZnO nanorods are ~150 nm and ~1 μm , respectively. Using the ZnO nanorod arrays as the working electrode, CdSe QD shells with controllable thicknesses can be further deposited galvanostatically onto the ZnO nanorods to form a core-shell nanostructure. The CdSe nanocrystals were precipitated on the surface of ZnO nanorods through the following redox reaction:(214)

Figure 4-2c shows the morphologies of the ZnO–CdSe nanorod arrays prepared after 250 seconds of CdSe deposition, with a total charge transport of about 0.138 C cm^{-2} . It can be observed that the surface of ZnO nanorods is fully covered with a dense and uniform outer shell, which is made up of numerous CdSe QDs with diameters around 10 ± 5 nm. The CdSe shell thickness is about 40 nm, which can be further tuned by adjusting the electrochemical deposition time.

Figure 4-3 TEM images of ZnO/CdSe nanorods

The cross-sectional FESEM image (Figure 4-2d) shows that the CdSe QDs are uniformly distributed along the entire length of the ZnO nanorods. The core-shell configuration is further revealed by transmission electron microscopy (TEM) measurement, shown in Figure 4-3 in which the compact cable-like nanostructure along with the tight interface formed between ZnO and CdSe can be clearly seen.

Figure 4-4 EDS spectrum and elemental composition of ZnO/CdSe core-shell nanorod arrays

Energy-dispersive X-ray spectroscopy (EDS) (Figure 4-4) affirms the atomic ratio between Cd and Se atoms close to unity, which is consistent with the theoretical stoichiometric ratio of CdSe.

Figure 4-5 XRD patterns of the ITO substrate, ZnO nanorod arrays and ZnO–CdSe nanorod arrays

Figure 4-5 shows the X-ray diffraction (XRD) patterns of the bare ITO substrate, ZnO nanorod arrays and ZnO–CdSe nanorod arrays. From the XRD spectrum of ZnO nanorod arrays, 6 diffraction peaks, namely (100), (002), (101), (102), (110) and (103) of wurtzite ZnO (JCPDS no. 79-2205), can be clearly identified. The predominant (002) peak indicates that the ZnO nanorods grow along the [001] direction with their growth axis nearly perpendicular to the ITO surface. After the deposition of CdSe QDs, major diffraction peaks of ZnO are still identifiable, suggesting that the electrochemical deposition does not affect the crystalline structure of ZnO. In addition, three new diffraction peaks centered at 24, 25.3 and 27.5°, which can be indexed to the (100), (002) and (101) planes of wurtzite CdSe (JCPDS no. 77-2307), are observed in the XRD spectrum of ZnO–CdSe nanorod arrays.

Figure 4-6 The HRTEM image of ZnO/CdSe core-shell nanorod arrays

As shown in Figure 4-6 high-resolution transmission electron microscopy (HRTEM) analysis was also performed to examine the crystal quality of ZnO–CdSe

nanorod arrays. The HRTEM image reveals the interplanar spacing of 0.26 nm and 0.35 nm, corresponding to the (002) crystal plane of wurtzite ZnO and the (002) crystal plane of wurtzite CdSe, respectively.

Figure 4-7 UV-visible absorption spectra of ZnO nanorod arrays, CdSe thin film and ZnO–CdSe nanorod arrays.

Figure 4-7 shows the optical absorption spectra of ZnO nanorod arrays, CdSe thin film and ZnO–CdSe nanorod arrays. A steep absorption edge at 390 nm was observed in ZnO nanorod arrays, which is consistent with the wide bandgap of ZnO (3.2 eV). After coating a thin layer of CdSe QD shells, the absorption edge of the core–shell ZnO–CdSe nanorod arrays was drastically extended to about 600 nm.

4.3.2 Photoelectrochemical tests

The photoelectrochemical measurements were carried out in a three-electrode cell, with the electrodeposited film (ZnO, CdSe and ZnO–CdSe) on ITO as the working electrode, a Pt plate as the counter electrode, and a SCE electrode (in 3 M

KCl) as the reference. The photoresponses were recorded in 0.2 M Na₂S aqueous solution under AM 1.5G simulated solar illumination.

Figure 4-8 a) Photocurrent -photovoltage (J - V) curves of ZnO/CdSe nanorod arrays prepared with different CdSe deposition time, and b) optimization curve

To obtain the optimum deposition conditions of CdSe QDs, ZnO–CdSe nanorod arrays with varied deposition time were prepared. Figure 4-8a shows the photocurrent–voltage (J - V) curves of ZnO–CdSe samples prepared with different CdSe deposition times ranging from 50 seconds to 400 seconds, corresponding to 0.028–0.22 C cm⁻² of total charge passing through the working electrode during the deposition. The observed photocurrent density first increases with increasing CdSe deposition time, reaching a maximum value, and then decreases as shown in Figure 4-8b. Initially, the amount of CdSe QDs deposited on the surface of ZnO nanorods increases with time, leading to better visible-light absorption and thus more efficient exciton-generation. However, if the deposition time is too long, an excessive amount of CdSe QDs deposited may cause the aggregation of CdSe QDs (Figure 4-9), which increases the recombination loss of photo-generated excitons (excitons have to diffuse longer to reach the CdSe–ZnO interface for charge separation).

Figure 4-9 ZnO nanorod arrays loaded with excessive amount of CdSe QDs (350 seconds)

As a result, the optimized CdSe QD deposition time would be around 225–275 seconds ($0.12\text{--}0.15 \text{ C cm}^{-2}$). Further experiments were carried out using the ZnO–CdSe nanorod arrays prepared with a CdSe deposition time of 250 seconds (0.138 C cm^{-2}).

Photovoltage responses of ZnO nanorod arrays, CdSe thin film and ZnO–CdSe nanorod arrays towards on–off cycles under AM 1.5G simulated solar illumination are shown in Figure 4-10a. The illuminated open-circuit potentials are 0.41, 0.32 and 0.15 V for ZnO–CdSe nanorod arrays, CdSe thin film and ZnO nanorod arrays, respectively. The ZnO–CdSe nanorod arrays and CdSe thin film exhibited steady and highly repeatable photovoltage responses during on–off cycles of irradiation. Figure 4-10b shows the photocurrent profiles of these photoanodes recorded under zero-bias (two-electrode, short circuit) condition. In each on–off cycle, a transient spike induced by the diffusion of charge carriers was observed. Thereafter, steady photocurrent was recorded, due to the formation of a diffusion layer at the interface between the electrode and electrolyte.(215)

Figure 4-10 (a) Illuminated open-circuit-potential and (b) zero-biased photocurrent responses of ZnO nanorod arrays, CdSe thin film and ZnO/CdSe nanorod arrays towards on-off cycles of AM 1.5 illumination. Photocurrent-photovoltage (J - V) curves of different photoanodes obtained (c) in the dark, and (d) under illumination conditions.

ZnO–CdSe nanorod arrays can produce a steady photocurrent density of about 1.22 mA cm^{-2} , which is 4.9 and 61 times higher than that of the CdSe thin film (0.25 mA cm^{-2}) and ZnO nanorod arrays (0.02 mA cm^{-2}), respectively.

The photocurrent–voltage (J - V) curves of the three photoanodes obtained in the dark and under illumination are shown in Figure 4-10c and d, respectively. In each measurement, the voltage was linearly swept from -0.4 V to 1.0 V (vs. RHE) at a scan rate of 50 mV s^{-1} . In the dark, the J - V curves of all samples exhibited typical rectifying behavior, with weak current responses less than 0.19 mA cm^{-2} . Under simulated solar illumination, the ZnO–CdSe nanorod arrays can generate a large photocurrent of 14.9 mA cm^{-2} at 0.8 V (vs. RHE), which is, to the best of our knowledge, the highest value ever reported for similar nanostructured materials (Table 4-1) and is 3.8 times and 86.9 times higher than the values of the CdSe thin film and ZnO nanorod arrays.

Table 4-1 Comparison of saturated photocurrent density with reported similar materials

Reported Material	Year	Light Source	Electrolyte	Saturated Photocurrent density (mA/cm ²)
ZnO/CdSe nanorod arrays^{a)}	2013	Simulated Sunlight	0.2M Na₂S	14.9
IrO _x .nH ₂ O-CdSe/CdS/ZnO nanowire (216)	2013	Simulated Sunlight	0.25M Na ₂ S and 0.35M Na ₂ SO ₃	13.9
Double-layered tubular CdSe/ZnO arrays (207)	2013	Xe Lamp	0.1M Na ₂ S	2.55
Double-shelled ZnO/CdSe/CdTe nanocable arrays (217)	2012	Simulated Sunlight	0.6M Na ₂ S, 0.2M S and 0.2M KCl	14.3
TiO ₂ /CdSeS (218)	2012	Xe Lamp	0.25M Na ₂ S and 0.35M Na ₂ SO ₃	6
CdSe/CdS sensitized ZnO/WO _x Nanowires (219)	2011	Simulated Sunlight	0.25M Na ₂ S and 0.35M Na ₂ SO ₃	11
CdS/ZnO nanotube arrays (220)	2011	Xe Lamp	1M Na ₂ S	10.64
CdSe QDs sensitized N-doped TiO ₂ (221)	2010	Xe Lamp	0.25M Na ₂ S and 0.35M Na ₂ SO ₃	2.75
Double sided CdS CdSe QD sensitized ZnO (126)	2010	Xe Lamp	0.25M Na ₂ S and 0.35M Na ₂ SO ₃	12
ZnO-CdSSe core-shell nanowire arrays (222)	2010	Xe Lamp	1M Na ₂ S	6.2
CdSe QD-sensitized ZnO nanowire arrays (215)	2010	Xe Lamp	0.25M Na ₂ S and 0.35M Na ₂ SO ₃	2.48
CdSe/CdS co-sensitized ZnO nanowire arrays (223)	2010	Simulated Sunlight	1M Na ₂ S	9.15
CdS nanoparticle/ZnO nanowire (224)	2009	Simulated Sunlight	1M Na ₂ S	4.5
ZnO/CdS core/shell nanowire arrays (202)	2009	Simulated Sunlight	1M Na ₂ S	7.23

^{a)} ZnO/CdSe nanorod arrays prepared in this work

These results affirm the efficient visible light absorption and interfacial charge transfer between CdSe QDs and ZnO nanorods. It is noteworthy that large amounts of H₂ bubbles were observed on the surface of the Pt counter electrode during the PEC tests of ZnO–CdSe nanorod arrays.

Figure 4-11 Photocurrent-voltage characteristics of ZnO/CdSe nanorod arrays in 0.5 M Na₂SO₄ under chopped AM 1.5 G light illumination, inset shows the corresponding LSV curves observed under dark (black) and illuminated (red) conditions in the same electrolyte.

To further investigate the application potential of ZnO–CdSe nanorod arrays in practical solar water splitting applications, we also performed PEC tests in a scavenger-free electrolyte (0.5 M Na₂SO₄, pH = 6.9) as shown in Figure 4-11. The result shows that the ZnO–CdSe nanorod arrays can produce a photocurrent of ~2.75 mA cm⁻² without using any sacrificial agents. A noticeable amount of H₂ bubbles can be observed on the Pt counter electrode during the test.

4.3.3 Stability test

Figure 4-12 Stability test of ZnO/CdSe nanorod arrays conducted under chopped AM1.5 illumination in zero-bias condition

The stability of ZnO–CdSe nanorod arrays was examined with chopped simulated solar illumination, under zero-bias condition in 0.2 M Na₂S. As shown in Figure 4-12, the ZnO–CdSe nanorod array photoanode can well retain ~95.1% of its initial response after 65 on–off chopped lighting cycles, with a total test duration of 2600 seconds. H₂ bubbles were generated on the surface of the Pt counter electrode upon illumination throughout the entire test, and there is no significant change in the color of ZnO–CdSe nanorod arrays after the stability test.

Figure 4-13 Stability test of ZnO/CdSe nanorod arrays under continuous AM 1.5G light illuminations for 1 hour

To further verify the stability of ZnO–CdSe nanorod arrays, we also conducted stability tests using continuous light illumination with the same sample. We found that ~86.2% of its initial photocurrent density can be retained after 3600 s (Figure 4-13).

4.3.4 Incident-photon-to-current-conversion efficiency (IPCE)

Figure 4-14 Dependence of the incident photon-to-current-conversion efficiency (IPCE) on the incident wavelength of different electrodes; the inset shows the scheme of charge transfer on ZnO–CdSe nanorod arrays under illumination.

Incident-photon-to-current-conversion efficiency (IPCE) measurements were performed under zero-bias condition to probe the origin of photocurrent generation as a function of incident light wavelength. As shown in Figure 4-14, the IPCE spectra of the three samples are consistent with their corresponding UV-vis spectra and J – V curves. The ZnO nanorod arrays show negligible IPCE below the ZnO band gap

energy of ~390 nm (bandgap of bulk ZnO is 3.2 eV), closely following their small photocurrent shown in Figure 4-10b. In comparison with pristine ZnO nanorods, the ZnO–CdSe nanorods showed a pronounced response in the visible light region, with a maximum IPCE value of 34.9% obtained at ~475 nm. The incorporation of the CdSe QD shell apparently enhanced the visible light absorption of the nanoarrays, thus leading to a significant increment in IPCE.

The inset in Figure 4-14 illustrates the energy diagram of ZnO– CdSe nanorod arrays. As shown in the diagram, both the conduction band minimum (CBM) and valence-band maximum (VBM) of CdSe are higher than those of ZnO, forming a typical type II band alignment (staggered gap). With this advantageous configuration, the photogenerated electrons can be efficiently transferred from the CdSe QDs to ZnO nanorods, and then transported to the substrate along the direct path provided by single-crystal ZnO nanorods. In addition, the excellent uniformity of CdSe QDs on ZnO nanorods further enhanced the photoconversion efficiency.⁽²²⁵⁾ The good distribution of CdSe QDs has been achieved by utilizing the electrochemical deposition approach, which allows the homogeneous deposition of CdSe to take place across the entire area on ZnO nanorods.

4.4 Conclusion

In summary, ZnO–CdSe core–shell nanorod arrays with excellent uniformity have been successfully fabricated through a facile and efficient all-electrochemical approach. The favorable band alignment and good CdSe QD distribution contribute to the effective separation of photogenerated electron–hole pairs and transportation of the electrons to the electrode surface, thus leading to a significantly enhanced photoelectrochemical performance and remarkable stability of the core–shell nanorod

arrays. This work shows the application potential of ZnO–CdSe nanorod arrays as photoanodes for efficient photoelectrochemical water splitting applications. In addition, we also demonstrated that the all-electrochemical deposition method utilized in this work could be a safe, efficient and cost-effective strategy for fabricating similar nanomaterials on a large scale.

