Synthesis of transition metal dichalcogenide-based heterostructures for efficient photocatalytic hydrogen evolution

Chen, Junze

2017

Chen, J. (2017). Synthesis of transition metal dichalcogenide-based heterostructures for efficient photocatalytic hydrogen evolution. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/72763>

<https://doi.org/10.32657/10356/72763>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**SYNTHESIS OF TRANSITION METAL
DICHALCOGENIDE-BASED HETEROSTRUCTURES FOR
EFFICIENT PHOTOCATALYTIC HYDROGEN
EVOLUTION**

CHEN JUNZE

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2017

**SYNTHESIS OF TRANSITION METAL
DICHALCOGENIDE-BASED HETEROSTRUCTURES FOR
EFFICIENT PHOTOCATALYTIC HYDROGEN
EVOLUTION**

CHEN JUNZE

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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

2017

Statement of Originality

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

.....
Date

.....
Chen Junze

Abstract

Exploiting low-cost and earth-abundant photocatalysts is of great importance to achieve highly efficient photocatalytic water splitting. Transition metal dichalcogenides (TMDs) already show excellent performance using as co-catalysts for hydrogen evolution reaction (HER). However, the synthesis of TMD-based heterostructure photocatalysts which possess rich active sites for HER remains urgent. The aim of this thesis is to develop novel TMD-based heterostructures which exposed large amount of active edge-sites to improve the activity toward photocatalytic HER under visible light irradiation. To achieve this goal, the following works have been done.

First, a facile one-pot method has been developed to synthesize nearly monodisperse CdS-MoS₂ and CdS-WS₂ heterostructures with an average diameter of about 6 nm. Monolayer MoS₂/WS₂ with a lateral size around 6 nm was grown on one side of bullet-like CdS particles. The direct contact of CdS and MoS₂/WS₂ monolayer improved the electron transfer and reduced the charge carrier recombination. What is more, these heterostructures possess lots of exposed edge sites in the MoS₂/WS₂ layers, which are also the active sites for HER. The photocatalytic activity of CdS-WS₂ and CdS-MoS₂ heterojunctions towards photocatalytic hydrogen production under light irradiation are about 16 and 12 times of that of pure CdS. The heterojunctions also shown improved durability, 70% of activity is still remained after long-time evaluation (total 16 h).

Second, for the first time, controlled synthesis of a new type of heterostructure was reported, in which TMD nanosheets (NSs) (i.e., MoS₂ and MoSe₂) vertically grown along the longitudinal direction of 1D Cu_{2-x}S nanowire (NW) in an epitaxial manner. The heterostructures were systematically characterized by the high-angle annular dark (bright)-field scanning transmission electron microscopy, which demonstrated that the well match of crystal symmetries and lattice fringes between the TMD and Cu₂S is critical for the construction of these epitaxial heterostructures. The architectures of the heterostructures can be well maintained after the composition and crystal structure of the original Cu_{2-x}S

nanowires were transformed by a well-known cation exchange method (e.g., Cu_{2-x}S to CdS). The as-obtained CdS-MoS_2 heterostructures with different loadings of MoS_2 are used as photocatalysts for photocatalytic HER, exhibiting enhanced photocatalytic activity towards HER under visible light irradiation as compared to the pure CdS nanowires. This synthetic strategy opens up a new way for the controlled synthesis of TMD-based heterostructures which could have various promising applications.

Acknowledgements

First of all, I am particularly grateful to my supervisor, Professor Zhang Hua, for his patient guidance and constant encouragement during my study and research in last four years.

I appreciate the help from my group mates and friends: Dr. Xuejun Wu, Dr. Yaping Du, Dr. Xun Hong, Dr. Xiao Huang, Dr. Zongyou Yin, Dr. Xiehong Cao, Dr. Hai Li, Dr. Zhimin Luo, Dr. Wei Zhao, Dr. Xiaoying Qi, Dr. Juqing Liu, Dr. Shikui Han, Dr. Zhanxi Fan, Dr. Chaoliang Tan, Dr. Jian Yang, Dr. Qipeng Lu, Dr. Meiting Zhao, Dr. Bing Zheng, Dr. Yixian Wang, Dr. Xiao Zhang, Dr. Feifei Cao, Dr. Bo Chen, Dr. Yifu Yu, Dr. Zhicheng Zhang, Dr. Qiyuan He, Mr. Zhuangchai Lai, Ms. Ying Huang, Mr. Gwang-Hyeon Nam, Ms. Ye Chen, Mr. Qinglang Ma, and all other colleagues.

The support from the technicians of the laboratories is also appreciated.

This thesis is dedicated to my family. Thank my mother, Mrs. Peixian, for her endless love. Thank my sisters for supporting my study. Thank my wife, Liping, this dissertation is dedicated to you.

Table of Contents

Abstract	i
Acknowledgements	iii
Table of Contents	v
Table Captions	ix
Figure Captions	xi
Abbreviations	xix
 Chapter 1 Introduction.....	 1
1.1 Hypothesis/Problem Statement	2
1.2 Objectives and Scope	6
1.3 Dissertation Overview	7
1.4 Findings and Outcomes/Originality	8
References	9
 Chapter 2 Literature Review	 13
2.1 Overview	14
2.2 Basic Principles of Photocatalytic Hydrogen Evolution	14
2.2.1 Fundamental Mechanism of Water Splitting	14
2.2.2 Main Processes of Photocatalytic Hydrogen Evolution	16
2.3 Co-catalysts in Photocatalytic Hydrogen Evolution	18
2.3.1 Heterostructure Photocatalysts.....	18

2.3.2	Roles of Co-catalysts in Photocatalytic Hydrogen Evolution.....	21
2.4	TMD as Co-catalysts in Photocatalytic Hydrogen Evolution	24
2.4.1	MoS ₂ as Co-catalyst for Photocatalytic Hydrogen Evolution	27
2.4.2	WS ₂ as Co-catalyst for Photocatalytic Hydrogen Evolution	31
2.5	Questions to answer based on literature.....	33
2.6	PhD in context of literature	34
	References.....	35
Chapter 3	Experimental Methodology.....	41
3.1	Rationale for Materials and Method Selection.....	42
3.2	Chemicals and Synthesis Process	42
3.2.1	Chemicals	42
3.2.2	Synthesis of CdS-WS ₂ Heterostructures.....	43
3.2.3	Synthesis of CdS-MoS ₂ Heterostructures	44
3.2.4	Synthesis of CdS NWs	44
3.2.5	Synthesis of Cu _{2-x} S NWs by Cation Exchange of CdS NWs	44
3.2.6	Synthesis of Cu _{2-x} S-MoSe ₂ Heterostructures	45
3.2.7	Synthesis of Cu _{2-x} S-MoS ₂ Heterostructures	45
3.2.8	Synthesis of CdS-MoS ₂ Heterostructures	46
3.2.9	Preparation of the Water-soluble CdS-MoS ₂ Heterostructures	46
3.2.10	Photocatalytic Hydrogen Evolution	46
3.3	Characterization	47
3.3.1	Transmission Electron Microscopy	47
3.3.2	X-ray Diffraction	48
3.3.3	X-ray photoelectron spectroscopy	49

References	50
Chapter 4 CdS-MoS₂ and CdS-WS₂ Heterostructures	53
4.1 Introduction	54
4.2 Results and Discussion	55
4.2.1 Synthesis and Characterization of CdS-WS ₂ Heterostructures	55
4.2.2 Formation process of CdS-WS ₂ Heterostructures	58
4.2.3 Synthesis and Characterization of CdS-MoS ₂ Heterostructures	61
4.2.4 Photocatalytic activity of CdS-WS ₂ and CdS-MoS ₂ Heterostructures	64
4.3 Conclusion	65
References	66
Chapter 5 Edge Epitaxy of 2D MoSe₂ and MoSe₂ NSs on 1D NWs	69
5.1 Introduction	70
5.2 Results and Discussion	72
5.2.1 Synthesis of CdS nanowires and their cation exchange to Cu _{2-x} S	72
5.2.2 Synthesis of Cu _{2-x} S-MoSe ₂ Heterostructure Nanowires	72
5.2.3 Synthesis of Cu _{2-x} S-MoS ₂ Heterostructure Nanowires	83
5.2.4 Photocatalytic Activity of CdS-MoS ₂ Heterostructure Nanowires	87
5.3 Conclusion	90
References	90
Chapter 6 Discussion and Future Work	93
6.1 General Discussion	94

6.1.1 Discussion on the preparation of CdS-MoS ₂ and CdS-WS ₂ Heterostructures for HER	94
6.1.2 Discussion on the Edge Epitaxy of 2D MoS ₂ and MoSe ₂ on 1D NWs	95
6.2 Reconnaissance	97
6.2.1 Synthesis of CdS _x Se _{1-x} -MoS ₂ Epitaxial Heterostructures	98
6.2.2 Preparation of Other TMD-Based Heterostructures	99
6.2.3 Preparation of 1 T TMD Based Heterostructures	100
References	100
Publication List	103

Table Captions

Table 5.1	The amount of MoSe ₂ and MoS ₂ in Cu _{2-x} S-MoSe ₂ , Cu _{2-x} S-MoS ₂ and CdS-MoS ₂ heterostructures determined by ICP-OES.	82
------------------	--	----

Figure Captions

Figure 1.1	The Sabatier plot for the HER.	4
Figure 1.2	(a) STM images of MoS ₂ nanosheet on gold [111]. (b) A schematic model of a nanosheet exposing both Mo and S edges.	5
Figure 2.1	Demonstration of photocatalytic water splitting on a semiconductor surface decorated with hydrogen and oxygen evolution co-catalysts.	15
Figure 2.2	Processes in photocatalytic water splitting.	17
Figure 2.3	Different types of semiconductor heterostructures.	19
Figure 2.4	Charge transfer in CdS/TiO ₂ heterostructure under visible-light irradiation.	20
Figure 2.5	(a). Schematic illustration and TEM images of the multicomponent heterostructure. Scare bar: 20 nm. (b) Relative quantum efficiency for HER using different samples.	21
Figure 2.6	Roles of catalyst in a catalyst reaction.	22
Figure 2.7	The relationship between the loading amount of co-catalyst and the activity for photocatalyst process.	23
Figure 2.8	Crystal structure of transition metal dichacogenides.	25
Figure 2.9	(a) STM image of MoS ₂ NSs on gold [111]. (b) A schematic model of a NSs exposing both Mo and S edges from top and side view.	25

Figure 2.10 Plot of Exchange current density with the coverage area of MoS ₂ (left) and (right) edge length of MoS ₂	26
Figure 2.11 (a) TEM image of 1 wt% MoS ₂ /CdS obtained at 733 K and (b) the HR-TEM image took in the white square in image (a).	27
Figure 2.12 Rate of photocatalytic HER rate on CdS decorated with 0.2 wt% of several types of co-catalysts.	28
Figure 2.13 Possible reaction mechanism for photocatalytic HER of the Ru(bpy) ₃ ²⁺ -MoS ₂ -H ₂ A system.	29
Figure 2.14 (a) Illustration of the charge transfer in the MoS ₂ /G-CdS heterostructure. (b) Amount of H ₂ generation in 5 h.	30
Figure 2.15 (a-b) TEM images of WS ₂ /CdS composite. (b) Photocatalytic activities of WS ₂ /CdS with different WS ₂ loading amount. (c) Proposed Reaction Mechanism for Photocatalytic H ₂ Production on WS ₂ /CdS Catalyst.	32
Figure 2.16 (a) Schematically illustrated the preparation methods. (b) Band structure of TiO ₂ -WS ₂	33
Figure 3.1 Schematic illustration of the Bragg diffraction.	49
Figure 4.1 TEM images and EDS mapping of CdS-WS ₂ heterostructures. (a, b) TEM images of CdS-WS ₂ . The arrows in b indicate the single-layer WS ₂ NSs, which grew on the Cd-rich (0001) surface of CdS NCs. (c, d) Representative high-resolution TEM images of CdS-WS ₂ viewed perpendicular and parallel to <i>c</i> axes, correspondingly. (e) DF-STEM image and EDS mapping of CdS-WS ₂ heterostructures (scale bar = 100 nm).	56