Chaper 5 Stable quantum dot photoelectrolysis cell for unassisted visible light solar water splitting³

5.1 Introduction

Sunlight is an inexpensive, non-polluting, abundant renewable source of energy. The amount of sunlight striking Earth for a given time period is approximately 10 thousand times greater than the total energy consumed on the planet.(12, 226) Thus, converting solar energy into an easily usable form has attracted substantial attention in past decades.(227) As society has become increasingly conscious of the adverse impacts of anthropogenic activities on the environment, the development of methods to efficiently harness solar energy has emerged as one of the central scientific challenges in the 21st century.(37, 228) Photosynthesis in plants underpins the existence of many life-forms on Earth,(229) where a remarkable chemical reaction lies at the core of photosynthesis: the solar energy conversion of water and carbon dioxide into oxygen and carbohydrates (fuel). The development of an artificial version of this reaction, based on splitting water into oxygen and hydrogen, is highly desirable, owing to the attraction of hydrogen as a fuel.(37, 230) The efficient conversion of sunlight into fuels through the photochemical splitting of water to generate hydrogen and oxygen is a critical factor for developing sustainable energy. Since Fujishima and Honda reported the first photoelectrochemical device for solar water splitting in 1972,(14) numerous research efforts have been devoted toward the development of efficient photocatalytic systems for hydrogen production.(38, 231) Among them, two photocatalytic systems, namely, the single-photon system (49, 54, 232) and two-photon system have been extensively studied.(15, 42, 103, 233) As

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compared to the single-photon system, the two-photon system allows capture of lower energy photons and thus a larger part of the solar spectrum, which can potentially lead to a higher solar-to-fuel conversion efficiency. Furthermore, the reduction and oxidation catalytic centres in the two-photon system are spatially separated, which not only minimizes the undesirable back-reaction but also separates the photosynthetic products. Regarding this two-photon system, a “Z-scheme” in artificial photosynthesis would be considered for solar water splitting,(234-237) in which the photogenerated minority carriers in two semiconductors move toward the semiconductor-electrolyte interface to carry out individual half reactions while the majority carriers recombine at the ohmic contact between the semiconductors.(238) Consequently, both photoreduction reaction and water oxidation reaction can spontaneously occur in corresponding inorganic semiconductors to evolve hydrogen and oxygen, respectively. Although unassisted solar water splitting has been achieved in previous studies of photoelectrochemical systems, some wide-band-gap semiconductors (e.g., TiO_2) had to be employed to capture sunlight,(239, 240) which only allows harvesting UV light in the solar spectrum and greatly limits their overall solar-to-fuel conversion efficiency. Regarding this issue, several strategies have been revealed to achieve the utilization of visible photons in sunlight.(40) Among which, inorganic quantum dot (QD) sensitization has been demonstrated as an effective way to extend the photoresponse of wide-band-gap semiconductors to visible light,(241, 242) because of the tunable band gap by controlling the QD's size and composition. However, it is worth pointing out that their photostability and long-term durability have to be considerably addressed for future applications since the photosystem needs to be operated under tough conditions and long-term illumination. Here, we develop a cadmium chalcogenide QD modified photoelectrochemical system consisting of a

CdS QD modified TiO₂ nanorod photoanode and a CdSe QD modified NiO nanosheet photocathode for spontaneous overall solar water splitting to produce H₂ and O₂ under visible light illumination, in which corresponding co-catalysts and surface protection were developed to considerably facilitate the stability of the system. This development is a remarkable step toward the demonstration of a complete QD-based artificial photosynthetic system that is efficient, durable, and cost-effective.

5.2 Experimental

5.2.1 Materials

Titanium isopropoxide, hydrochloric acid, cadmium chloride, sodium sulfide, sodium sulfate, sodium thiosulfate, zinc nitrate, nickel acetate, nickel nitrate, potassium persulfate, 3-mercaptopropionic acid ($\geq 99\%$, Aldrich), nitrilotriacetic acid, sodium hydroxide, and aqueous ammonia were used as received without any further purification.

5.2.2 CdS/TiO₂ photoanode preparation.

TiO₂ nanorod arrays were grown on fluorine-doped tin oxide (FTO) substrate using a hydrothermal method. In a typical synthesis, FTO substrate (Tec 15, 10 Ω /sq, Hartford Glass Company) was first cleaned with 5 wt. % detergent in an ultrasonic water bath for 30 min, followed by rinsing with DI water and sonicating for another 10 min. After being dried by a N₂ stream, the FTO substrate was placed in a sealed Teflon-lined autoclave (63 mL), containing 20 mL of HCl (37 wt. %), 20 mL of DI water, and 0.5 g of titanium isopropoxide. The hydrothermal reaction was conducted at 200 °C for 4 h. After the reaction, the TiO₂ nanorod covered FTO substrate was

rinsed with DI water, dried at 70 °C, calcined at a ramp of 1 °C/min to 500 °C, and kept at this temperature for 1 h before loading CdS quantum dots.

CdS QDs were electrochemically deposited onto TiO₂ nanorod arrays from a solution containing 0.2 M CdCl₂ and 0.05 M Na₂S₂O₃. The pH of the solution was adjusted to 2.1 by adding a few drops of 0.1 M HCl. The electrochemical deposition was conducted at 70 °C using a three-electrode setup, with TiO₂/FTO as the working electrode, Pt plate as the counter electrode, and a standard calomel electrode (SCE) as the reference electrode. During deposition, a constant voltage of -0.7 V vs SCE was applied to the TiO₂/FTO working electrode for different times to optimize the coverage of CdS QDs on TiO₂ nanorod arrays.

A thin ZnS protective layer was coated on the as-prepared CdS/TiO₂ photoelectrode using a successive ionic layer adsorption and reaction (SILAR) technique to improve the photostability. CdS/TiO₂ films were sequentially dipped into four different solutions of 0.05 M Zn(NO₃)₂, DI water, 0.05 M Na₂S, and DI water, respectively. The thickness of the ZnS protective layer was controlled by the number of dipping cycles.

5.2.3 CdSe/NiO photocathode preparation

NiO nanosheet arrays were grown on an FTO substrate using a chemical bath deposition technique. Prior to CBD growth, a compact NiO layer was deposited on the FTO substrate by spin-coating a nickel acetate (98%, Aldrich) ethanolic solution (0.4 M) on FTO at 2000 rpm and sintering at 350 °C for 30 min. Thermal annealing converts nickel acetate to nickel oxide through

A solution for CBD growth of NiO nanosheets was prepared by mixing 80 mL of 1 M nickel nitrate, 60 mL of 0.25 M potassium persulfate, and 20 mL of aqueous ammonia (25-28%) in a 250 mL Pyrex beaker at room temperature. The NiO compact layer covered FTO substrates were placed vertically in the freshly prepared solution and kept at room temperature for 20 min to grow a NiOOH nanosheet precursor film. Then, the NiOOH nanosheet film was dried at 70 °C, heated at a ramp of 1 °C/min to 450 °C, and kept at this temperature for 1 h to convert NiOOH to NiO.

CdSe nanoparticles were coated on NiO nanosheet arrays using a CBD technique. Prior to CBD growth of CdSe nanoparticles, the NiO nanosheet film was immersed in 10 mM 3-mercaptopropionic acid (MPA) solution for 1 h at 40 °C under a nitrogen atmosphere to anchor a monolayer of MPA molecules onto NiO through $-\text{COO}-\text{NiO}$ binding. The films were then transferred into a 25 mM CdCl_2 aqueous solution for 1 h at 40 °C under a nitrogen atmosphere to adsorb Cd^{2+} ions on the surface of the NiO nanosheets, which serve as nucleation centres for CdSe nanoparticle growth. The CBD growth solution was prepared by mixing 10 mL of 80 mM CdCl_2 and 10 mL of 80 mM sodium selenosulfate (Na_2SeSO_3) solution with 10 mL of 120 mM trisodium nitrilotriacetate [$\text{N}(\text{CH}_2\text{COONa})_3$]. The CBD growth was conducted at 10 °C for different times to grow CdSe nanoparticles with different CdSe coverage.

5.2.4 Preparation and loading of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) co-catalysts.

NiS nanoparticles were used as the co-catalysts for the hydrogen evolution reaction. Loading of NiS nanoparticles onto a CdSe/NiO photocathode was performed using the SILAR technique by alternatively dipping the photocathode into 0.05 M $\text{Ni}(\text{NO}_3)_2$ and 0.05 M Na_2S ethanolic solutions for 2 min per dip and subsequently

rinsing with ethanol. Afterward, the electrode was washed a few times with deionized water and blow-dried with nitrogen.

$\text{IrO}_x \cdot n\text{H}_2\text{O}$ nanoparticles were used as the co-catalysts for the oxygen evolution reaction. The colloidal $\text{IrO}_x \cdot n\text{H}_2\text{O}$ suspension was prepared by hydrolysis of a 2 mM K_2IrCl_6 aqueous solution at $\text{pH} = 13$. The hydrolysis was carried out at $90\text{ }^\circ\text{C}$ for 20 min. Then, the pH of the solution was rapidly adjusted to 1 by adding a 3 M HNO_3 aqueous solution in an ice bath and maintained for 80 min to induce acid condensation. After adjusting the suspension pH to 7, the ZnS-protected CdS/TiO_2 nanorod array was immersed into the $\text{IrO}_x \cdot n\text{H}_2\text{O}$ colloidal suspension for 1 h to adsorb $\text{IrO}_x \cdot n\text{H}_2\text{O}$ nanoparticles onto the electrode. Afterward, the electrode was washed a few times with deionized water and blow-dried with nitrogen.

5.2.5 Material characterizations

The crystal structure and morphology of cadmium chalcogenide QD modified photoelectrodes were examined with X-ray diffraction (Bruker AXS D8 Advance), field emission scanning electron microscopy (JEOL JSM-6700F), and transmission electron microscopy (TEM, JEOL JEM-2100F), respectively. Absorption spectra were recorded using a PerkinElmer Lambda 900 UV-vis-NIR spectrometer equipped with an integrating sphere. Photoluminescence spectra and photoluminescence lifetime spectroscopy were measured at room temperature using a commercial laser-flash photolysis spectrometer (Edinburgh Instruments LP920-KS), a photomultiplier tube (Hamamatsu R928), a gated CCD (Princeton Instruments, PI-MAX ICCD camera), and a digital oscilloscope (Tektronix TDS-3012C). The sample was prepared by attaching a calculated amount of CdS or CdSe QDs synthesized from a hot injection method onto TiO_2 nanorods or NiO nanosheets and excited using a 420 nm

laser pulse (5 ns duration, $\sim 2 \text{ mJ cm}^{-2}$). Detailed chemical composition of samples was obtained by X-ray photoelectron spectroscopy (XPS) measurements on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) at $2.4 \times 10^{-10} \text{ mbar}$ using a monochromatic Al K α X-ray beam (1486.60 eV). All binding energies were referenced to the C 1s peak (284.60 eV) arising from adventitious hydrocarbons.

5.2.6 Photoelectrochemical measurements.

Photoelectrochemical properties of individual cadmium chalcogenide QD modified photoanode and photocathode were measured using an electrochemical workstation (WonA tech, ZIVE SP2) in a standard three-electrode setup with a Pt plate as the counter electrode and Ag/AgCl as the reference electrode. Reproducibility of all measurements was precisely controlled within 10 % for different batch samples to achieve significant comparisons. The short-circuit measurements of the externally wired CdS/TiO₂ nanorod photoanode and CdSe/NiO nanosheet photocathode were performed using a two-electrode setup, in which the electrochemical workstation remained short-circuited and behaved as an ammeter. The two photoelectrodes were in the same reactor and placed in a tandem configuration (CdS/TiO₂ photoanode as front cell and CdSe/NiO photocathode as back cell), as illustrated in Figure 5-1. In all cases, a 0.5 M Na₂SO₄ aqueous solution (pH = 6.8) was used as the electrolyte. The light source used for simulated sunlight was a 300 W xenon lamp (Newport, Oriel, 91160) equipped with an AM1.5G filter (Newport, 81094) and a UV filter (Newport, FSQ-GG400) ($>400 \text{ nm}$). Prior to each measurement, the light intensity was determined by a calibrated silicon photodiode. The incident photon-to-current conversion efficiency was measured under zero-bias (two-electrode, short-circuit) condition. The monochromatic light was supplied by a xenon lamp (450 W, Oriel)

illuminating through a monochromator (Newport) with a bandwidth of 5 nm. The photoactivity of the two short-circuited photoelectrodes was characterized by measuring the gaseous products using a commercial compact glass photoreactor system (Makuhari Rikagaku Garasu Inc. CCS-N-66-76). The setup comprises a quartz batch reactor, a circulation system, a vacuum pump, and a gas chromatograph (Agilent 490 Micro GC) for inline measurements.

5.2.7 Calculation of the Energy Conversion Efficiency and Faradic Efficiency

The energy conversion efficiency of the solar-driven water splitting (η) was calculated based on the measured photocurrent density, using the following equation:

$$\eta = \frac{1.23(V) \times I(mA/cm^2)}{P(mW/cm^2)} \times 100 \% \quad (9)$$

in which I is the photocurrent density and P is the light intensity.

For the calculation of the faradic efficiency of the water splitting (η_{faradic}) in the configuration of short-circuited electrodes, the following equation was applied:

$$\eta_{\text{faradic}} = \frac{2 \times n_{H_2}(mol) \times 96485 (C/mol)}{Q(C)} \times 100 \% \quad (10)$$

in which Q is the total amount of charge passed through the external circuit during the same time period as the measurement of evolved H₂ gas.

5.3 Results and discussions

5.3.1 Characterization of photoelectrodes.

Figure 5-1 (a) Cadmium chalcogenide QD modified photoelectrolysis cell system constructed with an array of CdS QD modified TiO₂ nanorods serving as the photoanode and CdSe QD modified NiO nanosheets serving as the photocathode. (b) Energy band diagram of a cadmium chalcogenide QD modified photoelectrolysis cell system for direct solar-driven water splitting. The photogenerated holes in the CdS QD modified TiO₂ nanorod photoanode and electrons in the CdSe QD modified NiO nanosheet photocathode move to the quantum dot surface to perform water splitting, while the electrons in TiO₂ and holes in NiO recombine at the external circuit. (c) Tauc plot of CdS and CdSe QDs. (d and e) Photoluminescence emission spectra of CdS QDs, CdS QDs adsorbed on TiO₂ nanorods, CdSe QDs, and CdSe QDs adsorbed on NiO nanosheets. Insets in d and e are time-resolved photoluminescence decays of CdS QDs and CdS QDs adsorbed on TiO₂ nanorods and CdSe QDs and CdSe QDs adsorbed on a NiO nanosheet

The photoelectrochemical system, which uses cadmium chalcogenide QDs as light absorbers, is depicted in Figure 5-1a. TiO₂ nanorods grown on transparent conductive fluorine-doped tin oxide (FTO) substrate decorated with CdS QDs served as an O₂-generating photoanode, while the photocathode for hydrogen evolution

consisted of a NiO nanosheet array with modification of CdSe QDs. An energy diagram of the present CdS and CdSe QD modified TiO₂ and NiO photoelectrodes is plotted in Figure 5-1b, and the band gaps of CdS and CdSe QDs are estimated to be ~2.46 and 2.0 eV, respectively, which are larger than their bulk values due to the quantum confinement effect (Figure 5-1c). NiO is a wide-band-gap (~3.6 eV) p-type semiconductor, widely used as an electron-blocking and hole-transporting layer in polymer and dye-sensitized solar cells.(126, 243-245) The frequently cited Fermi level of undoped NiO is about 5.0 eV, while the valence band maximum (VBM) is 0.4 eV below the Fermi level.(92, 246-248) CdSe can form a type II heterojunction upon NiO with band offsets of -2.4 eV (vacuum level: -4.2 eV/-1.8 eV) and +0.8 eV (vacuum level: -6.2 eV/-5.4 eV) at the conduction and valence band, respectively. Because of the type II band alignment, photoexcited carriers in CdSe can effectively dissociate at the CdSe/NiO interface.(249) Furthermore, the conduction band of CdSe is more negative (0.3 eV) than the redox potential of H⁺/H₂, making photocatalytic H₂ evolution thermodynamically favourable. In the case of the photoanode, TiO₂ (rutile) is a wide-band-gap (~3.0 eV) n-type semiconductor, able to form a type II heterojunction with CdS as well.(103) Upon exposure to visible light, the photo-excited carriers generated in CdS and CdSe would diffuse to CdS/TiO₂ and CdSe/NiO interfaces and dissociate into free electrons and holes. The photogenerated holes in CdS migrate to the CdS/electrolyte interface and oxidize water to generate O₂. Meanwhile, the photogenerated electrons in CdSe reduce protons to evolve H₂. In this design, the injection of sensitized electrons and holes from adsorbed CdS and CdSe QDs into TiO₂ and NiO can be revealed by time-resolved photoluminescence spectroscopy measurements. As shown in Figure 5-1d and e, the photoluminescence intensities of CdS and CdSe QDs were quenched by 75 % and 65 % once they were

attached to TiO_2 and NiO photoelectrodes, respectively. Accompanying the formation of CdS/TiO_2 and CdSe/NiO junctions, a significant decrease in photoluminescence lifetime from 14.5 and 10.2 ns to 7.6 and 6.0 ns can be attributed to effective charge-carrier transferring through junctions.