Figure 4.2	XRD pattern of CdS-WS ₂	57
Figure 4.3	EDS spectrum of CdS-WS ₂ heterostructures deposited on Si/SiO ₂ copper grid. The Cu signal is from the copper grid substrate.	57
Figure 4.4	TEM images of CdS-WS ₂ heterostructures prepared at different reaction time. (a) 5 min, (b) 30 min, (c) 60 min. (d) Schematic illustration of the shape evolution of CdS-WS ₂ heterostructures.	58
Figure 4.5	TEM images of the product of decomposition of (NH ₄) ₂ WS ₄ (a,b) in the absence of TOP (c,d) in the presence of TOP at 5 min.	59
Figure 4.6	TEM image of the CdS-MoS ₂ when 0.3 mmol of (NH ₄) ₂ WS ₄ was injected.....	60
Figure 4.7	TEM images of CdS- MoS ₂ heterostructures. (a, b) TEM images of CdS-MoS ₂ heterostructures. (c) HR-TEM images of CdS-MoS ₂ viewed perpendicularly to the c axis of CdS NCs. The arrows in b and c shows the single-layer MoS ₂ NSs which grew on the Cd-rich (0001) surface of CdS NCs.	62
Figure 4.8	XRD pattern of CdS-MoS ₂ heterostructure.	62
Figure 4.9	EDS spectrum of CdS-MoS ₂ heterostructures deposited on Si/SiO ₂ substrate. The Si signal is from the Si/SiO ₂ substrate.	63
Figure 4.10	XPS survey spectrum (a) and high-resolution XPS spectra of CdS-MoS ₂ heterostructures: (b) Mo 3d, (c) S 2p, (d) Cd 3d.	63

Figure 4.11 Photocatalytic activity of CdS-MS₂ heterostructures for HER. (a) Time-dependent photocatalytic H₂ production for CdS-WS₂, CdS-MoS₂ and pure CdS, respectively. (b) Comparison of the H₂-production rate under the light irritation for CdS-WS₂, CdS-MoS₂ and pure CdS. (c) Cycling test of photocatalytic HER for CdS-WS₂. (d) Illustration of the photocatalytic process in CdS-MoS₂ heterostructures.64

Figure 5.1 (a) XRD pattern of CdS NWs. The standard diffraction pattern of wurtzite CdS (JCPDS No. 41-1049) is used as reference. (b) Low magnification TEM image of CdS NWs with diameter of 30–50nm and lengths up to 3 μ m. (c) TEM image and (d) corresponding SAED pattern of a typical CdS NW. Inset in (c): HR-TEM image of the CdS NW showing the well crystalline structure. The measured lattice fringe of 0.33 nm is ascribed to (002) plane of wurtzite CdS, indicating that the CdS NW grew along the *c* direction.71

Figure 5.2 (a) XRD pattern of the Cu_{2-x}S NWs. The standard diffraction pattern of djurleite Cu_{2-x}S (JCPDS No. 20-0365) is used as reference. (b) Low magnification TEM image of Cu_{2-x}S NWs. It is found that the size and shape of obtained Cu_{2-x}S NWs are well maintained compared to the original CdS NWs. (c) TEM image and (d) the corresponding SAED pattern of a typical Cu_{2-x}S NW, proving its well crystalline structure.72

Figure 5.3 (a) Schematic illustration of the synthesis of Cu_{2-x}S-MoX₂ (X=S or Se) heterostructure. (b) HAADF-STEM image of a typical Cu_{2-x}S-MoSe₂ heterostructure. (c) TEM image of Cu_{2-x}S-MoSe₂ heterostructure. The circles indicate the Cu_{1.94}S, component i and Cu₂S, component ii. The black arrows indicate the MoSe₂, component iii. Inset: corresponding FFT pattern of the Cu_{2-x}S-MoSe₂. (d) HR-TEM image of Cu_{2-x}S-MoSe₂ taken in the square in (c). (e-g) Bragg-filtered image derived by inverse FFT in component i, ii and iii. The Bragg-filtered images are derived by using the (080) reflection of component i (e), the (110) reflection of component ii (f) and the (002) reflection of component iii (g). The images were then processed with a Sobel filter to enhance their boundaries. (h) Overlap of the Bragg-filtered images of the three components.73

Figure 5.4 (a, b) Low magnification TEM images of Cu_{2-x}S - MoSe_2 heterostructures. (c, d) TEM images of Cu_{2-x}S - MoSe_2 heterostructures. High-density MoSe_2 NSs grown on the tip (c) and body (d) of Cu_{2-x}S NWs are clearly observed.74

Figure 5.5 XRD pattern of Cu_{2-x}S - MoSe_2 heterostructures. The standard diffraction pattern of djurleite Cu_{2-x}S (JCPDS No. 20-0365) is used as reference. Not obvious peaks from MoSe_2 are detected.75

Figure 5.6 TEM image of Cu_{2-x}S - MoSe_2 composites obtained at 260 °C.76

Figure 5.7 (a) Experimental electron diffraction pattern of Cu_{2-x}S - MoSe_2 heterostructures. (b) Simulated electron diffraction pattern (Kinematical) of djurleite ($\text{Cu}_{1.94}\text{S}$). The SAED pattern of the Cu_{2-x}S - MoSe_2 heterostructures (a) indicates the major component of the Cu_{2-x}S - MoSe_2 heterostructures is djurleite $\text{Cu}_{1.94}\text{S}$, which is well accord with the simulate electron diffraction pattern (b).76

Figure 5.8 (a) The FFT pattern taken at the circle (i) in Figure 5.3c, indicating the major component of Cu_{2-x}S - MoSe_2 heterostructures is the djurleite $\text{Cu}_{1.94}\text{S}$. (b) FFT pattern of Cu_2S , component ii. (c) FFT pattern of MoSe_2 , component iii.77

Figure 5.9 FFT pattern of Cu_{2-x}S - MoSe_2 heterostructure. The enlarged image (right) indicates the difference between the (080) reflection of djurleite $\text{Cu}_{1.94}\text{S}$ (i) and the (110) reflection of high chalcocite Cu_2S (ii). The djurleite $\text{Cu}_{1.94}\text{S}$ (i) and high chalcocite Cu_2S (ii) almost have the same lattice fringes, and the lattice mismatch between the (080) planes of djurleite phase (1.97 nm) and the (110) planes of high chalcocite phase (2.02 nm) is only about 2.5%.77