Figure 5-2 FESEM images of (a) FTO and (b) NiO compact layer coated FTO. Scale bar: 100 nm

In a typical procedure of QD-modified photoelectrodes, a NiO nanosheet array and CdSe QDs were grown on an FTO substrate in sequential order using a modified chemical bath deposition (CBD) method.(250, 251) Notably, a 100 nm thick NiO compact layer (Figure 5-2) has to be prepared on the FTO surface prior to the CBD growth of NiO nanosheets, since the compact layer is able to avoid a direct contact between CdSe and the FTO electrode.

Figure 5-3 Photocurrent vs. time plot of CdSe/NiO photoelectrode without NiO compact layer at zero bias condition

A control experiment shows a considerably anodic response in the CdSe/NiO nanosheet photoelectrode without a NiO compact layer owing to the direct electron injection from CdSe QDs to FTO (Figure 5-3).

Figure 5-4 (a) XRD patterns of NiO nanosheet array, CdSe QDs-modified NiO nanosheet array, TiO₂ nanorod array, and Cd QDs-modified TiO₂ nanorod array. (b) XRD patterns of CdSe (chemical bath deposition) QDs (CBD-CdSe) and CdS (electrodeposition) QDs (ED-CdS) prepared under the same conditions. (c) High-resolution TEM images of CdS QD modified TiO₂ nanorods. (d) High-resolution TEM images of CdSe QD modified NiO nanosheets.

The deposition of CdSe and CdS QDs on NiO and TiO₂ photoelectrodes was studied with X-ray diffraction (XRD), as shown in Figure 5-4a. The diffraction patterns of QD modification on the surface of TiO₂ or NiO were absent of obvious diffraction contribution from QDs, which can be attributed to the characteristics of the nanocrystalline nature of QDs. As a result, CdSe and CdS QDs were prepared under identical conditions to further verify their structures (Figure 5-4b). Several feature diffraction peaks at $\sim 25.0^\circ$ and 26.5° in the XRD patterns could be assigned to the

(111) diffraction of zinc blende CdSe (JCPDS No. 19-0191) and the (002) diffraction of wurtzite CdS (JCPDS No. 41-1049), respectively.

Figure 5-5 High-magnification SEM images of (a) CdS QDs-modified TiO₂ nanorods and (b) CdSe QDs-modified NiO nanosheets. Scale bar is 100 nm.

High-resolution scanning and transmission electron microscope images reveal a close contact between CdS (CdSe) QDs and TiO₂ nanorods (NiO nanosheets) (Figure 5-4c and d and Figure 5-5). Notably, apparent contrasts between QDs and TiO₂ nanorods (NiO nanosheets) were clearly observed, which provided more compelling evidence that QDs were remarkably attached onto the substrate surfaces (Figure 5-6).

Figure 5-6 (a) & (b) TEM images of CdS QDs-modified TiO₂ nanorods and CdSe QDs-modified NiO nanosheets. (c) & (d) TEM images showing the decoration of ZnS protective layer and loading of IrOx and NiS co-catalysts. (e) & (f) HRTEM images showing the crystallize sizes of CdS and CdSe quantum dots.

Furthermore, the estimated crystalline sizes of QDs through Scherrer's formula from XRD were approximately 6.5 and 5.0 nm for CdS and CdSe, which were consistent with the observation from HRTEM images. The significant QD decoration could be further revealed by the fact that well-resolved interplanar spacings of 0.325,

0.336, 0.241, and 0.348 nm correspond to the (110) plane of rutile TiO_2 , the (002) plane of wurtzite CdS, the (111) plane of NiO, and the (111) plane of zinc blende CdSe, respectively.

Figure 5-7 (a) UV/vis spectra and photographs of CdS QD modified TiO_2 photoanode and CdSe QD modified NiO photocathode. (b) IPCE spectra of CdS QD modified TiO_2 photoanode and CdSe QD modified NiO photocathode measured at -0.3 V vs Ag/AgCl.

Figure 5-7a shows the absorption spectra of bare NiO nanosheets, TiO_2 nanorods, CdSe QD modified NiO nanosheets, and CdS QD modified TiO_2 nanorods. The inset in Figure 5-7a displays photographs of a CdSe QD modified NiO photocathode and a CdS QD modified TiO_2 photoanode. The absorption spectra of the CdSe QD modified NiO photocathode and CdS QD modified TiO_2 photoanode exhibited a significant increase in the visible region, owing to the presence of either CdS or CdSe QDs, implying that the use of CdS or CdSe QDs as sensitizer enables a wider range of visible photons in sunlight to be harvested. The CdS QD modified TiO_2 photoanode and CdSe QD modified NiO photocathode absorb in the visible region with an onset at ~ 500 nm and ~ 630 nm, corresponding to the presence of CdS QDs and CdSe QDs, respectively, consistent with the observation in the absorption spectra (Figure 5-1c). To quantify the photoresponse of QD-sensitized photoelectrodes, incident photon-to-current-conversion efficiency (IPCE) measurements were made to examine their

photoresponses as a function of incident light wavelength (Figure 3b). IPCE can be expressed as: (115, 124, 126)

$$IPCE = [1240 \times I(\lambda)] / [\lambda \times P(\lambda)] \quad (11)$$

where $I(\lambda)$ is the photocurrent, $P(\lambda)$ is the illumination power, and λ is the wavelength of incident light. The photoresponses of TiO_2 and NiO photoelectrodes were drastically extended to the visible light region of the solar spectrum after modification of cadmium chalcogenide QDs, indicating that photogenerated charge carriers by excitation of cadmium chalcogenide QDs can efficiently inject into both TiO_2 and NiO and considerably contribute to photocurrent generation. Notably, a TiO_2 nanorod photoanode sensitized with CdS QDs exhibited a substantially higher IPCE than a CdSe QD modified NiO photocathode, attributed primarily to their intrinsic n-type nature of cadmium chalcogenide QDs. In the case of the CdS QD modified TiO_2 photoanode, the band-bending effect within CdS QDs is able to facilitate the charge separation and advance charge transfer in the interface of the QDs and electrolyte. However, the n-type nature of CdSe QDs as a photocathode sensitizer might generate a negative effect on their charge transferring within the semiconductor surface and electrolyte interface. To eliminate this negative effect, co-modification of ZnS and gas evolution co-catalysts are consequently utilized in the following section. Overall, the IPCE of a CdS QD modified TiO_2 photoanode and a CdSe QD modified NiO photocathode revealed significant photoresponses in the visible light region, which is consistent with the observed increase in visible light absorption after CdS or CdSe QD modification.

Figure 5-8 SEM images of (a) NiO nanosheet array and (b-d) CdSe QD modified NiO nanosheet array with various CBD growth times of CdSe (b, 12 h; c, 24 h; and d, 36 h). (e) Transient photocurrent response curves of CdSe-modified NiO photocathode prepared with various CdSe deposition times at 0 V vs Ag/AgCl.

Chemical bath deposition growth of CdSe QDs was optimized as well since decoration of QDs would strongly affect the photoelectrochemical performance of the CdSe/NiO photocathode. Figure 5-8(a-d) shows the SEM images of a CdSe QD modified NiO nanosheet photocathode with various CBD growth times. A CdSe QD single layer could be uniformly loaded on both sides of the NiO nanosheet if the deposition time was less than 24 h, which is beneficial for efficient charge carrier separation at the interface of the CdSe QDs/NiO nanosheet. However, in the case of longer CBD growth (more than 36 h), the formation of CdSe QD aggregations on the NiO nanosheets forced the charge carriers to diffuse longer distances, resulting in a greater recombination loss and thus poorer photoelectrochemical performance.^(243, 252) The best cathodic photocurrent at 0 V vs Ag/AgCl for the CdSe/NiO photocathode is $\sim 0.13 \text{ mA/cm}^2$, in which the photoelectrode was prepared with 24 h CBD growth of CdSe (Figure 5-8e). On the other hand, CdS QDs were used to modify the TiO_2 nanorod photoanode to extend the optical response to visible light in this work, where CdS QDs were deposited onto a TiO_2 nanorod array by using a modified electrochemical deposition method.⁽²⁵³⁾ The optimized CdS/ TiO_2 photoanode delivers a photocurrent density of $\sim 0.30 \text{ mA/cm}^2$ at 0 V vs Ag/AgCl

under 1 sun visible light illumination (1 sun illumination with UV $\lambda < 400$ nm filtered off) (Figure 5-9).

Figure 5-9 (a) SEM image of bare TiO₂ nanorod array. (b) SEM image of CdS QD (200 s) coated TiO₂ nanorod array. (c) Transient photocurrent response curves of CdS-modified TiO₂ photoanode prepared with various electrodeposition times at 0 V vs Ag/AgCl.

5.3.2 Passivation of photoelectrodes

Since cadmium chalcogenide QDs commonly suffer from photodecomposition and/or photocorrosion in aqueous media under illumination, a sacrificial reagent such as sulfide or selenium ions was generally employed to protect QDs from undesired photogenerated effects. However, sacrificial reagents normally contain reductant, electron donors, or hole-scavengers; photogenerated charge carriers consequently react with sacrificial reagents rather than water, resulting in the fact that either a cathodic or anodic reaction can be performed under a sacrificial environment. As a result, a sacrificial system cannot be operated to protect QDs for solar water splitting. Although optimized decoration of QDs can facilitate effective charge transferring to improve their stability,⁽²⁴²⁾ this still cannot offer sufficient stability for long-term irradiation. Consequently, an easily synthesized corrosion-resistant layer that can protect the underlying semiconductor QDs while not inhibiting charge carrier (electron or hole) transport and photon absorption will be extremely essential. In the

present study, a thin protecting layer of ZnS and NiS or iridium oxide nanoparticles as hydrogen or oxygen evolution co-catalysts was sequentially decorated on the surfaces of CdSe/NiO and CdS/TiO₂ photoelectrodes.

Figure 5-10 (a) The effect of oxygen-generating IrO_x·nH₂O nanoparticles on ZnS/CdS/TiO₂ nanorod photoanode, and (b) the effect of hydrogen-generating NiS nanoparticles on ZnS/CdSe/NiO nanosheet photocathode.

Iridium oxide and NiS have been demonstrated to significantly catalyze oxygen evolution and hydrogen evolution reactions, (254-256) which allow us to improve their activities in both the photoanode and photocathode (Figure 5-10). The ZnS layer has been reported to act as a passivation layer to protect QDs and increase photocurrent in solar cells, where the ZnS layer can prevent the recombination of photogenerated electrons with oxidizers on the surface of QDs.(203, 257) It has to be pointed out here that the stabilizing treatment of photoelectrodes in solar water splitting has to be different from solar cells, and both a ZnS overlayer and co-catalyst decoration are essential and critical for stabilizing cadmium chalcogenide QDs in solar water splitting systems, in which ZnS passivation and co-catalysts are responsible for QD protection and charge carrier extraction, respectively (as shown in Figure 5-11).

Figure 5-11 (a) Photocurrent density versus time of ZnS coating and IrO_x co-catalyst loading on a CdS/TiO₂ nanorod photoanode measured at 0 V vs Ag/AgCl. (b) Photocurrent density versus time of ZnS coating and NiS co-catalyst loading on a CdSe/NiO nanosheet photocathode measured at 0 V vs Ag/AgCl. Simulated 1 sun illumination (AM1.5G) with UV cutoff ($\lambda > 400$ nm) was used, and the scan rate is 10 mV/s.

This commodification of the ZnS layer and gas evolution cocatalysts can perform a nearly identical photoresponse within the measured period in both the photoanode and photocathode. By contrast, the QD-modified photoanode and photocathode without ZnS and co-catalyst decoration exhibited a substantial and rapid decrease in photocurrent, which verified that bare cadmium chalcogenide QD modified photoelectrodes are unable to achieve practical solar water splitting, as shown in Figure 5-11a and b. In the solar water splitting system, ZnS passivation alone cannot provide sufficient efforts for enhancing performance since both anodic and cathodic reactions need to be simultaneously considered. If only a ZnS layer is employed to passivate QDs from surface recombination, further increasing the thickness of the

passivation layer will result in a negative effect and lead to a decrease in photocurrent (not shown here), since a thicker ZnS layer simultaneously suppresses both anodic and cathodic reactions to reduce the overall performance of water splitting.

Figure 5-12 *J-V* scans of CdS QD modified TiO₂ nanorod photoanode (a) and CdSe QD modified NiO nanosheet photocathode (b) under chopped illumination (all samples were co-modified with ZnS and gas evolution cocatalysts).

For example, ZnS passivation can suppress the recombination at surface trapping states on CdS QDs and facilitate the electron flow from CdS to TiO₂, but anodic reaction (water oxidation for oxygen evolution) would be simultaneously passivated as well. Toward this end, cocatalysts (iridium oxide) are essentially utilized to facilitate the collection of holes and to improve oxygen evolution in water splitting. Effectively collecting charge carriers can not only improve the photocurrent but also avoids the undesired photogenerated effect on QDs. Co-modification of ZnS and gas evolution cocatalysts are greatly able to suppress surface state trapping to enhance photocurrent and efficiently collect carriers to improve gas evolution in a solar water splitting system. As a result, the optimized photocurrent-photovoltage (*J-V*) data under chopped illumination are plotted in Figure 5-12 a and b. The onset potential and saturation photocurrent for the CdS/TiO₂ photoanode were found to be -0.83 V vs Ag/AgCl and 0.21 mA/cm², respectively. The CdSe/NiO photocathode gave a

cathodic photocurrent with an onset potential at 0.23 V vs Ag/AgCl and a photocurrent density of 0.30 mA/cm² at -0.4 V vs Ag/AgCl.

5.3.3 Wire-linked photoelectrodes

Figure 5-13 (a) SEM images of CdS QD modified TiO₂ nanorod (top) and CdSe QD modified NiO nanosheet (bottom) electrodes. Scale bar: 500 nm. (b) Photocurrent density of CdS QD modified TiO₂ nanorod photoanode and CdSe QD modified NiO nanosheet photocathode in 0.5 M Na₂SO₄ solution versus the applied voltage referenced to a reversible hydrogen electrode (RHE). (c) *J-V* curve of a photoelectrolysis cell with CdS QD modified TiO₂ nanorod and CdSe QD modified NiO nanosheet photoelectrodes.

To further reveal solar driven water splitting, a wire-linked photoelectrolysis cell was obtained (as shown in Figure 5-13a), in which the optimized individual *J-V* curve for the CdSe/NiO photocathode and CdS/TiO₂ photoanode under simulated sunlight with UV filtered-off was measured (Figure 5-13b). In this individual measurement, a current density intersection of 0.19 mA/cm² (as indicated by the arrow) suggests a

nonzero current flow under visible light illumination once the CdSe/NiO photocathode and CdS/TiO₂ photoanode are directly linked.

Figure 5-14 Photovoltage vs. time curves of NiO photocathode and TiO₂ under visible light in 0.5 M Na₂SO₄ electrolyte solution

Further measuring the *J-V* curve of the wire-linked photoelectrolysis cell in a tandem configuration demonstrated the open-circuit voltage (V_{oc}) of the photoelectrolysis cell is ~ 0.53 V (Figure 5-13c), which can be attributed to the sum of photovoltages of the CdS/TiO₂ photoanode (~ -0.42 V) and CdSe/NiO photocathode (~ 0.13 V) (Figure 5-14). This phenomenon is clearly consistent with the observation in Figure 5-13b, implying that overall solar-driven water splitting can be spontaneously performed without applied external energy in a tandem configuration of CdSe/NiO and CdS/TiO₂ photoelectrodes. A short-circuit current density of ~ 0.125 mA/cm² is obtained under 1 sun visible light illumination, which is further confirmed through corresponding transient photocurrent response of this tandem cell under chopped visible light illumination (Figure 5-15).

Figure 5-15 Transient photocurrent response curve of wire linked photoanode and photocathode system at zero bias condition under 1 sun visible light illumination in 0.5 M Na₂SO₄ electrolyte solution.

Prolonged testing of the two illuminated cadmium chalcogenide QD modified photoelectrodes under short-circuit conditions was also performed; a photocurrent versus time evolution of the photoelectrolysis system under chopped illumination over 20 min is shown in Figure 5-16a.

Figure 5-16 (a) Photocurrent density versus time of externally short-circuited CdS QD modified TiO₂ nanorod and CdSe QD modified NiO nanosheet photoelectrodes under chopped light exposure. Inset: Digital photographs of CdS/TiO₂ photoanode and CdSe/NiO photocathode before and after 30 min of continuous photoreaction. Photocurrent responses of (b) bare TiO₂ nanorod array and optimized CdS/TiO₂ nanorod photoanode and (c) bare NiO nanosheet array and optimized CdSe/NiO nanosheet photocathode at 0 V vs Ag/AgCl.

The photocurrent first decreased and then stabilized at $\sim 70\%$ of its original performance, rendering a stabilized photocurrent density of 0.11 mA/cm^2 under simulated 1 sun illumination with UV filtered-off, indicating that this co-modification can significantly stabilize the cadmium chalcogenide QDs under long irradiation. Furthermore, no obvious change in appearance of the QD-modified photoelectrodes after 30 min of continuous photoreaction was observed (inset), indicating that this co-modification of ZnS and gas evolution cocatalysts can significantly improve their properties in both surface passivation of QDs and charge-carrier transferring between QDs/TiO₂(NiO) and exhibit a good system photostability. In addition, the photocurrent contributions from bare NiO and TiO₂ photoelectrodes are merely 9 and $7 \text{ } \mu\text{A/cm}^2$ (Figure 5-16b and c); this finding revealed that wide-bandgap materials (TiO₂ and NiO) generated an extremely low photoresponse ($\sim 4\%$ and $\sim 5\%$) compared to that of a QD-modified photocathode and photoanode, indicating that the photoresponse from TiO₂ or NiO is negligible and all photocurrent results from the photo-generation process of cadmium chalcogenide QDs in the visible light region. Consequently, a visible light-driven spontaneous water splitting has been realized, while the calculated overall solar-to-chemical conversion efficiency based on photocurrent density is $\sim 0.17\%$, which is comparable to the efficiency of natural photosynthesis.(226, 236)

Figure 5-17 Comparison of the evolved hydrogen and oxygen gases and the charge through the external circuit. Inset shows the photocurrent versus time measurement.

Figure 5-17 displays the evolution of H_2 and O_2 gases in a 0.5 M Na_2SO_4 aqueous solution. A stoichiometric amount of H_2 and O_2 with a hydrogen-to-oxygen ratio of 2:1 was observed, which is expected as a result of spontaneous water splitting. Moreover, the amount of H_2 evolved is almost equal to half of the charges that passed through the external circuit, giving a high charge-to-chemical faradic efficiency of ~95%.

5.4 Summary

In summary, a photoelectrolysis cell with a cadmium chalcogenide QD modified TiO_2 nanorod photoanode and a NiO nanosheet photocathode was developed for spontaneous overall water splitting to produce H_2 and O_2 under visible light illumination. Such a self-driven water splitting system provides desired charge transfer paths to achieve high-efficiency H_2 and O_2 generation at zero external bias condition. The optimized CdSe QD modified NiO photocathode combined with a current matched CdS QD modified TiO_2 photoanode gave rise to the highest efficiency of overall solar water splitting, about 0.17%. Average gas evolution rates of 2.24 (hydrogen) and 1.07 (oxygen) $\mu mol\ h^{-1}\ cm^{-2}$ at zero bias condition have been achieved, with almost 95% faradic efficiency. In addition, this research provides a

new concept of co-modification of the passivation layer and cocatalysts to suppress surface-state trapping and to efficiently collect charge carriers for enhancing overall efficiency of solar water splitting. Although this maiden concept focuses on cadmium chalcogenide quantum dots and TiO_2/NiO photoelectrodes, we believe that our strategy is fundamental to the design of solar energy devices and should become an accepted technique for solar energy utilization in spontaneous solar water splitting.

Chaper 6 Hierarchical Ni-Mo-S nanosheets on carbon fiber cloth: a flexible electrode for efficient hydrogen generation in neutral electrolyte

6.1 Introduction

On the journey to pursue clean and sustainable energy resources, electrocatalytic and photoelectrocatalytic water splitting have attracted growing attention because of their potential applications in producing hydrogen with ultrahigh purity while generating negligible greenhouse gases.(15, 258) Hydrogen evolution reaction (HER), in which protons are reduced to molecular hydrogen, is a critical process for electrocatalytic water splitting.(258) Although platinum (Pt) is the most effective HER electrocatalyst, the scarcity and expensiveness limit its practical applications for large-amount hydrogen generation. (259, 260) Therefore, exploration of alternative earth-abundant materials with low cost and high catalytic activity is essential for developing high performance electrocatalyst toward large-amount hydrogen production.

MoS₂, a layered transition metal dichalcogenide, has been shown as a versatile functional material for various applications,(261-263) including lithium-ion batteries,(264-266) nanoelectronics,(267, 268) hydrodesulphurization,(269) and HER catalysts(270). The earliest observation of hydrogen evolution on MoS₂ can be dated back to more than 40 years ago.(271) Later, in 1991, Sobczynski reported MoS₂ as an HER co-catalyst for water photodecomposition on semiconductors.(272) Since then, MoS₂-based catalysts have been thoroughly studied and widely recognized as an ideal catalyst for hydrogen generation in acidic medium.(273) More recently, a number of computational and experimental studies suggest that the HER activities of

nano-sized MoS₂ particles are originated from the edge sites while their basal planes are catalytically inactive.(154) To fully exploit the advantageous catalytic properties, well-defined MoS₂ nanostructures with abundant exposed catalytic active sites and enhanced intrinsic properties should be rationally designed. Various strategies have been proposed and reported for improving the catalytic activity of MoS₂-based HER catalysts. For example, Li et al. reported the synthesis of MoS₂ nanoparticles anchored on graphene through a solvothermal approach. The composite catalyst showed superior catalytic performance owing to the abundant exposed edges as well as the strong chemical and electronic coupling between graphene oxide (GO) and MoS₂.(84) Kibsgaard et al. successfully engineered MoS₂ into highly ordered double-gyroid network, in which active edge sites in MoS₂ are preferentially exposed for electrocatalysis.(274) Recently, Wang et al. showed the preparation of vertically aligned MoS₂ nanofilms with improved HER activity by electrochemical lithium intercalation.(275) Zhu et al. demonstrated that the aerophobic surface of nanostructured MoS₂ is more beneficial for releasing gas bubbles during HER as compared to the planar thin film.(276) Besides the aforementioned design and construction of nanostructures, controllable disorder engineering is another approach that can be utilized to improve the catalytic activities of MoS₂. For example, Xie et al. reported the syntheses of defect-rich MoS₂ ultrathin nanosheets through controlling experimental conditions such as precursor concentration and reaction temperature.(156, 277) They discovered that the introduction of defect sites could lead to the exposure of additional catalytic centers, thus significantly improving the catalytic performance of MoS₂.

All of the aforementioned strategies are important and provide us valuable guidelines to further excavate the potential of MoS₂-based electrocatalysts. However,

most of the current studies on MoS₂-based electrocatalysts are only viable for lab-scale applications under ideal experimental conditions, which are not ready to be applied in practical industrial appliances. For the purpose of developing qualified H₂ gas-evolving electrodes that can be integrated in large-scale reactors, the following criteria have to be fulfilled. First, the attached HER catalyst must exhibit extraordinary catalytic activity and reasonable stability for long-term operation. Second, the catalysts and their supporting materials should be abundant and cost-effective that can be massively produced. Third, the catalysts, substrates and the operating environment have to be nontoxic and eco-friendly, in accordance with the intention of developing sustainable energy resources. Last, the electrodes should possess excellent mechanical strength and physical flexibility, which allow them to be integrated in varied reactors to meet different requirements and standards. Owing to the rapid advancement in theoretical calculations as well as experimental techniques, the progresses of developing gas-evolving electrodes for practical applications have been significantly accelerated over the past few years. (278-281)

Herein, we report a facile synthetic strategy to directly grow nanostructured Ni-Mo-S on three-dimensional (3D) flexible and conductive carbon fiber cloth substrate. It was found that the introduction of nickel ion (Ni²⁺) in the precursor solution played a crucial role in tailoring the morphology and intrinsic properties of MoS₂, hence effectively affecting their catalytic behaviors. The optimized Ni-Mo-S/C electrode showed pronounced HER electrocatalytic activity in neutral electrolyte with remarkable stability. The as-synthesized Ni-Mo-S catalysts were characterized by scanning and transmission electron microscopy, Raman spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy.

Importantly, a prototype of lab-scale H₂ generator was designed to show the applicability of the Ni-Mo-S/C electrode for future large-scale applications.

6.2 Experimental

6.2.1 Materials

Woven carbon fiber cloth with evenly sized pores was purchased from GasHub Technology. Sodium molybdate dihydrate (Na₂MoO₄·2H₂O), nickel sulfate hexahydrate (NiSO₄·6H₂O), L-cysteine (L-Cys, HSCH₂CHNH₂COOH), sulfuric acid (H₂SO₄, ≥ 98%), sodium phosphate monobasic (NaH₂PO₄), and sodium phosphate dibasic (Na₂HPO₄) were purchased from Sigma-Aldrich. Hydrogen peroxide (H₂O₂) was purchased from Alfa Aesar, and acetone ((CH₃)₂CO) was purchased from Acros Organics. All chemical reagents were used directly without further purification. Milli-Q water (resistivity over 18 MΩ cm) from a Millipore Q water purification system was used in all experiments.

6.2.2 Syntheses of MoS₂ and Ni-Mo-S on carbon fiber cloth

Carbon fiber cloth substrates were washed consecutively with acetone, H₂SO₄ (1 M) and DI water under sonication for 2 hours in each solution to thoroughly remove organic residues and other impurities. The substrates were then soaked in “piranha” solution, i.e. the mixture of concentrated sulfuric acid and 30% hydrogen peroxide with volume ratio of 3 : 1, for overnight to further improve their hydrophilicity. The clean substrates were kept in Milli-Q water to avoid regaining hydrophobicity.

The MoS₂, NiS_x and Ni-Mo-S were grown on the cleaned carbon fiber cloth using a biomolecule-assisted hydrothermal synthetic route. Briefly, sodium molybdate dihydrate (Na₂MoO₄·2H₂O) and nickel sulfate hexahydrate (NiSO₄·6H₂O) were used as Mo and Ni sources, respectively, while L-cysteine (L-Cys, HSCH₂CHNH₂COOH) was used as S source and reducing agent. To study the effect

of the Ni-to-Mo precursor ratio on the morphology and performance of the as-prepared functional electrodes, 6.05 mg/ml of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (25 mM), 6.57 mg/ml of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (25 mM) and 16 mg/ml of L-Cys (132 mM) aqueous solutions were prepared and mixed according to Table 6-1, while the sum of molar amounts of Ni and Mo was kept as constant in the precursor solutions for all samples.

Table 6-1 Preparation of MoS_2 , NiS_x and Ni-Mo-S on carbon fiber cloth

Precursor Sample	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (25 mM)	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (25 mM)	L-Cys (132 mM)
MoS_2	20 ml	0	20 ml
Ni-Mo-S (Ni : Mo = 1 : 3)	15 ml	5 ml	20 ml
Ni-Mo-S (Ni : Mo = 1 : 1)	10 ml	10 ml	20 ml
Ni-Mo-S (Ni : Mo = 3 : 1)	5 ml	15 ml	20 ml
NiS_x	0	20 ml	20 ml

The precursor solutions have to be mixed rapidly and subjected to vigorous stirring to prevent the formation of precipitates. Then the solution was transferred to a 50 ml Teflon-lined stainless autoclave. Thereafter, a piece of pre-cleaned carbon fiber cloth was vertically aligned in the growth solution. The autoclave was heated at 200 °C for 24 hours. After naturally cooling down to room temperature, the sample was washed thoroughly with Milli-Q water, and dried using compressed air flow at

room temperature. The weight of carbon fiber cloth electrodes was precisely recorded before and after reaction using an Ohaus analytical balance to calculate the actual catalyst-loading amount. The calculation of actual loadings for MoS₂/C, NiS_x/C and different Ni-Mo-S/C samples can be found in Table 6-2.

Table 6-2 Calculation of actual catalyst-loadings for MoS₂/C, NiS_x/C and different Ni-Mo-S/C samples

Sample	Calculated Mass Loading (mg/cm ²)				Standard Deviation
	Test 1	Test 2	Test 3	Average	
MoS ₂	1.64	1.56	1.63	1.61	0.044
Ni-Mo-S/C (Ni:Mo = 1:3)	0.96	0.84	0.87	0.89	0.062
Ni-Mo-S/C (Ni:Mo = 1:1)	0.52	0.54	0.5	0.52	0.02
Ni-Mo-S/C (Ni:Mo = 3:1)	0.35	0.31	0.3	0.32	0.027
NiS _x	0.44	0.37	0.42	0.41	0.036

6.2.3 Sample characterizations

The morphology and elemental composition of samples were examined using field emission scanning electron microscopy (FESEM, JEOL JSM-6700F), transmission electron microscopy (TEM, JEOL JEM-3010) and energy dispersive X-ray spectroscopy (EDS, JEOL JED-2300 Analysis Station). BET measurements were performed using the Autosorb-1 system (*Quantachrome Instruments*). X-ray diffraction (XRD) measurements were conducted on Bruker AXS D8 Advance and D2 Phaser to study the crystal structures and phase compositions. X-ray photoelectron spectroscopy (XPS) measurements were carried out 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). All binding energies were referenced to the C 1s peak (284.60 eV) arising from the adventitious hydrocarbons. Raman spectra of the samples were measured using a research laser Raman microscope (Reinshaw RM1000), with a 514.5 nm excitation laser. The Raman band of Si at 520 cm⁻¹ was used as the reference to calibrate the spectrometer. A series of extended x-ray absorption fine structure (EXAFS) measurements were made using synchrotron radiation. Measurements were made at the Ni K edge (8333 eV) and the Mo K edge (20,000 eV) with the sample held at room temperature. The 01C beam line in the National Synchrotron Radiation Research Center (NSRRC) in Taiwan has been designed for such experiments. The backscattering amplitude and phase shift functions for specific atom pairs were calculated ab initio using the FEFF8 code. X-ray absorption data were analyzed following standard procedures, including pre-edge and post-edge background subtraction, normalization with respect to edge height, Fourier transformation and nonlinear least-squares curve fitting. The normalized k^3 -weighted EXAFS spectra, $k^3\chi(k)$, were Fourier-transformed in the k range from 3.1 to 12.7 Å⁻¹ to reveal the contribution of each bond pair on the Fourier transform (FT) peak. The experimental Fourier-filtered spectra were obtained by performing an inverse Fourier transformation with a Hanning window function with r between 1.1 and 2.4 Å. The S_0^2 (amplitude reduction factor) values of Mo and Ni atoms were fixed at 0.9 and 0.91, to determine the structural parameters of each bond pair.