Figure 5.10 (a) HR-TEM image taken at the tip of Cu_{2-x}S - MoSe_2 heterostructure. Few-layer MoSe_2 NSs grown on the tip of Cu_{2-x}S NW are observed. (b) Bragg-filtered image from the (080) reflection of djurleite $\text{Cu}_{1.94}\text{S}$. The yellow area clearly indicates the presence

of djurleite $\text{Cu}_{1.94}\text{S}$ (i). (c) Bragg-filtered image from the (110) reflection of high chalcocite Cu_2S . The green area indicates the presence of high chalcocite Cu_2S (ii). (d) Bragg-filtered image from the (002) reflection of MoSe_2 . The location of MoSe_2 (iii) is indicated by the red area in the tip of NW. (e) Overlap of the Bragg-filtered images (b-d).78

Figure 5.11 (a) High-resolution XPS spectra of Cu 2p. (b) High resolution XPS spectra of Mo 3d. (c) High resolution XPS spectra of S 2p. The two peaks located at 161.9 eV and 163.1 eV can be assigned to the presence of S. (d) High resolution XPS spectra of Se 3d.79

Figure 5.12 TEM analyses and crystal model of Cu_{2-x}S - MoSe_2 heterostructure NWs. (a, b) HAADF-STEM image of Cu_{2-x}S - MoSe_2 taken at the centre (a) and the end (b) of Cu_{2-x}S - MoSe_2 heterostructure NWs, the white triangles indicate the position of MoSe_2 NSs. (c) HAADF-STEM (left) and ABF-STEM image (right) of Cu_{2-x}S - MoSe_2 heterostructure NW. (d) Schematic illustration of the crystal structure of Cu_{2-x}S - MoSe_2 at the interface of Cu_2S and MoSe_280

Figure 5.13 (a-c) TEM images of the Cu_{2-x}S - MoSe_2 heterostructures obtained at different injection volume of Se precursor solution: (a) 0.5 mL, (b) 1 mL and (c) 1.75 mL. (d) The plot of the weight percentage (wt%) of MoSe_2 in Cu_{2-x}S - MoSe_2 heterostructures, measured by ICP-OES, versus the volume of Se precursor solution.81

Figure 5.14 (a) TEM image of a typical Cu_{2-x}S - MoS_2 heterostructure, obtained by using 1.5 mL of S precursor solution. (b, c) HAADF-STEM images of Cu_{2-x}S - MoS_2 heterostructures taken at the tip (b) and the body (c) parts. The red triangles indicate the position of MoS_2 NSs. (d-f) TEM images of the Cu_{2-x}S - MoS_2 heterostructures obtained by using different injection volume of S precursor solution: (d) 0.5, (e) 1.0, and (f) 2 mL. (g) The plot of the weight percentage (wt%) of MoS_2 in Cu_{2-x}S - MoS_2 heterostructures, measured by ICP-OES, versus the volume of S precursor solution.84

Figure 5.15 (a) High-resolution XPS spectra of Cu 2p. The peaks located at 932.3 eV and 952 eV can be ascribed to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively. (b) High resolution XPS spectra of Mo 3d. The peaks of Mo 3d appear at binding energy of 228.4 eV (Mo3d_{5/2}) and 231.8 eV (Mo3d_{3/2}), indicating that Mo⁴⁺ is the dominant oxidation state. (c) High resolution XPS spectra of S 2p. The two peaks located at 161.6 eV and 162.6 eV can be assigned to the presence of S²⁻.85

Figure 5.16 XRD pattern of Cu_{2-x}S-MoS₂ heterostructures. The standard diffraction pattern of djurleite Cu_{2-x}S (JCPDS No. 20-0365) is used as reference. The experimental XRD pattern matches well with the standard one. No obvious peaks from MoS₂ were detected.85

Figure 5.17 (a) HAADF-STEM and (b-d) the corresponding STEM-EDS images of (b) Cu, (c) Mo and (d) S in the Cu_{2-x}S-MoS₂ heterostructures, indicating the existence of Cu, S and Mo, and suggesting the uniform growth of MoS₂ NSs on Cu_{2-x}S NWs.86

Figure 5.18 (a) High-resolution XPS spectra of Cd 3d. (b) High resolution XPS spectra of Mo 3d. (c) High resolution XPS spectra of S 2p.87

Figure 5.19 (a) HAADF-STEM and (b-d) the corresponding STEM-EDS images of (b) Cd, (c) S and (d) Mo in CdS-MoS₂ heterostructures, indicating the existence of Cd, S and Mo, and suggesting the successful transformation of Cu_{2-x}S-MoS₂ to CdS-MoS₂ heterostructures.88

Figure 5.20 XRD pattern of CdS-MoS₂ heterostructures. The standard diffraction pattern of wurtzite CdS (JCPDS No. 41-1049) is used as reference. Experimental XRD pattern matches well with the standard one, indicating the successful cation exchange from Cu_{2-x}S-MoS₂ to CdS-MoS₂ heterostructures.88

Figure 5.21 (a) TEM image of CdS-MoS₂ heterostructures. (b) HAADF-STEM and (c) ABF-STEM images of the tip area of CdS-MoS₂ heterostructures. The red triangles

indicate the position of MoS₂ NSs. (d) Comparison of H₂ production activities using CdS NW and CdS-MoS₂ heterostructures with different loading amount of MoS₂ NSs as catalysts. (e) Produced H₂ amount after 5 h photocatalytic HERs using CdS NW and CdS-MoS₂ heterostructures with different loading amount of MoS₂ NSs as catalysts. (f) Cycling test of photocatalytic H₂ evolution using CdS-MoS₂ heterostructures with 7.7 wt% MoS₂ NSs as catalyst.89

Figure 6.1 Synthesis and characterization of CdS_xSe_{1-x}-MoS₂ heterostructure. (a, b) TEM image of CdS_xSe_{1-x}-MoS₂ heterostructures. (c) A typical side view HR-TEM image of CdS_xSe_{1-x}-MoS₂ heterostructure. (d) A typical top view HR-TEM image of CdS_xSe_{1-x}-MoS₂ heterostructure. (e) Dark-field STEM image and corresponding EDS mapping images of CdS_xSe_{1-x}-MoS₂ heterostructures. (f-g) XRD pattern of CdS_xSe_{1-x}-MoS₂ heterostructure with different S/Se ratio.....99