6.2.4 Electrochemical measurements

Electrochemical measurements were carried out on an electrochemical workstation (CHI 760E) with a three-electrode set-up, consisting of an as-prepared electrode as the working electrode, a graphite foil (2 cm × 3 cm) as the counter electrode and a saturated calomel electrode (SCE, in saturated KCl) as the reference

electrode. To assess the catalytic activity in neutral medium, electrochemical tests were primarily carried out in 0.5 M sodium phosphate buffer solution prepared by mixing 0.5 M NaH_2PO_4 and 0.5 M Na_2HPO_4 aqueous solutions with an appropriate ratio. The HER performance was also studied in 0.5 M H_2SO_4 electrolyte. The electrolytes were deaerated by purging nitrogen for 30 minutes prior to the electrochemical measurement. The pH values of different electrolytes were carefully measured using a calibrated pH meter (Mettler Toledo SevenCompact), and were determined to be 0.18 and 6.94 for 0.5 M H_2SO_4 and 0.5 M sodium phosphate buffer solution, respectively.

Reference electrode calibrations were performed using a standard Pt plate electrode as the working electrode. Cyclic voltammetry scans were performed at a scan rate 1 mV/s, and the average of the two potentials at which the current crossed zero was taken to be the experimentally determine 0 V vs. RHE (or $V_{\text{HOR/HER}}$). Based on this value, we have calculated the electrode potential of the SCE that we used in this work using the equation shown below:

$$V_{\text{SCE}}^0 (V) = V_{\text{HOR/HER}} - 0.059 V \times pH \quad (12)$$

The theoretical electrode potential of SCE (in saturated KCl) was reported to be 0.241 ~ 0.244 V vs. RHE. But the values that we determined experimentally, say 0.238 V vs. RHE in 0.5 M H_2SO_4 and 0.234 V vs. RHE in 0.5 M sodium phosphate buffer solution, are slightly differed from the theoretical values.

The catalytic behaviors of different materials were studied and compared using linear sweep voltammetry (LSV) at scan rate of 5 mV/s, while the stability was

studied using amperometric technique. The measured voltage values were converted to reversible hydrogen electrode (RHE) scale by applying the following calculation:

$$V_{RHE} = V_{measured} + V_{SCE}^0 + 0.059 \times pH \quad (13)$$

where V_{RHE} is the converted potential value vs. RHE, $V_{measured}$ is the voltage reading from potentiostat and V_{SCE}^0 is the experimentally determined electrode potential of SCE.

To study the electrode kinetics, electrochemical impedance spectroscopy (EIS) was performed at -0.3 V vs. RHE in a range from 100K to 0.1 Hz with AC amplitude of 15 mV, using an electrochemical workstation (Zive SP2, Wonatech). The data were analyzed and fitted in equivalent circuits using ZView® software, and the Nyquist plots were used to study the charge transport properties.

In this work, AC impedance technique was used to obtain the uncompensated resistance (R_u) of the working electrodes before carrying out the LSV measurements, and all polarization curves were iR-corrected with a compensation level of 90%.

6.2.5 Faraday efficiency measurement

Faraday efficiency measurement was performed inside a multi-purpose compact glass photo-/electro-catalysis reactor, integrated with a single-chamber electrolysis cell. The sample line of the reactor was linked to an online gas chromatograph (GC, Agilent 490), which is equipped with a molecular sieve column and a thermal conductivity detector (TCD), allowing the real-time detection of gas products. Inside the electrolysis cell, the Ni-Mo-S/C, graphite foil and SCE were used as working, counter and reference electrodes, respectively, while deaerated 0.5 M sodium

phosphate buffer was used as the electrolyte. Prior to the measurement, the system was evacuated thoroughly using a high-efficiency vacuum pump, and then charged with ultra-pure Argon (Ar, 99.9995%) gas to 1 atm. Constant potential was applied to the working electrode using an electrochemical workstation (CHI 760E). The compositions and concentrations of the gas products were analyzed with GC through automatic sampling in every 4 minutes.

6.3 Results and discussion

6.3.1 Aggregation of MoS₂ on carbon fiber cloth

Figure 6-1 SEM image of carbon fiber cloth. SEM image of carbon fiber cloth used for fabrication of functional electrodes. Inset: SEM image of typical carbon fiber.

In this work, our first attempt was to synthesize nanostructured MoS₂ onto various carbon-based substrates, including carbon fiber cloth (Figure 6-1) and graphite foil, which can be directly used as functional electrodes for hydrogen

evolution. In these experiments, a biomolecule-assisted hydrothermal synthetic route with $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and L-cysteine (L-Cys) as the Mo and S sources, respectively, was used to synthesize nanostructured MoS_2 . As one type of amino acids, the L-Cys molecules can be assembled into polymeric network structure through the formation of peptide bonds and disulfide bonds from the dehydration condensation and sulfhydryl (-SH) group oxidation reactions. The as-formed 3D network is beneficial for the construction of nanostructured materials. Upon heating to a certain temperature, L-Cys starts to decompose and releases H_2S that is capable of reducing MoO_4^{2-} to MoS_2 based on the following reactions:(264, 282)

However, after several trials, we noticed that bulky aggregates of MoS_2 with wide size distributions could be easily formed during the hydrothermal process, similar to those reported previously.(84, 264) These aggregates may bury the active sites-containing edges and create micro-cavities, which can trap evolved H_2 bubbles, thus significantly limiting the catalytic activity of MoS_2 . We then took different measures for the purpose of preventing the formation of bulky aggregates on carbon fibers, including reducing the precursor concentration, varying the precursor ratio and tuning the reaction temperature. However, none of these approaches worked effectively to meet our expectation.

After careful analysis, we attribute the aggregation of MoS_2 to the epitaxial nucleation/growth of layered MoS_2 on the rough carbon fibers. Figure 6-1 shows the

SEM image of the carbon fiber cloth which was used to fabricate functional electrodes. The inset of Figure 6-1 illustrates the morphology of a single carbon fiber, from which the oriented striations comprising wrinkles and ridges can be clearly observed. Figure 6-2 shows the MoS₂/C synthesized with reduced precursor concentration (10 mM Na₂MoO₄ · 2H₂O + 50 mM L-Cys), which shows that carbon fiber is only partially covered by nanostructured MoS₂. Based on these observations, the following aggregation mechanism is proposed.

Figure 6-2 SEM image of MoS₂/C synthesized with reduced precursor concentration. MoS₂/C synthesized with reduced precursor concentration (10 mM Na₂MoO₄ · 2H₂O + 50 mM L-Cys), showing the evidences of the formation mechanism of bulky MoS₂ aggregates.

Initially, MoS₂ nuclei formed by heterogeneous nucleation attach onto the hydrophilic surface of carbon fibers, and then firmly bind with it through van der Waals interaction. The sizes of nuclei may vary, due to the propagation of

heterogeneous nucleation at different rates on distinct sites. In the structure of MoS₂, Mo (IV) centers occupy the trigonal prismatic coordination sphere, which bound to six neighboring sulfide atoms, while each pyramidal sulfur center is connected to three neighboring Mo centers. With this spatial arrangement, MoS₂ tends to form layered structures through the interconnection between trigonal prisms.(283) Due to its layered structure, MoS₂ crystals will grow epitaxially along the hydrophilic surface, forming film-like structures that partially cover the carbon fibers. However, the surface of carbon fibers is not ideally smooth for the development of continuous thin film, due to the presence of random allocated striations. The epitaxial growth of MoS₂ layers will be hindered once those expanding edges step onto the wrinkles or ridges near the striations. Due to the weakening of van der Waals interaction near these sites, certain expanding edges are lifted from the surface of carbon fibers. The redirected crystal growth along the lifted edges will continue when there are sufficient precursors present in the solution, and these lifted edges will gradually folded into aggregates. Meanwhile, newly generated nuclei may continuously attach onto the carbon fibers or stack onto the existing MoS₂ sheets on carbon fibers. Due to the unevenly distributed film thickness, the stacked MoS₂ layers will start to crack by random tearing and squeezing forces, hence leading to the formation of new expanding crystal edges. Eventually, the MoS₂ layers will assemble into bulky aggregates on carbon fibers. As shown in Figure 6-3, we found that the aggregation of MoS₂ is time-dependent.

Figure 6-3 SEM images of MoS₂/C synthesized after different durations of hydrothermal treatment. SEM images of MoS₂ nanostructures on carbon fiber cloth synthesized after different durations of hydrothermal treatment, showing that the development of bulky MoS₂ is a time-dependent process. All scale bars represent 500 nm.

6.3.2 Development of Ni-Mo-S/C electrodes and material characterizations

To tailor the morphologies and intrinsic properties of MoS₂ on carbon fibers, the synthetic strategy was modified by introducing Ni²⁺ into the precursor solution. As shown in Figure 6-4 A, MoS₂ and Ni-Mo-S samples with different Ni-to-Mo precursor ratios, namely 3 : 1, 1 : 1 and 1 : 3, were directly synthesized on carbon fiber cloth, designated as MoS₂/C, and Ni-Mo-S/C (3:1), Ni-Mo-S/C (1:1) and Ni-Mo-S/C (1:3), respectively. For comparison purpose, NiS_x/C was also synthesized using the similar hydrothermal approach. Figure 6-4 B shows a photographic image of a freshly synthesized Ni-Mo-S/C (1:1) with dimension of 5 cm × 3 cm.

Figure 6-4 Synthesis processes of MoS_2/C and $\text{Ni-Mo-S}/\text{C}$. (A) Schematic illustration of syntheses of MoS_2 and Ni-Mo-S on carbon fiber cloth. (B) Photographic image of freshly prepared $\text{Ni-Mo-S}/\text{C}$ (1:1).

Figure 6-5 shows the typical low-magnification SEM images of bare carbon fiber from the cloth, NiS_x/C , $\text{Ni-Mo-S}/\text{C}$ and MoS_2/C . As displayed in Figure 6-5 A, the diameter of a single carbon fiber is $\sim 10\ \mu\text{m}$. Oriented striations that formed during the manufacturing process are along the entire surface of fibers. Figure 6-5 B shows the morphology of as-prepared NiS_x/C , where the irregular-shaped NiS_x particles with sizes ranging from 100 nm to 1 μm , forming a shell-like outer layer that covers the carbon fiber surface. However, the NiS_x particles are loosely attached to the surface of carbon fibers with clear cracks formed between them. The introduction of Ni^{2+} in the precursor solution plays a critical role in tuning the nanoarchitectures of $\text{Ni-Mo-S}/\text{C}$. At Ni-to-Mo precursor ratio of 3 : 1, the surface of carbon fibers were firstly covered with a rough and tight nanostructured film, followed by particles attachment with random shape and size (Figure 6-5 C). The nanostructured film, showing clear visible striations, is thinner as compared to NiS_x/C . When the Ni-to-Mo precursor ratio is reduced to 1 : 1, a uniform and continuous nanostructured film could be grown on the entire surfaces of carbon fibers (Figure 6-5 D). However, further increase in the Mo content (Ni: Mo = 1: 3) in the growth solution leads to the

formation of large aggregates (Figure 6-5E). Moreover, if no Ni^{2+} was added in the growth solution, non-uniform MoS_2 aggregates would cover the entire surface of carbon fibers.

Figure 6-5 Low-magnification scanning electron microscopy images. (A) bare carbon fiber cloth, (B) NiS_x/C , (C) Ni-Mo-S/C (3:1), (D) Ni-Mo-S/C (1:1), (E) Ni-Mo-S/C (1:3), and (F) MoS_2/C . All scale bars represent 2 μm .

To gain more detailed insights into the morphological evolution, we further compared the high-magnification SEM images of different Ni-Mo-S/C samples. Figure 6-6 A reveals that the nanostructured film in Ni-Mo-S/C (3:1) is comprised of numerous nanosheets and large aggregated nanoparticles, which stack tightly onto

the surface of carbon fibers. When Ni to Mo ratio in the precursor solution is reduced to 1 : 1, a uniform nanostructured film composed of abundant edge-exposing nanosheets with an average thickness of 8-10 nm is formed, which develops into a nanoscale 3D network (Figure 6-6 B). The 3D nanostructure of Ni-Mo-S/C (1:1) is expected to benefit its HER application.(276) Further increase in the Mo content in the growth solution (Ni : Mo = 1 : 3) results in the formation of bulky aggregates which significantly decreases the density of exposed edge structures (Figure 6-6 C). If no Ni^{2+} is introduced into the synthesis, freely grown MoS_2 can easily form large aggregates, which folded together and resembled the morphology of crumpled paper balls (Figure 6-6 D). The average thickness of MoS_2 nanosheets is around 20-30 nm, which is about 3 times thicker than the edges in Ni-Mo-S (1:1) (Figure 6-6 B).

Figure 6-6 High-magnification scanning electron microscopy images. (A) Ni-Mo-S/C (3:1), (B) Ni-Mo-S/C (1:1), (C) Ni-Mo-S/C (1:3) and (D) MoS_2 /C. All scale bars represent 500 nm.

The morphologies of different aggregates in different samples were compared (Figure 6-7). It was found that the aggregates in MoS₂/C, Ni-Mo-S/C (1:3) and Ni-Mo-S/C (1:1) are morphologically similar, which are all evolved from crumpled 2D-layered structures. In contrast, although the aggregates in Ni-Mo-S/C (3:1) and NiS_x are similar in appearance, both of the aggregates are formed from nanoparticles. Obviously, the introduction of Ni²⁺ during the synthesis plays important roles in regulating the development of Ni-Mo-S nanostructures. The added Ni²⁺ may suppress the MoS₂ crystal growth along the basal planes, thus lowering the probability of formation of stack-ups and coalescences among the nanosheets. However, overwhelming Ni²⁺ will prevent the formation of preferable 3D nanostructures on carbon fibers. Therefore, the optimized Ni-to-Mo precursor ratio in our synthesis is 1 : 1.

Figure 6-7 SEM images of aggregates. SEM images of the aggregates in different samples

Energy-dispersive X-ray spectroscopy (EDS) measurements were performed to study the elemental composition of the samples (Figure 6-8). The spectrum of MoS₂/C affirms the atomic ratio of Mo : S is close to 1 : 2, which is consistent with the stoichiometric ratio of MoS₂. However, the measured Ni-to-Mo ratios in Ni-Mo-S/C (3:1), Ni-Mo-S/C (1:1) and Ni-Mo-S/C (1:3) are 1 : 4.5, 1 : 8.3 and 1 : 11.3, respectively, which differ from their corresponding precursor ratios. Based on these observations, we believe that the predominant constituents in all Ni-Mo-S/C samples should be Ni incorporated MoS_x.

Figure 6-8 EDS spectra of different samples. EDS spectra of (A) carbon fiber cloth, (B) NiS_x/C, (C) Ni-Mo-S/C (3:1), (D) Ni-Mo-S/C (1:1), (E) Ni-Mo-S/C (1:3), and (F) MoS₂/C.

Point EDS was performed to further confirm the composition of aggregates in Ni-Mo-S/C (3:1). As shown in Figure 6-9, it is observed that the ratio of Ni:Mo on the aggregate is ~ 1.61:1, significantly higher than the non-aggregated area (~ 0.47:1). It suggests that the aggregates in Ni-Mo-S/C (3:1) are Ni-rich, most probably due to the presence of NiS_x nanoparticles that were adsorbed onto the electrode surface.

Figure 6-9 Point-EDS spectra of Ni-Mo-S/C (3:1). Point-EDS spectra of Ni-Mo-S/C (3:1). (A) SEM image of Ni-Mo-S/C (3:1) and point-EDS analyses performed on (B) aggregated (labeled as 001) and (C) non-aggregated (labeled as 002) areas.

Figure 6-10 Transmission electron microscopy images. Low magnification TEM images of (A) MoS₂/C and (B) Ni-Mo-S/C (1:1); and HRTEM images of (C) MoS₂/C and (D) Ni-Mo-S/C (1:1). Insets: the corresponding cross-sectional HRTEM images. Dashed circles in (d) indicate the structure defects of Ni-Mo-S/C (1:1).

To better elucidate the morphological distinction between Ni-Mo-S/C (1:1) and MoS₂/C, transmission electron microscopy (TEM) images were carried out. Figure 6-10 A and B show TEM images of MoS₂/C and Ni-Mo-S/C (1:1). MoS₂ has continuous and corrugated layered-structures, where restacked and wrinkled parts can be clearly observed. In contrast, the introduction of Ni²⁺ during the synthesis leads to the formation of interconnected Ni-Mo-S flake-like structures. In the high-resolution TEM (HRTEM) images (Figure 6-10 C and D), lattices with a spacing of 0.27 nm, which can be assigned to the (100) plane of 2H-MoS₂, are identified in both

samples. However, as compared to MoS_2/C , the crystalline quality of Ni-Mo-S/C was significantly reduced. Numerous structure defects, as indicated by dashed circles in Fig. 4D, can be observed in the surface of nanoflakes (see Figure 6-11). The insets in Figure 6-10 C and D show the cross-sectional views of stacked MoS_2/C and Ni-Mo-S/C (1:1), respectively. It is found that the (002) plane spacing of Ni-Mo-S/C (1:1), which correlates to the interlayer distance, is significantly enlarged to 0.92 nm from 0.63 nm observed in MoS_2/C .

Figure 6-11 HRTEM images of Ni-Mo-S/C (1:1). HRTEM image of Ni-Mo-S/C (1:1), showing random defects in the entire basal plane of Ni-Mo-S .

In order to assess the distribution of Ni across the basal plane of Ni-Mo-S/C (1:1), EDS mappings have been performed on the sample. As shown in Figure 6-12, both Mo and S are uniformly distributed across the entire detected region. Meanwhile, the distribution of incorporated Ni atoms on the structure is mostly homogeneous, but its concentration is slightly higher near the defect-rich regions.

Figure 6-12 Elemental mapping of Ni-Mo-S/C (1:1). The TEM image and its corresponding elemental mapping of Ni-Mo-S/C (1:1).

Porosity is also an important property for electrocatalysts, since porous structures could provide channels that allow the fast access to electrolytes and efficient transport of reactants and products. The nitrogen adsorption/desorption analysis was conducted to analyze the porosity of the as-synthesized Ni-Mo-S/C (1:1) as shown in Figure 6-13. The curve appears to be a type III isotherm hysteresis according to IUPAC classification,(284) and the hysteresis loop affirms the presence of mesopores in nanostructured Ni-Mo-S/C (1:1). As indicated by the inset of Figure 6-13, the size of most pores formed on Ni-Mo-S/C (1:1) falls in the range between 2 nm and 10nm. This conclusion is consistent with our previous observation made using TEM, from which pores due to the defect formation can be clearly observed on the basal plane of Ni-Mo-S/C (1:1). Apart from the mesopores, adjacent nanosheets in the structure can lead to the formation of numerous macropores ranging from 50 to 100 nm. However, these macropores could not be detected using the BET method precisely. The porous

nature of Ni-Mo-S/C (1:1) could significantly benefit the electrocatalytic hydrogen evolution process.

Figure 6-13 BET measurements of Ni-Mo-S/C (1:1). The nitrogen adsorption-desorption isotherm of Ni-Mo-S/C (1:1) and the inset shows its corresponding pore size distribution.

To understand the crystal structure of Ni-Mo-S/C samples, X-ray diffraction (XRD) patterns were studied in detail. As the XRD pattern of Ni-Mo-S/C (1:1) shows a predominant diffraction peak at 26° that can be indexed to the (002) plane of carbon (inset of Figure 6-14), the XRD pattern of Ni-Mo-S (1:1) was precisely extracted using Bruker EVA software by subtraction of the signal from carbon fiber cloth (Figure 6-14). The broadened diffraction peaks imply the nanoscale dimensions of Ni-Mo-S flakes on carbon fiber cloth. Compared to the reference XRD pattern (JCPDS card No. 73-1508), the (002) peak of pristine 2H-MoS_2 at 14.39° is absent in the Ni-Mo-S/C (1:1) sample. Instead, two new diffraction peaks at 9.22° and 17.64°

can be observed, which are most probably corresponding to the first and second order reflections from (002) plane of layered Ni-Mo-S, respectively.

Figure 6-14 X-ray diffraction analysis. XRD pattern of Ni-Mo-S/C (1:1) after subtraction of carbon fiber cloth signal. Inset: the original XRD pattern of Ni-Mo-S/C (1:1).

Our observation is similar to the MoS₂ nanosheets with enlarged interlayer spacing that was recently reported by Xie et al.(277) In this case, the spacing between two adjacent Ni-Mo-S layer can be calculated using Bragg's Law:(285)

$$n\lambda = 2d\sin\theta \quad (16)$$

where n is the order of reflection, λ is the wavelength of incident X-ray (Cu K α , 0.154 nm), d is the interlayer spacing, and θ is the angle between the incident X-ray

and the scattering planes. The calculated spacing between Ni-Mo-S layers is around 0.94-0.95 nm, consistent with our observations in HRTEM images. Moreover, two diffraction peaks centered at 32° and 57° can be well indexed to (100) and (110) planes of 2H-MoS₂, showing that the atomic arrangement of Ni-Mo-S (1:1) should be similar to that of pristine MoS₂. In addition, the asymmetric features of these two peaks reflect the turbostratic stacking characteristic of Ni-Mo-S flakes, which is commonly observed in other layered compounds.(286) The absence of other high-angle diffraction peaks suggests the structure-disordering feature of Ni-Mo-S, due to the presence of abundant defect sites across its basal planes. It is worth mentioning that diffraction peaks that correlate to nickel sulfide and its non-stoichiometric forms were absent in the XRD pattern of Ni-Mo-S/C (1:1).

Figure 6-15 shows the Raman spectra of Ni-Mo-S/C (1:1) and MoS₂/C. Two distinct peaks at $\sim 380\text{ cm}^{-1}$ and $\sim 405\text{ cm}^{-1}$, corresponding to the in-plane E_{2g}^1 and out-of-plane A_{1g} vibrational modes of 2H-MoS₂, can be clearly identified in the spectra of both MoS₂/C and Ni-Mo-S/C (1:1).(274, 287, 288) The slightly red shift and broadening of A_{1g} peak in Ni-Mo-S/C (1:1) can be attributed to reduced numbers of stacked layers along the *c*-axis.(287) Besides, the increased width along with reduced intensity of the E_{2g}^1 peak in Ni-Mo-S/C (1:1) reveals the presence of in-plane defect sites,(289) which is consistent with our aforementioned experimental observations.

Figure 6-15 Raman spectroscopy. Raman spectra of Ni-Mo-S/C (1:1) and MoS₂/C. Inset: the schematic illustration of E_{2g}^1 and A_{1g} vibrational modes in layered 2H-MoS₂.

To further confirm the chemical composition and elemental chemical states of Ni-Mo-S/C (1:1), X-ray photoelectron spectroscopy (XPS) measurements were carried out. As shown in Figure 6-16 A, the survey spectrum recorded from 0 to 1200 eV reveals the presence of Mo, Ni, S, C and O elements. From the high-resolution XPS spectrum of Mo 3d scan (Figure 6-16 B), two major peaks at 228.9 and 232 eV are observed and can be assigned to the Mo^{IV} 3d_{5/2} and Mo^{IV} 3d_{3/2} in MoS₂, affirming the dominance of Mo^(IV) in Ni-Mo-S/C.⁽²⁷⁴⁾ Besides the Mo^{IV} 3d_{5/2} signal, there exists a small peak at 266.2 eV resulted from the S 2s orbital. Another doublet at relatively higher binding energy (Mo 3d_{5/2} = 233.1 eV, Mo 3d_{3/2} = 235.9 eV) can be assigned to the Mo ions in the +6 oxidation state, which may be due to the

inadequate reduction of MoO_4^{2-} species during the hydrothermal synthesis. The high-resolution S 2p spectrum clearly shows a doublet with the S 2p_{3/2} falling on 161.9 eV (Figure 6-16 C), revealing the -2 oxidation state of sulfur in MoS_2 , which is consistent with previous reports.(274, 277) The appearance of a shoulder at higher binding energies in the S 2p region can serve as another evidence for the presence of Mo with higher oxidation states. As shown in Figure 6-16 D, the intensity of Ni spectrum is much lower than other elements, due to its lower content in Ni-Mo-S/C. The calculated Ni-to-Mo ratio is about 1:8.56, which matches well with the estimated value from EDS measurements. The Ni spectrum shows a major peak and a satellite peak at 854.3 and 861 eV, respectively, attributed to Ni 2p_{3/2} orbital, which are close to the previously reported values of sulfide Ni-Mo alloys.(290)

Figure 6-16 X-ray photoelectron spectroscopy. (A) Survey XPS spectrum of Ni-Mo-S/C (1:1). High resolution scans of (B) Mo 3d, (C) S 2p and (D) Ni 2p.

6.3.3 Electrochemical tests

To investigate the role of incorporated Ni on the catalytic activity of Ni-Mo-S, electrochemical measurements were designed and carried out. It is important to mention that all as-fabricated materials were directly used as working electrodes for HER without annealing or calcination. Neutral phosphate buffer solution, which could minimize the adverse environmental impacts in practical applications,(291) was chosen as the primary electrolyte in this work.

Figure 6-17 Electrochemical performances. (A) Polarization curves of carbon fiber cloth, NiS_x/C, MoS₂/C and different Ni-Mo-S/C in neutral electrolyte, and (B) the corresponding Tafel plots obtained using slow-scan rate polarization curves.

All electrochemical tests were carried out using the same set-up, with consistent cell configuration, electrode positions and electrolyte volume. The HER activities of different electrodes were investigated by comparing the polarization curves obtained with linear sweep voltammetry (LSV). In each measurement, the voltage applied on working electrode was linearly swept from 0.2 to -0.5 V vs. RHE at a scan rate of 5 mV/s. As shown in Figure 6-17 A, all Ni-Mo-S/C electrodes have typical onset overpotentials of 130 to 150 mV, which are apparently smaller than that of MoS₂/C (~200 mV), while the bare carbon fiber cloth electrode shows negligible HER catalytic activity. Among all studied samples, Ni-Mo-S/C (1:1) shows the best HER

catalytic activity with a considerably smaller η_{10} (overpotential at 10 mA/cm²) of 200 mV. At an applied potential of -0.35V vs. RHE, Ni-Mo-S/C (1:1) can produce a cathodic current density as large as 36.5 mA/cm², which is two times of that produced by MoS₂/C. During the test, tremendous amount of H₂ bubbles was observed on the surface of Ni-Mo-S/C (1:1).

To better understand the different catalytic behaviors of these electrodes, their corresponding Tafel plots were obtained from the slow-scan rate (1 mV/s) polarization curves. As shown in Figure 6-17 B, various Tafel slopes, ranging from 85.3 to 107.2 mV/dec, were found on different electrodes. These values are apparently larger than those reported recently for MoS₂-based electrocatalysts in acidic electrolytes (39-65 mV/dec), (154, 156, 277, 292) but are comparable with those values reported using neutral electrolytes.(291, 293, 294) The increase in Tafel slopes is due to the much lower proton concentration ($\sim 1 \times 10^{-7}$ M, standard conditions) in neutral electrolytes than in acidic solutions, in which electrochemical hydrogen adsorption (Volmer reaction) and electrochemical desorption (Heyrovsky reaction) processes proceed at comparable rates.(293) Although it is not possible to precisely determine the rate-determining step and exact reaction mechanism in this case, Tafel slopes of different electrodes are still important indicators for comparative analyses. Among all tested electrodes, Ni-Mo-S/C (1:1) exhibits the smallest Tafel slope (~ 85.3 mV/dec), which well correlates with its remarkable HER catalytic behavior originating from the abundant exposed edge sites and excellent material uniformity. In addition, the defect sites found in the basal plane of Ni-Mo-S/C (1:1) could also provide substantial extra active sites that can further enhance its HER performance. The slightly steeper Tafel slopes observed on MoS₂/C (94.4 mV/dec) and Ni-Mo-S/C (1:3) (88.4 mV/dec) may be possibly due to the formation

of bulky aggregates, which in turn hinders the interactions between protons and effective active sites to certain extent. Compared to MoS₂/C and other Ni-Mo-S/C samples, most probably resulting from their relatively poorer intrinsic catalytic activities, Ni-Mo-S/C (3:1) and NiS_x/C showed much higher Tafel slopes, which are ~103.7 mV/dec and ~107.2 mV/dec, respectively. Table 6-3 lists the exchange current densities (j_0) of different samples calculated using the Tafel equation. Ni-Mo-S/C (1:1) showed the largest j_0 among the tested electrode, which is 4.89×10^{-2} mA/cm². The j_0 values for other samples follow the order of Ni-Mo-S/C (3:1) > NiS_x > Ni-Mo-S/C (1:3) > MoS₂.

Table 6-3 Exchange current densities of MoS₂/C, NiS_x/C and Ni-Mo-S/C in neutral electrolyte

Sample	Exchange Current Density (10^{-2} mA/cm ²)
MoS ₂	2.13
Ni-Mo-S/C (Ni:Mo = 1:3)	3.43
Ni-Mo-S/C (Ni:Mo = 1:1)	4.89
Ni-Mo-S/C (Ni:Mo = 3:1)	3.94
NiS _x	3.54

For comparison purposes, electrochemical tests were also carried out in acidic electrolyte, as illustrated in Figure 6-18A, which exhibit a similar general trend to that observed in neutral electrolyte, in which Ni-Mo-S/C (1:1) still shows the best catalytic performance characterized by a low onset overpotential (~-0.14 V) and a reasonably small Tafel slope (~48 mV/dec). The Tafel slope values obtained in acidic electrolyte are closer to those reported previously,(84, 273, 295, 296) indicating that electrochemical desorption (Heryrovsky reaction) is the rate-determining step for HER catalyzed by Ni-Mo-S/C (1:1) through the Volemr-Herovsky mechanism.

Figure 6-18 Electrochemical tests in 0.5 M H₂SO₄. (A) Polarization curves of different samples and (B) the corresponding Tafel plots obtained in 0.5 M H₂SO₄.

6.3.4 Electrochemical impedance spectra

Figure 6-19 (A) Electrochemical impedance spectra of different electrodes at -0.3 V vs. RHE. Inset: the equivalent circuit used for data analyses. (B) Plot of charge transport resistance of different samples.

Moreover, electrochemical impedance spectroscopy (EIS) analyses were performed to study the electrode kinetics of these samples under the HER mode.^(293, 297) All measurements were performed at -0.3 V vs. RHE from 100 K to 0.1 Hz with alternating current (AC) amplitude of 15 mV in neutral buffer (Figure 6-19 A). A Randle circuit (Figure 6-19 A), which is commonly used in analyzing charge

transport on single electrodes, was used to fit our experimental results.(298) All electrodes show small and similar series resistance (R_s), from 1.9 to 2.2 Ω , mainly originated from uncompensated solution resistance, suggesting a consistency of our experimental set-up. The slightly variation of R_s in different electrodes can be partially attributed to the differences in electrode resistance. The kinetics of electrocatalysis on different electrodes can be reflected from their charge transfer resistance (R_{ct}), and a lower R_{ct} value corresponds to a faster reaction rate.(293) The R_{ct} values of MoS_2/C , NiS_x/C and all Ni-Mo-S/C electrodes are summarized in Figure 6-19 B, which show a similar tendency as we observed previously in HER tests (Figure 6-17A), with Ni-Mo-S/C (1:1) exhibiting the lowest R_{ct} of 39.48 Ω .

6.3.5 Intuitive comparison test

Figure 6-20 Precise onset comparison between MoS_2/C and Ni-Mo-S/C (1:1).

The onset potentials of different samples were measured using tangent method. As shown in Figure 6-20, the determined onset potential of Ni-Mo-S/C (1:1) and

MoS₂/C are -0.132 and -0.193 V vs. RHE, respectively, in neutral electrolyte. Compared to MoS₂/C, the absolute onset potential value of Ni-Mo-S/C (1:1) is 61 mV smaller, arising from its significantly improved HER catalytic activity. However, it is not always fair to judge the catalytic behavior on different electrodes solely based on their differences in onset potential and Tafel slope, especially for the practical gas-evolving reaction.