Abbreviations

1D	One-dimensional
2D	Two-dimensional
CB	Conduction Band
Cd(Ac) ₂	Cadmium acetate
CdS	Cadmium Sulfide
CdO	Cadmium Oxide
CuCl ₂	Copper(II) Chloride
Cu ₂ S	Copper Sulfide
Cu _{2-x} S	Copper Sulfide
DDT	Tert-Dodecylmercaptan
H ₂ O	Water
HAAD	High-angle Annular Dark
HER	Hydrogen Evolution Reaction
HR-TEM	High-resolution Transmission Electron Microscopy
N ₂	Nitrogen
Na ₂ S	Sodium Sulfide
Na ₂ SO ₃	Sodium Sulfite
NCs	Nanocrystals
(NH ₄) ₂ MoS ₄	Ammonium Tetrathiomolybdate
(NH ₄) ₂ S	Ammonium Sulfide Solution
NSs	Nanosheets
NW	Nanowire
MoO ₂ (acac) ₂	Bis(acetylacetonato)dioxomolybdenum
MoS ₂	Molybdenum Disulfide
MoSe ₂	Molybdenum Diselenide
MPA	3-Mercaptopropionic Acid
OA	Oleic Acid
ODE	1-Octadecene
OM	Oleylamine

PdSe	Diphenyl Diselenide
PEC	Photoelectrochemical
rGO	Reduced Graphene Oxide
STM	Scanning Transmission Electron Microscopy
TOP	Trioctylphosphine
TMD	Transition Metal Dichalcogenide
TEM	Transmission Electron Microscopy
VB	Valence Band
WS ₂	Tungsten Disulfide
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy

Chapter 1

Introduction

Construction of semiconductor heterostructure photocatalysts is a very promising way to improve the activity for photocatalytic hydrogen production. Such a hypothesis guides the content of this thesis, which is designed for two objectives. First, the MoS_2 or WS_2 nanosheets with ultra-small lateral size and single layer structure will be decorated on CdS nanoparticle surface, and the obtained CdS- MoS_2/WS_2 heterostructures will be used as photocatalysts for photocatalytic hydrogen production under visible light irradiation. Second, a new type of epitaxial heterostructure consisting of two-dimensional (2D) transition metal dichalcogenides (TMDs, i.e., MoSe_2 and MoS_2) and one-dimensional (1D) non-layered Cu_{2-x}S nanowires will be synthesized by using Cu_{2-x}S nanowires as seeds. The 2D TMD nanosheets are vertically grown along the longitudinal direction of 1D Cu_{2-x}S nanowire in an epitaxial manner. The obtained Cu_{2-x}S - MoS_2 heterostructures can be transformed to a CdS- MoS_2 heterostructures by a cation exchange method, and the vertical structure can be preserved. The obtained CdS- MoS_2 heterostructures with different loadings of MoS_2 will be used as photocatalysts for photocatalytic hydrogen evolution.

1.1 Hypothesis/Problem Statement

To find a sustainable energy supply for the development of human society is one of the greatest challenges being confronted by scientists in the 21st century. At present, about 80% of the total world energy supply is depended on limited and non-renewable fossil fuels.^[1] Moreover, the usage of fossil fuels has leads to a series of environmental problems, such as air/water contamination, global warming. Thus, there is an urgent need to find an alternative resource which is renewable, cheap and environment friendly to replace the fossil fuels and meet the energy demands. Among the various energy strategies, hydrogen economy which delivery energy using hydrogen as primary carrier connecting a host of energy source enable a secure and clean energy future. Currently, the industrial production of H₂ depends on steam reforming of hydrocarbon fuels such as naturel gas, which still relies on fossil fuels and causes serious environmental problems. On the contrary, water splitting into H₂ and O₂ driven by renewable energy resources are promising pathway for sustainable H₂ production.

Electrochemical water splitting, photoelectrochemical water splitting and photocatalytic water splitting are three important ways for sustainable H₂ production. The electrochemical water splitting, first observed in 1789, including two half reactions: the hydrogen evolution reaction (HER, Equation 1.1) and the oxygen evolution reaction (OER Equation 1.2).

Under standard conditions, the free energy change for conversion of one molecule of water into hydrogen and oxygen is +237.2 kJ per mol of H₂. This value correspond to a reversible electrolysis cell voltage of 1.23 V. Thus, in an idea case, the application of 1.23 V of external potential would be enough to trigger the water splitting reaction in an electrochemical cell. In practice, water electrolysis is less efficient and external potentials lager than 1.23 V are required. However, electricity is secondary energy source, which has to be generated by primary energy sources such as coal, natural gas and so on.

In the contrary, solar energy is widely considered as free, clean, abundant and inexhaustible primary resource.^[2, 3] Hydrogen production driven by solar energy is a promising way to solve the energy crisis. Since the first discovery of photoelectrochemical (PEC) water-splitting over TiO₂ electrode by Fujishima and Honda in 1972,^[4] water splitting into hydrogen and oxygen using semiconductor photocatalysts under light irradiation has attracted a lot of attention. Generally, there are three critical steps in the overall photocatalytic water splitting reaction: firstly, photoexcitation of charge carriers; secondly, charge carriers separate and transfer to the surface of the semiconductor; thirdly, oxidation and reduction reaction happen on the catalyst surface.^[5] The balance of thermodynamics and kinetics of these three steps determines the overall efficiency of a photocatalytic water splitting process. Tremendous efforts have been made to improve the overall efficiency in the past several decades. To improve the light absorption of photocatalysts, a series of strategies have been employed, including bandgap engineering,^[6, 7] dye sensitization,^[8, 9] surface plasmonic enhancement^[10, 11] and coupling with narrow-bandgap semiconductors.^[12] On the other hand, great achievements have been made to gain efficient charge separation and transportation. Semiconductors with high crystallinity and few defects as well as small size designed to shorten charge diffusion length have been fabricated.^[13, 14] Furthermore, the formation of semiconductor heterostructures also show promising results to improve the charge separation and transfer.^[15] Co-catalysts which can extract photo-generated electrons or holes for H₂ or O₂ evolution, greatly promote the efficiency. The photo-corrosion is suppressed by co-catalysts, thus the stability of photocatalysts can also be improved. Therefore, co-catalysts play a very important role in the improvement of both the activity and durability of semiconductor photocatalysts.