Figure 6-21 Electrode for intuitive comparison test. The electrode design for intuitive comparison of the gas-evolving profiles between MoS₂/C and Ni-Mo-S/C (1:1).

Therefore, we developed a simple strategy that allows us to intuitively compare the onset potentials and gas-evolving profiles of different electrodes at the same time. As shown in Figure 6-21, a special electrode was designed to visualize the HER processes taking place on different samples simultaneously. Single bundles of MoS₂/C and Ni-Mo-S/C (1:1) with same length (2 cm) and similar appearance were

firstly extracted from their corresponding carbon fiber cloth electrodes, and then firmly attached to the same home-made titanium (Ti) connector. Within the Ti connector, the distance between the ends of two samples was fixed at 3 mm for ease of comparison, while the angle between the two bundles was set at 30° for better observation of the gas-evolving events along their entire length.

Figure 6-22 Intuitive comparison test for HER. The first hydrogen bubbles observed on (A) Ni-Mo-S/C (1:1) at -0.13 V vs. RHE and (B) MoS₂/C at -0.2 V vs. RHE. (C) Hydrogen bubbling from both samples at higher applied bias.

The HER study was then carried out using the parallel linked single-bundle electrodes as the working electrode, in which the synchronized potential bias can be applied to MoS₂/C and Ni-Mo-S/C (1:1) simultaneously. In a typical comparative test, the working electrode was linearly swept in a potential window of 0 to -0.8 V vs. RHE at a scan rate of 10 mV/s using LSV technique, and the whole process was recorded using a digital camera. The first observable gas bubbles were found on Ni-Mo-S/C (1:1) and MoS₂/C at -0.13 and -0.2 V vs. RHE, respectively (Figure 6-22 A and B), matching well with the results obtained from electrochemical tests. During the test, H₂ bubbles on Ni-Mo-S/C (1:1) were generated faster and more continuously along the entire bundle. At larger applied biases (-0.8 to -0.4 V vs. RHE), it was found that the color of MoS₂/C bundle turned pale white due to the adhesion of numerous freshly evolved gas bubbles (Figure 6-22 C). While the appearance of Ni-Mo-S/C bundle (1:1) remained consistent throughout the test with a much more fluent gas-evolving profile. The macroscopic differences between the two electrodes observed by naked eyes are originated from their microscopic distinctions. The aggregates formed in MoS₂/C, as discussed above, may evidently decrease the exposed active sites, leading to the attenuated catalytic activity. Meanwhile, these bulky structures will also hinder the effective proton adsorption and H₂ desorption processes, due to the presence of trapped bubbles within them. Therefore, the microscopic gas bubbles have to gain their volume before they can be successfully released from these trap sites. Furthermore, these accumulated bubbles on the surface of MoS₂/C will make the electrode less aerophobic and more hydrophobic in appearance, as observed during the test. In brief, significant deduction in overall efficiency is expected when all these unfavorable factors are combined. In contrast, the significantly improved catalytic performance of Ni-Mo-S/C (1:1) results from the

exposure of abundant uniform edge structures along with additional active sites arising from the defect sites in the basal plane, while the more fluent gas-evolving profile observed on it may benefit from its sharper and thinner edges, which will ease the gas releasing (desorption) process.(276)

6.3.6 Electrochemically active surface area (EASA) measurements

Figure 6-23 Electrochemically active surface area (EASA) measurements for MoS₂/C and Ni-Mo-S/C (1:1). (A) and (B) are the cyclic voltammograms taken in a potential range where no faradic processes were observed to measure the capacitive current from double layer charging-discharging process for MoS₂/C and Ni-Mo-S/C (1:1), respectively. (C) The capacitive currents of the two electrodes measured at 0.03 V vs. SCE were plotted as a function of scan rate. (D) The polarization curves of MoS₂/C and Ni-Mo-S/C (1:1) normalized by the total EASA of the two electrodes, inset shows the comparison of onset overpotential.

To affirm that the catalytic enhancement is mainly originated from the more exposed edge sites and defects formed along the basal plane, it's necessary to normalize the electrode HER activities of MoS₂/C and Ni-Mo-S/C (1:1) to their total

electrochemically active surface area (EASA). In order to obtain the total EASA, cyclic voltammetry with different scan rates were performed to calculate the electrochemical double layer capacitance according to the method discussed by Trasatti and Petrii in 1991.(299) More recently, this method was also applied by Benck et al. to calculate the EASA of MoS₂-based HER catalysts.(300) In our case, the capacitive currents for MoS₂/C and Ni-Mo-S/C (1:1) were measured in 0.5 M sodium phosphate buffer solution with different scan rates (1~10, 15, 20, 25 mV/s) in a potential range of -0.02 ~ 0.08 V vs. SCE, since there are no obvious electrochemical features corresponding to faradaic current within this range. The non-faradic capacitive current, which is proportional to both the scan rate and EASA, can be calculated from these two sets of CV curves as shown in Figure 6-23 A and B. The capacitive currents of the two electrodes measured at 0.03 V vs. SCE were plotted as a function of scan rate as shown in Figure 6-23 C. It was noticed that the dependence of the current on the scan rate in this region is linear for both materials, which is consistent with capacitive charging behavior. From the slopes of the linear curves, the unit electrode capacitances were calculated to be 82.78 mF/cm² and 27.74 mF/cm² for MoS₂/C and Ni-Mo-S/C (1:1), respectively. In most previous reported studies,(300) the calculated capacitance of single-layer/flat MoS₂ is ~60 μF/cm². By adapting this number, the total EASA of MoS₂/C and Ni-Mo-S/C (1:1) are 1379.67 cm² and 462.33 cm², respectively on the electrodes with geometric area of ~1 cm². This result suggests that the total electrochemically surface area of MoS₂/C is three times that of Ni-Mo-S/C (1:1). Figure 6-23 D shows the polarization curves of MoS₂/C and Ni-Mo-S/C (1:1) normalized by their corresponding total EASA, from which the performance of Ni-Mo-S/C (1:1) is overwhelmingly better than its

counterpart. These results suggest that there would be much more active sites on Ni-Mo-S/C (1:1) compared to MoS₂/C on the electrodes with the same EASA.

6.3.7 Electrochemical irreversible oxidation

Besides the EASA measurements, the edge-rich feature of Ni-Mo-S/C (1:1) was also confirmed using the irreversible electrochemical oxidation method proposed by Bonde et al. (301)

Figure 6-24 Irreversible electrochemical oxidation cyclic voltammetry curves. Irreversible electrochemical oxidation of MoS₂/C and Ni-Mo-S/C (1:1) in 0.5 M H₂SO₄ at a scan rate of 50 mV/s.

Irreversible electrochemical oxidations were also performed on both samples (with same geometric surface area) using 0.5 M H₂SO₄ as the electrolyte at a scan rate of 50 mV/s to assess their structural differences. Figure 6-24 shows the cyclic voltammetry (CV) curves of MoS₂/C and Ni-Mo-S/C (1:1). For comparison study, we assume that the major component in Ni-Mo-S (1:1) is MoS_x, confirmed by XRD and XPS. Two peaks centered at ~0.72 and 1.14 V (vs. RHE) in the CV curve of

MoS₂/C can be ascribed to the oxidation of edges and basal planes of MoS₂, respectively. In contrast, only one apparent oxidation peak centered at ~0.72 V vs. RHE can be observed in the CV of Ni-Mo-S/C (1:1), possibly due to its edge-rich (including both sheet edges and defect edges) features, as edges of MoS₂ nanostructures are expected to be more readily oxidized than does the basal plane.⁽³⁰¹⁾ Based on these results, the edge-rich characteristic of Ni-Mo-S (1:1) is again confirmed.

6.3.8 Stability tests

Stability is another critical factor for designing gas-evolving electrodes that are eligible for long-term operation. In our work, the durability of Ni-Mo-S/C (1:1) and MoS₂/C electrodes (1 cm × 1 cm) were assessed using potential controlled electrolysis in neutral electrolyte. The two electrodes were operated at their corresponding η_{20} (overpotential at current density of 20 mA/cm²) for 30,000 s. Continuous gas bubbling was observed on both Ni-Mo-S/C (1:1) and MoS₂/C throughout the test.

Figure 6-25 (A) Stability tests of Ni-Mo-S/C (1:1) and MoS₂/C in neutral electrolyte. (B) The LSV curves of Ni-Mo-S/C (1:1) before and after stability tests.

As shown in Figure 6-25 A, Ni-Mo-S/C (1:1) can well retain about 97.5% of its initial current density after the test, which is apparently better than the 85% current density retention of MoS₂/C. For comparison, we also performed the stability of commercial Pt plate electrode (1 cm × 1 cm) in neutral electrolyte. It was found that only 15% of the initial current density was retained after 1-hour potential controlled electrolysis. The excellent stability of Ni-Mo-S/C (1:1) was further affirmed using LSV technique after potential controlled electrolysis. As shown in Figure 6-25 B, the polarization curve obtained after stability test was almost identical with the initial scan, without obvious shift in onset potential and curve shapes. In addition, as shown in Figure 6-26, no obvious changes in the oxidation states of Mo, S and Ni were detected in the XPS measurements after the stability test, affirming the excellent stability of Ni-Mo-S/C (1:1).

Figure 6-26 High-resolution XPS spectra of Ni-Mo-S/C (1:1) after stability test. High-resolution XPS spectra of Mo 3d, S 2p and Ni 2p before (gray) and after (colored) stability test.

6.3.9 Faraday efficiency

The Faraday efficiency of Ni-Mo-S/C (1:1) was measured using a multi-purpose compact glass photo-/electro-catalysis reactor, integrated with a single-chamber bulk electrolysis cell. Potential controlled electrolysis was performed on Ni-Mo-S/C (1:1) in neutral electrolyte, with a moderate applied bias of -0.2 V vs. RHE for 4000 s. Figure 6-27 shows that the actual detected H_2 amount was well correlated with the theoretical value calculated based on the charge transferred, resulting in a high Faraday efficiency of 98.2%. From the GC spectra, H_2 and O_2 (evolved on graphite foil) were the only two detected gaseous products throughout the test, which affirms the capability of Ni-Mo-S/C (1:1) as a HER electrode in producing high-purity H_2 gas.

Figure 6-27 Comparison the detected amount of evolved H_2 and the theoretical value in Faraday efficiency measurement.

6.3.10 Lab-scale hydrogen generator

Lab-Scale Ni-Mo-S/C Hydrogen Generator

Figure 6-28 Lab-scale Ni-Mo-S/C hydrogen generator. Illustration of the design of a lab-scale Ni-Mo-S/C hydrogen generator.

Figure 6-29 Assembly of lab-scale Ni-Mo-S/C hydrogen generator. Photos of (A) Ni-Mo-S/C electrode, (B) homemade Ti holder, (C) 5 ml round bottom tube used as hydrogen collector, and (D) the set-up for practical operation.

To further demonstrate the potential of Ni-Mo-S/C in practical applications, a simple prototype of lab-scale hydrogen generator was designed. Figure 6-28 and Figure 6-29 showed the schematic and actual assembly of the lab-scale Ni-Mo-S/C hydrogen generator, respectively. To prepare this reactor, a piece of Ni-Mo-S/C (1:1) (2 cm × 4 cm) was first rolled up into a column shape, and then firmly fixed on a homemade Ti holder, which also worked as the lead and electrode connector (Figure 6-29 B). A 5 ml sterile round bottom tube was used as the electrode housing and the primary gas collector (Figure 6-29 C). The Ti holder together with the clamped Ni-Mo-S/C was loaded into the tube and fixed using Scotch tape. In order to integrate the reactor with the gas-evacuation system or secondary gas collector, a round hole with diameter of 1 mm was drilled on its top. In this work, a 5 ml syringe, functioned as a simplified gas-evacuation system, was tightly sealed onto the reactor (Figure 6-29 D). For the practical operation, the H₂ generator should be vertically inserted into the electrolyte. The air remaining in the tube was then evacuated using the syringe, while the electrolyte was sucked upwards to fill the entire tube. When the system is operated at a moderate bias of -0.5 V vs. RHE, the 5 ml tube can be filled with H₂ in ~150 s.

6.3.11 Formation mechanisms of high-performance Ni-Mo-S on carbon cloth

On the basis of experimental findings, we propose a hypothetical growth mechanism to explicate the development of high-performance Ni-Mo-S HER electrocatalyst. Without the incorporation of Ni²⁺, the growth of layered MoS₂ crystals proceeds in a fast and uncontrollable fashion. The rapidly grown MoS₂ sheets tend to aggregate in solution, thus leading to the formation of bulky coalescences. We noticed that the morphological evolution of Ni-Mo-S/C strongly depended on the Ni-to-Mo precursor ratio. It is believed that the introduced Ni²⁺

could bond to the free sulfur during the growth or nucleation of MoS₂ nanocrystals, subsequently leading to the formation of substitutional and Schottky defects that instantly interrupt the regular atomic arrangement in MoS₂.

Figure 6-30 EXAFS spectra of Ni-Mo-S/C (1:1). R-space EXAFS spectra of Mo K-edge and Ni K-edge for Ni-Mo-S sample and the corresponding structural parameters extracted from EXAFS spectra fitting procedures.

The formation of Ni-S bonds was confirmed by X-ray absorption measurement (**Error! Reference source not found.**), in which the Ni-S path (~ 2.23 Å) has a smaller atomic radius than that of Mo-S path (~ 2.39 Å). Note that this difference can be attributed to the ionic radial discrepancy between Mo⁴⁺ (70 pm) and Ni²⁺ (83 pm), which is consistent with the observation from XPS. As a classic hydrodesulphurization (HDS) catalyst model, the Co-Mo-S has been thoroughly studied over the past few decades.(269, 302-304) Based on the density function theory (DFT), Byskov et al. found that the substitutional Co atoms in Co-Mo-S resulted in significantly lower sulfur binding energy as well as shorter bond length near the

vacancies.(305) In our case, Ni atoms shall play similar roles in tuning the Ni-Mo-S framework, i.e. the change in bond length and binding energy near the incorporated Ni atoms may lead to an extensive distortion across the basal plane, thus hindering the rapid growth of continuous MoS₂ film, while creating extra edges with more exposed active sites.

Figure 6-31 Formation mechanism of Ni-Mo-S nanostructure. Schematic illustration of a MoS₂ nanosheet surrounded by random Ni²⁺ ions that are executing Brownian motion. Ni will be incorporated into the MoS₂ framework upon the successful collision.

Figure 6-31 shows the schematic illustration of a MoS₂ nanocrystal surrounded by Ni²⁺ executing Brownian motion, where Ni could be incorporated into the existing MoS₂ framework upon its successful collision to the free sulfur ends. The distribution of Ni²⁺ around the MoS₂ nanocrystals is critical in determining the eventually evolved morphology of Ni-Mo-S structure on carbon fibers, since the frequency of successful bond formation largely depends upon their concentrations, according to the collision theory in chemical kinetics.(306) When MoS₂ nanocrystals are surrounded by excessive Ni²⁺ ions, vigorous collisions may take place, thus accelerating the formation of substitutional and vacancy defects, which in turn constrain the

continuous growth of the layered structure of Ni-Mo-S. On the contrary, the inadequate Ni^{2+} will only introduce random allocated defect sites with lower density, which cannot significantly alter the growth of the layered structures observed in MoS_2 . These assumptions well explain the morphological evolution that we observed in different Ni-Mo-S/C samples. Optimum Ni-to-Mo precursor ratio will lead to the formation of moderate defect sites along the basal plane, which simultaneously introduce additional active sites and constrain the growth rate of Ni-Mo-S layers.

Figure 6-32 Molecular models. Top views of molecular models of (A) pristine MoS_2 and (B) defect-rich Ni-Mo-S after geometric optimization. Side views of two adjacent layers of (C) pristine MoS_2 and (D) defect-rich Ni-Mo-S.

Based on these assumptions, we constructed the models of MoS_2 and Ni-Mo-S, and performed molecular mechanical simulation (MM + force field) using HyperChem.(266) Figure 6-32 A and B show the molecular models after geometric optimization for MoS_2 and Ni-Mo-S, respectively. Compared to the pristine MoS_2 ,

the random defects formed in Ni-Mo-S can cause a significant geometric distortion on the basal plane, due to the change in bond length and the presence of vacancies. The increase in molecular complexity along with the distortions across the entire basal plane may further weaken the interaction between the adjacent Ni-Mo-S layers, thus leading to an enlargement of the interlayer spacing (Figure 6-32 D), which is consistent with the observation in Fig. 4D. Based on these findings, we know that optimizing the Ni-to-Mo precursor ratio is important in tailoring the nanostructure of Ni-Mo-S at atomic scale. Apart from the structural effects, the incorporated Ni atoms may also function as promoters that further enhance the intrinsic catalytic activities, especially in neutral electrolyte, similar to that proposed by Daniel et al.(293) Besides, Lin et al. reported the atomic mechanism of the semiconducting (2H)-to-metallic (1T) phase transition in single-layered MoS₂.(266) In our case, the bond-length shortening introduced by the Ni atom may also initiate the gliding of sulfur plane near the defect sites, further resulting in the localized phase transition that partially converts 2H MoS₂ to meta-stable 1T MoS₂. As discussed previously by Lukowski et al., the metallic 1T MoS₂ may exhibit enhanced electrocatalytic activity along with the improved stability.(307) In addition, the incorporation of Ni atoms may alter the binding energy of pristine MoS₂, further improving the reaction kinetics.

6.4 Summary

In conclusion, we have developed a facile synthetic strategy to directly grow nanostructured Ni-Mo-S on carbon fiber cloth as a high-efficiency functional electrode for hydrogen generation in neutral electrolyte. The incorporated Ni atoms play vital roles in constructing Ni-Mo-S nanostructures, through forming substantial desirable defect sites as well as regulating the growth rate of layered MoS₂. The

optimized Ni-Mo-S/C exhibits excellent HER catalytic performance, characterized by its low onset potential of -0.132 V vs. RHE and a small Tafel slope of 85.3 mV/dec in the neutral electrolyte. The reduced stacking and aggregations in Ni-Mo-S/C effectively prevent the accumulation of instantly evolved H₂ bubbles during electrolysis, hence improving the performance and stability of Ni-Mo-S/C in long-term hydrogen production. The remarkable HER performance in acidic and neutral medium of Ni-Mo-S/C is comparable with other state-of-the-art HER electrocatalysts (see Table 6-4 and Table 6-5). To further demonstrate its potential application in practical appliances, a lab-scale hydrogen generator with rolled Ni-Mo-S/C electrode was designed to carry out the potential controlled electrolysis. Owing to the ultimate flexibility and excellent mechanical strength offered by the carbon fiber cloth, the functional Ni-Mo-S/C electrode developed in this work should be easily integrated into existing H₂ generators with appropriate modification to meet their specified standards and requirements. We believe that better electrode performance could be achieved through engineering the carbon fiber cloth, such as widening the inter-strand spacing and reducing the packing density of the carbon fiber.

Catalyst	Electrode	Electrolyte	Onset overpotential (vs. RHE)	η_{10} (vs. RHE)	Tafel slope (mV/dec)	IR correction	Catalyst loading (mg/cm ²)	Reference No.
Ni-Mo-S	Carbon fiber cloth	0.5 M Sodium phosphate buffer solution (pH 6.9)	-0.132 V	-0.2 V	85.3	Yes	0.52	This work
Co-S film	FTO	1 M Potassium phosphate buffer solution (pH 7)	-0.043 V	-0.17 V	93	Yes	-	(291)
Cu ₂ MoS ₄	FTO	0.1 M Phosphate buffer solution (pH 7)	-0.135 V	-0.337 V	95	Not mentioned	0.0416	(294)
Ni nanowires	-	1 M Na ₂ SO ₄ (pH 7)	-0.59 V	-	-	Not mentioned	-	(308)
WC (grain size = 16.5 nm)	Graphite disk	0.1 M Sodium phosphate buffer solution (pH 7)	-	< -0.3 V	-	Not mentioned	-	(309)
H ₂ -NiCat	FTO	0.1 M NaBi Electrolyte containing 1 M Ni ²⁺ (pH 9.2)	-0.25 V	-	226	Not mentioned	-	(78)
H ₂ -CoCat	FTO	0.5 M Potassium phosphate buffer solution (pH 7)	-0.29 V	-	140	Not mentioned	-	(310)
MoP nanosheets	Biomass-derived carbon flake	1 M Phosphate buffer solution (pH 7)	-0.15 V	-	77.8	Not mentioned	0.36	(311)
FeP Nanoparticles	Ti Foil	1 M Phosphate buffered saline (pH 6.5)	-	-0.102 V	-	Yes	1.0	(312)
Ni-S	FTO	Phosphate buffer solution (pH 7, concentration not mentioned)	-0.237 V	-0.337 V	77	Yes	0.0815 (for Ni only)	(313)
Co-B nanoparticles	-	0.5 M Potassium phosphate buffer solution (pH 7)	-0.07 V	-0.251 V	75	Yes	-	(314)

Table 6-4 Comparison of electrocatalysts for hydrogen evolution reaction in neutral or near neutral electrolytes

Catalyst	Electrode	Electrolyte	Onset overpotential (vs. RHE)	η_{10} (vs. RHE)	Tafel slope (mV/dec)	IR correction	Catalyst loading (mg/cm ²)	Reference No.
Ni-Mo-S	Carbon fiber cloth	0.5 M H ₂ SO ₄	-0.14	-0.154	48	Yes	0.52	This work
MoS ₂ /RGO	Carbon fiber paper	0.5 M H ₂ SO ₄	-0.14	-0.16	-	Yes	1.0	(84)
Double-gyroid MoS ₂ film	FTO	0.5 M H ₂ SO ₄	From -0.15 to -0.2	~-0.23	50	Yes	-	(315)
Vertically-aligned MoS ₂ nanofilms (1.1 V)	Mirror polished glassy carbon (MPGC)	0.5 M H ₂ SO ₄	~-0.15	~-0.22	44	Yes	0.022	(275)
“Superaerophobic” nanostructured MoS ₂ film	Ti foil	0.5 M H ₂ SO ₄	-0.15	~-0.22	51	Yes	0.12	(276)
Defect-rich MoS ₂ ultrathin nanosheets	Glassy carbon	0.5 M H ₂ SO ₄	-0.12	~-0.20	50	Not mentioned	0.285	(156)
Edge-oriented MoS ₂ nanoporous film	Mo foil	0.5 M H ₂ SO ₄	-0.20	-0.275	50	Yes	-	(286)
Edge-terminated MoS ₂	Glassy carbon	0.5 M H ₂ SO ₄	~-0.25	-	86	Yes	0.0085	(289)
Core-shell MoO ₃ -MoS ₂ nanowires	FTO	0.5 M H ₂ SO ₄	From -0.15 to -0.2	~-0.27	50-60	Yes	-	(292)
MoS ₃ -CV	Glassy carbon	1 M H ₂ SO ₄	~-0.18	~-0.21	40	Yes	-	(316)
MoS ₂ /Au	Glassy carbon	0.5 M H ₂ SO ₄	-0.205	~-0.35	56.97	Not mentioned	-	(317)

Table 6-5 Comparison of various MoS_x-based electrocatalysts for hydrogen evolution

Chaper 7 General conclusions and recommendations for future research directions

7.1 General conclusions

In this dissertation, the working principles, materials selections and up-to-date development of different sustainable water splitting systems have been discussed in detail. More specifically, we have thoroughly reviewed the importance of nanoarchitectural design in developing effective and efficient semiconductor-based photoelectrodes. Throughout this four-year program, unique nanostructured functional materials, with controllable catalytic properties have been successfully designed, synthesized and applied in different applications, including photocatalysis, photoelectrochemical water splitting and electrochemical hydrogen production.

The significant contributions of this research project towards the development of effective water splitting systems can be summarized as follows:

1. It's a well-known fact that the catalytic activity of anatase TiO_2 depends strongly on the crystallinity, size and surface states. Both theoretical and experimental studies show that the (001) surface of anatase TiO_2 is much more reactive than the thermodynamically more stable (101) surface. A facile hydrothermal method has been developed for synthesizing anatase TiO_2 microspheres with >90% exposed {001} facets.
2. The high percentage of exposed {001} facets makes the anatase TiO_2 an efficient photocatalyst in degrading toxic organic contaminants and producing hydrogen from water under UV light irradiation. Owing to the large exposure

of highly reactive {001} facets, the TiO₂ microspheres can be served as an ideal model system in studying the surface-related properties in the future.

3. One-dimensional nanostructures, such as nanorods, nanowires and nanotubes, of wide bandgap semiconductors have been successfully developed and applied in various emerging PEC applications. Compared to their bulk counterparts, these single-crystalline nanostructures can orthogonalize the directions of light absorption and minority carrier transport, thus enhancing the utilization of minority carriers and improve the overall performance of photoelectrochemical devices. However, the power conversion efficiency of pure ZnO and TiO₂ nanostructures is limited by their poor absorption of visible light, due to their relatively large bandgap. ZnO-CdSe core-shell nanorod arrays with excellent uniformity have been successfully fabricated through a facile and efficient all-electrochemical approach.
4. As a photoanode, the favorable band alignment and good distribution of CdSe QDs contribute to the effective separation of photogenerated electron-hole pairs as well as the efficient transportation of the electrons to the FTO substrate, thus leading to a significantly enhanced photoelectrochemical performance and remarkable stability of the core-shell nanorod arrays.
5. In order to achieve our ultimate goal for designing a photolysis cell that can perform overall water splitting, we have fabricated cadmium chalcogenide QD modified TiO₂ nanorod photoanode and a NiO nanosheet photocathode. The two electrodes were linked together to function as a self-driven water splitting system. The optimized CdSe QD modified NiO photocathode combined with a current-matched CdS QD modified TiO₂ photoanode gave rise to the highest efficiency of overall solar water splitting, about 0.17%.

6. The linked system provides a new concept of co-modification of the passivation layer and co-catalysts to suppress surface-state trapping and to efficiently collect charge carriers for enhancing overall efficiency of solar water splitting. Although this maiden concept focuses on cadmium chalcogenide quantum dots and TiO_2/NiO photoelectrodes, we believe that this strategy is fundamental to the designing of solar energy devices and should become an accepted technique for solar energy utilization in spontaneous solar water splitting systems under visible light illumination.
7. In the development of solar water splitting systems, it's of equal importance to design effective electrocatalysts that can be applied in large-scale applications. A facile synthetic strategy has been developed to directly grown nanostructured Ni-Mo-S on carbon fiber cloth as a high-efficiency functional electrode for hydrogen generation in neutral electrolyte. The incorporated Ni atoms play vital roles in constructing Ni-Mo-S nanostructures, through forming substantial desirable defect sites as well as regulating the growth rate of layered MoS_2 .
8. Optimized Ni-Mo-S/C showed excellent HER catalytic performance, characterized by its low onset potential of -0.132 V vs. RHE and a small Tafel slope of 85.3 mV/dec in the neutral electrolyte. The reduced stacking and aggregations in Ni-Mo-S/C effectively prevent the accumulation of instantly evolved H_2 bubbles during electrolysis, hence improving the performance and stability of Ni-Mo-S/C in long-term hydrogen production.
9. To further demonstrate the potential of Ni-Mo-S/C in practical applications, a lab-scale hydrogen generator with rolled Ni-Mo-S/C electrode was designed to carry out the potential controlled electrolysis. In order to bring the

functional electrode one-step closer to a more practical stage, we also performed HER tests using Ni-Mo-S/C electrode in natural seawater.

7.2 Recommendations for future research directions

As the “holy grail” of solar energy conversion, artificial photosynthesis technologies have attracted increasing attentions from researchers across different disciplines, and even from the non-scientist communities. The rapid advancement in material sciences has catalyzed the development of state-of-the-art functional materials; however the design of an optimal system that can achieve effective unassisted solar water splitting still remains a great challenge. To date, many groups of scientists have announced the successful development of sustainable overall water splitting systems; however most of them still suffered from varied issues, such as poor device stability, expensive fabrication cost, low energy conversion efficiency and sometimes extreme operating environment. For example, we have developed overall water splitting that consisted of nanostructured photocathode and photoanode to perform unassisted photolysis, however the efficiency is only 0.17%, resembles that of typical plants but still far below our target solar to hydrogen efficiency. Another issue that severely limits the progress in developing artificial photosynthesis is the lack of globally recognized testing standards and experimental apparatus. Photocatalytic and photoelectrochemical water splitting tests are being carried out very differently in different labs, making it difficult to make fair comparisons. It’s great to see that many leading groups have discussed over the issue and came up with a guideline for us to carry out relevant researches.(318) Meanwhile, in order to accelerate the development of water splitting electrocatalysts, some pioneer researchers have carried out a series of benchmarking experiments. (319, 320)

From our side, the specific recommendations for future research directions are highlighted below:

1. Extensive efforts are still required to design state-of-the-art hydrogen-evolving electrodes for practical water splitting applications. In Chapter 6, we have discussed the development of a functional HER electrode that shows the potential to be applied in practical applications. We believe that the catalytic performance of such electrodes can be further enhanced to meet the standards of practical devices. The carbon fiber cloth can be further engineered using different approaches, such as widening the inter-strand spacing and reducing the packing density of the carbon fibers. Besides, the surface properties of carbon fibers can be further modified using functional coatings. The engineered carbon-based substrates with optimized interfacial properties could support more efficient electron transportation between the catalysts and substrates. In addition, more efficient HER catalysts have been reported recently. For instance, metal phosphide-based electrocatalysts, such as Ni_2P ,⁽³²¹⁾ CoP ⁽³²²⁾ and FeP ,⁽³²³⁾ have been proved to be more stunning HER catalysts in both neutral and acidic medium. It's would be an ideal opportunity to design more efficient practical hydrogen-evolving electrodes using this novel HER catalysts.
2. 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. Recently, our group members have fabricated a flexible high-performance oxygen-

evolving electrode based on the transition metal oxide NiCo_2O_4 , which showed extraordinary OER performance. (324) The superior flexibility of the electrode may benefit the design of integrated sustainable energy systems in future. However, most of current OER studies, including ours, are being carried out in alkaline electrolytes, which may pose adverse environmental impacts. For the purpose of designing a truly sustainable water splitting system, it's necessary to develop effective OER catalyst that can produce oxygen gas from neutral media. Kanan and Nocera have reported the in-situ formation of an OER co-catalyst from neutral water that contains phosphate anion and cobalt anion,(325) and later have studied functioning mechanisms in depth. (326) This is a very important discovery and it could be a possible future direction for us to design practical OER electrodes based on cobalt-phosphate electrocatalysts.

3. The fast progresses made in solar cell technologies would greatly benefits the future development of sustainable water splitting systems. Based on the latest chart of “Best Research-Cell Efficiencies” provided by National Renewable Energy Laboratory (NREL) earlier this year,(327) a multi-junction solar cell based on III-V semiconductor compounds has broken the world record, reaching a breathtaking efficiency of 46%. This brilliant achievement reminds us that we still have better alternative strategy to realize unassisted water splitting, which is to link the photovoltaic cells directly to high-efficiency water electrolyzers. Grätzel and his team have demonstrated water photolysis at 12.3% using the similar concept,(328) however, the system was

demonstrated in alkaline environment. In future, we could design improved systems that are capable of performing photolysis in mild environments.

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