To date, noble-metal based co-catalysts have been adopted in most of photocatalyst systems to achieve high photocatalytic efficiency. Noble metal such as Pt,^[16, 17] Pd,^[18] Au,^[19] Ag,^[20] Ru^[21] and Rh^[22] have been extensively studied and proved as efficient co-catalysts for photocatalytic hydrogen evolution reaction (HER). Among them, Pt is the most active material for hydrogen evolution. Figure 1.1 gives the famous volcano curve for the most reported catalysts, which is obtained by plotting the activity of the materials against the corresponding hydrogen bonding free energy as calculated by DFT.^[23] This

volcano curve clearly illustrates why Pt is the best choice for HER. Until now, the highest photocatalytic activity for visible light derived H_2 evolution is obtained from photocatalyst which decorated Pt as the co-catalyst. Other noble-metals such as Pd, Rh are also located at the top of the volcano curve. Unfortunately, the above mentioned metals are too scarce in the earth crust, for example, Pt is only $0.005 \text{ mg} \cdot \text{kg}^{-1}$, which is too expensive to be used for large-scale energy production. Therefore, lots efforts have been made to seek an earth-abundant, stable, non-toxic and cheap replacement.

Figure 1.1 The Sabatier plot for the HER. Reprinted with permission from ref. 23.

In order to develop noble-metal free co-catalysts with high catalytic activity and low cost for photocatalytic hydrogen evolution, many kinds of novel co-catalysts composed of earth-abundant elements have been developed. For example, $\text{Cu}(\text{OH})_2$ ^[24] and $\text{Ni}(\text{OH})_2$ ^[25] clusters have been used as highly active co-catalysts to improve the photocatalytic performance of semiconductor photocatalysts, e.g. TiO_2 , CdS and so on. Among those co-catalysts, transition metal dichalcogenide (TMD) nanosheets (NSs) with layered structures, such as MoS_2 and WS_2 , shows very good performance in electrocatalytic H_2 evolution.^[26, 27] DFT studies showed that the hydrogen binding energy of MoS_2 is located at the top of the volcano shape curve, as shows in Figure 1.1.

Figure 1.2 (a) STM image of MoS₂ nanosheet on gold [111]. (b) A schematic model of a nanosheet exposing both Mo and S edges. Reprinted with permission from ref 23.

MoS₂ has a crystal structure with layered hexagonally packed composed of S-Mo-S sandwich structure. As an indirect-gap semiconductor, bulk MoS₂ has a band gap of 1.29 eV. However, when MoS₂ is thinned to single layer, it becomes a direct bandgap semiconductor (band gap ~1.7 eV).^[28] The use of MoS₂ as catalyst for electrochemical hydrogen evolution was started in the 1970s by Tribustsch and co-workers.^[29] According to DFT studies,^[30] the edges of MoS₂ sheets are the active sites for hydrogen evolution, especially the [1 010] Mo-edges have the most advantageous hydrogen binding energy. This theoretical calculation indicates that the edges are responsible for the activity, which was verified by Thomas and co-workers.^[23] In this study, single layer MoS₂ with a truncated triangular shape exposing the [1 010] Mo-edges and [1 110] S-edges was deposited on Au [111] surface (Figure 1.2). The total edge length was quantified by scanning transmission electron microscopy (STM), and electrochemical measurements showed that the current density for hydrogen evolution increases linearly with the length of the exposed edge of MoS₂.

WS₂ is also a layered material with a structure very similar with that of MoS₂, which also shows efficient catalytic activity towards HER. In electrocatalytic hydrogen evolution, the lowest Tafel slope of 1T WS₂ electrodes is about 60 mV per decade.^[27] For 1T MoS₂ electrodes, the Tafel slop is about 55 to 60 mV per decade.^[23] These values are quite comparable, indicating that the mechanism responsible for hydrogen evolution may be similar.

A large number of semiconductor materials have been developed for photocatalytic HER in past decades.^[31-33] Among them, CdS has attracted great attention since it possesses an optimal band gap (~2.4 eV) for effective absorption of solar energy and suitable band structure for HER.^[34-36]

1.2 Objectives and Scope

MoS₂ and WS₂ plays there different roles in a photocatalytic system. First, due to their special 2D layered structure, MoS₂ and WS₂ can be used as supports for the nucleation and growth of CdS nanoparticles, which would reduce avoid the arrogation of the semiconductors. Second, a semiconductor-semiconductor junction can be formed by loading MoS₂ or WS₂, thus can enhance the charge separation and migration in the heterostructures. Therefore, the hydrogen production activity can be enhanced. Third, as MoS₂ and WS₂ have been proved to be active for the electrochemical hydrogen evolution reaction. Their exposed active edge sites could lower the activation energy for photocatalytic H₂ evolution. The objective of this study is to synthesize CdS-MS₂ (M=W or Mo) heterostructures for photocatalytic hydrogen evolution. Up to now, several reports have demonstrated that a p-n junction can be formed by integrating CdS nanocrystals (NCs) with MoS₂ NSs, which great enhance the performance towards the photocatalytic HER.^[37-40] However, MoS₂ NSs in the heterostructures often exhibit large lateral size or/and multilayered structure, which lead to the low exposure of the active edge sites and limit their activity towards HER. The synthesis of photocatalysts containing layered MS₂ NSs with abundant of active sites remains challenge. Furthermore, previous works about the preparation of CdS-MS₂ heterostructures were realized through a high temperature treatment in the presence of toxic H₂S gas, using (NH₄)₂MS₄ as precursor. Multi-step experiments are needed. Thus, a relatively simple method to synthesis CdS-MS₂ heterostructures is highly desired.

Based on the hypotheses that are proposed above, the objectives and scope of this thesis are listed as below:

First, MoS₂ or WS₂ NSs with ultra-small lateral size and single layer structure will be decorated on CdS nanoparticle surface, and the obtained CdS-MoS₂/WS₂ heterostructures will be used as photocatalyst for HER under visible light irradiation. The as-prepared CdS-MoS₂/WS₂ heterostructures will be characterized by transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Then the obtained heterostructures will be transferred to water phase and the hydrogen production activity will be evaluated.

Second, a new type of epitaxial heterostructure consisting of two-dimensional (2D) TMD NSs (i.e., MoSe₂ and MoS₂) and one-dimensional (1D) non-layered Cu_{2-x}S nanowire (NW) will be synthesized by using Cu_{2-x}S nanowires as seeds. The 2D TMD NSs are vertically grown along the longitudinal direction of 1D Cu_{2-x}S nanowire in an epitaxial manner. The loading amount and lateral size of TMD NSs will be carefully tuned to obtain an optimized composition for application. The obtained Cu_{2-x}S-MoS₂ heterostructures will be transformed to CdS-MoS₂ heterostructures by a cation exchange method. These heterostructures will be characterized by TEM, HR-TEM, STEM, XPS and XRD. Finally, the CdS-MoS₂ with different loading amount of MoS₂ will be transferred to water phase and the hydrogen production activity will be evaluated.

1.3 Dissertation Overview

This thesis demonstrates the synthesis of novel TMD-based heterostructure photocatalysts via wet chemical method. CdS-MoS₂, CdS-WS₂, Cu_{2-x}S-MoS₂ and Cu_{2-x}S-MoSe₂ with different structures have been synthesized. To improve their performance for photocatalytic hydrogen evolution reaction, the lateral size and loading amount of TMD on CdS and Cu_{2-x}S have been optimized. And the potential of these novel heterostructures as catalysts in photocatalytic HER will be demonstrated.

Chapter 1 describes a rational analysis for the research. The hypothesis, objectives, and scope of the thesis are introduced.

Chapter 2 first reviews the literatures concerning the mechanism and main processes of photocatalytic water splitting. After that, the roles of co-catalysts in heterostructure photocatalysts will be introduced. Then special attention is paid to TMD materials. Recent research progress of design and synthesis of high efficient photocatalysts using TMD as co-catalysts will be reviewed.

Chapter 3 discusses the rational analysis for material selection. Why CdS and TMD were chosen as target materials to construct heterostructures are discussed. The detailed synthetic procedure, characterization techniques as well as the method for evaluating the photocatalytic hydrogen evolution activity are described in detail.

Chapter 4 elaborates the preparation of CdS-MoS₂ and CdS-WS₂ heterostructures, which characteristic with single layer TMD selectively grown on the Cd-rich (0001) surface of wurtzite CdS nanocrystals. The lateral size of single layer TMD is only 4–10 nm, which indicates that large percentage of the exposed surface are active edge sites. Their photocatalytic activity towards HER were evaluated.

Chapter 5 elaborates the synthesis of a new kind of heterostructure, composed of Cu_{2-x}S and MoS₂/MoSe₂. The 2D TMD NSs are vertically grown along the longitudinal direction of 1D Cu_{2-x}S nanowire in an epitaxial manner. Their cation exchange to CdS-MoS₂ heterostructures were performed. The utilization of CdS-MoS₂ as photocatalyst for HER has been studied.

Chapter 6 concludes the whole thesis and elaborates the reconnaissance studies with could be conducted in the near future.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. A facile one-pot method has been developed to synthesis nearly monodisperse CdS/MoS₂ and CdS-WS₂ heterostructures with an average diameter of about 6 nm.

Monolayer MoS₂/WS₂ with a lateral size around 6 nm was grown on one end of bullet-like CdS particles. The direct contact of CdS and MoS₂/WS₂ monolayer improved the electron transfer and reduced the charge carrier recombination. Thus, the photocatalytic activity of CdS-WS₂ and CdS/MoS₂ heterojunctions for HER were found to increase about 16 and 13 times compared with pure CdS, respectively. The advantage of this study lies in the following aspects. First of all, one-pot wet chemical method was used to in-situ growth MoS₂/WS₂ monolayer on CdS nanoparticles, which not only simplify the fabrication process, but also offers more opportunity to tailor the structure in solution phase. Secondly, the lateral size of MoS₂ and WS₂ was less than 10 nm, which expose lots of active sites toward HER since the active sites are locate at the edges of the TMD sheet. Thirdly, the direct contact between CdS and MoS₂/WS₂ formed a p-n junction, which greatly improve the separation of photo-generated electrons and holes.

2. For the first time, a new type of heterostructure, in which TMD NSs (i.e., MoS₂ and MoSe₂) vertically grown along the longitudinal direction of 1D Cu_{2-x}S nanowire in an epitaxial manner were synthesized. The heterostructures were systematically characterized by the high-angle annular dark (bright)-field scanning transmission electron microscopy, which demonstrated that the well match of crystal symmetries and lattice fringes between the TMD and Cu₂S is critical for the construction of this kind of epitaxial heterostructures. The architectures of the heterostructures can be well maintained after the composition and crystal structure of the original Cu_{2-x}S nanowires are transformed by the well-known cation exchange method (e.g., Cu_{2-x}S to CdS). As a proof-of-concept application, the as-obtained CdS-MoS₂ heterostructures with different loading amount of MoS₂ are used as photocatalyst for photocatalytic HER, exhibiting enhanced photocatalytic activity toward HER under visible light irradiation as compared to the pure CdS nanowires. The synthetic strategy in this thesis opens up a new way for the controlled synthesis of TMD-based heterostructures which could have various promising applications.

References

- [1] J. Goldemberg, *Science* **2007**, *315*, 808-810.

- [2] J. C. Colmenares, R. Luque, *Chemical Society Reviews* **2014**, 43, 765-778.
- [3] Y. Qu, X. Duan, *Chemical Society Reviews* **2013**, 42, 2568-2580.
- [4] A. Fujishima, *Nature* **1972**, 238, 37-38.
- [5] J. Ran, J. Zhang, J. Yu, M. Jaroniec, S. Z. Qiao, *Chemical Society Reviews* **2014**.
- [6] E. Borgarello, J. Kiwi, M. Graetzel, E. Pelizzetti, M. Visca, *Journal of the American Chemical Society* **1982**, 104, 2996-3002.
- [7] F. Zuo, L. Wang, T. Wu, Z. Zhang, D. Borchardt, P. Feng, *Journal of the American Chemical Society* **2010**, 132, 11856-11857.
- [8] E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca, M. Grätzel, **1981**;
- [9] Y. I. Kim, S. Salim, M. J. Huq, T. E. Mallouk, *Journal of the American Chemical Society* **1991**, 113, 9561-9563.
- [10] C. u. Gomes Silva, R. Juárez, T. Marino, R. Molinari, H. García, *Journal of the American Chemical Society* **2010**, 133, 595-602.
- [11] E. Thimsen, F. Le Formal, M. Grätzel, S. C. Warren, *Nano letters* **2010**, 11, 35-43.
- [12] A. Kongkanand, K. Tvrđy, K. Takechi, M. Kuno, P. V. Kamat, *Journal of the American Chemical Society* **2008**, 130, 4007-4015.
- [13] N. Wu, J. Wang, D. N. Tafen, H. Wang, J.-G. Zheng, J. P. Lewis, X. Liu, S. S. Leonard, A. Manivannan, *Journal of the American Chemical Society* **2010**, 132, 6679-6685.
- [14] H. B. Wu, H. H. Hng, X. W. D. Lou, *Advanced Materials* **2012**, 24, 2567-2571.
- [15] X. Wang, Q. Xu, M. Li, S. Shen, X. Wang, Y. Wang, Z. Feng, J. Shi, H. Han, C. Li, *Angew. Chem. Int. Ed.* **2012**, 51, 13089-13092.
- [16] Q. Li, B. Guo, J. Yu, J. Ran, B. Zhang, H. Yan, J. R. Gong, *Journal of the American Chemical Society* **2011**, 133, 10878-10884.
- [17] K. Wu, H. Zhu, Z. Liu, W. Rodríguez-Córdoba, T. Lian, *Journal of the American Chemical Society* **2012**, 134, 10337-10340.
- [18] F. N. Sayed, O. Jayakumar, R. Sasikala, R. Kadam, S. R. Bharadwaj, L. Kienle, U. Schürmann, S. r. Kaps, R. Adelung, J. Mittal, *J. Phys. Chem. C* **2012**, 116, 12462-12467.
- [19] M. Murdoch, G. Waterhouse, M. Nadeem, J. Metson, M. Keane, R. Howe, J. Llorca, H. Idriss, *Nature chemistry* **2011**, 3, 489-492.

- [20] S. Onsuratoom, T. Puangpetch, S. Chavadej, *Chemical Engineering Journal* **2011**, *173*, 667-675.
- [21] I. Tsuji, H. Kato, A. Kudo, *Angewandte Chemie* **2005**, *117*, 3631-3634.
- [22] K. Maeda, N. Sakamoto, T. Ikeda, H. Ohtsuka, A. Xiong, D. Lu, M. Kanehara, T. Teranishi, K. Domen, *Chemistry-a European Journal* **2010**, *16*, 7750-7759.
- [23] T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Hørch, I. Chorkendorff, *Science* **2007**, *317*, 100-102.
- [24] J. Yu, J. Ran, *Energy. Environ. Sci.* **2011**, *4*, 1364-1371.
- [25] J. Yu, Y. Hai, B. Cheng, *J. Phys. Chem. C* **2011**, *115*, 4953-4958.
- [26] X. Huang, Z. Zeng, S. Bao, M. Wang, X. Qi, Z. Fan, H. Zhang, *Nature communications* **2013**, *4*, 1444.
- [27] D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. Alves, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda, *Nature materials* **2013**, *12*, 850-855.
- [28] K. Kam, B. Parkinson, *The Journal of Physical Chemistry* **1982**, *86*, 463-467.
- [29] H. Tributsch, J. Bennett, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1977**, *81*, 97-111.
- [30] B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Hørch, I. Chorkendorff, J. K. Nørskov, *Journal of the American Chemical Society* **2005**, *127*, 5308-5309.
- [31] A. Kudo, Y. Miseki, *Chemical Society Reviews* **2009**, *38*, 253-278; bF. E. Osterloh, *Chemistry of Materials* **2007**, *20*, 35-54.
- [32] F. E. Osterloh, *Chemistry of Materials* **2007**, *20*, 35-54.
- [33] X. Chen, S. Shen, L. Guo, S. S. Mao, *Chemical reviews* **2010**, *110*, 6503-6570.
- [34] Y. Li, L. Tang, S. Peng, Z. Li, G. Lu, *Crystengcomm* **2012**, *14*, 6974-6982.
- [35] T. Peng, K. Li, P. Zeng, Q. Zhang, X. Zhang, *J. Phys. Chem. C* **2012**, *116*, 22720-22726.
- [36] C. Nasr, S. Hotchandani, W. Y. Kim, R. H. Schmehl, P. V. Kamat, *The Journal of Physical Chemistry B* **1997**, *101*, 7480-7487.
- [37] X. Zong, H. Yan, G. Wu, G. Ma, F. Wen, L. Wang, C. Li, *J. Am. Chem. Soc.* **2008**, *130*, 7176-7177.

- [38] K. Chang, Z. Mei, T. Wang, Q. Kang, S. Ouyang, J. Ye, *ACS nano* **2014**, 8, 7078-7087.
- [39] J. Zhang, Z. Zhu, X. Feng, *Chemistry-a European Journal* **2014**, 20, 10632-10635.
- [40] X. Zong, J. Han, G. Ma, H. Yan, G. Wu, C. Li, *J. Phys. Chem. C* **2011**, 115, 12202-12208.

Chapter 2

Literature Review

This chapter first reviews the mechanism and main processes of photocatalytic water splitting. After that, the roles of co-catalysts in heterostructure photocatalysts will be introduced. Then special attention is paid to transition metal dichalcogenides (TMDs) materials. Recent research progress of design and synthesis of high efficient photocatalysts using TMDs as co-catalysts will be reviewed. Although using TMDs as co-catalysts greatly improve the activity of semiconductor photocatalyst, there are some questions that need to be addressed. For example, the used MoS₂ nanosheets as co-catalyst often show large lateral sizes and/or multilayered structures, which greatly limit their application as co-catalysts towards hydrogen evolution reaction (HER) due to the low exposure of active edge sites. Thus, the synthesis of photocatalysts containing layered TMD nanosheets with large number of active sites remains a challenge. The focus of this thesis is the synthesis of TMD based heterostructures which expose abundant active sites for photocatalytic hydrogen evolution.

2.1 Overview

Today, most of the energy consumption depend on the nonrenewable fossil fuels. The combustion of fossil fuels, such as coal, nature gas and oil, has led to serious environmental problems, ranging from air/water pollution to global warming. To solve the energy crisis and environmental problems for our modern society, it's important to find a clean, sustainable energy resource to replace the fossil fuels. Solar energy has long been considered as endless and clean energy resource. Photovoltaic devices which can transform the solar energy into electricity is now the most popular way to harvest solar energy. However, the electricity must be used immediately or stored in a secondary device. An alternative and more attractive strategy to harvest solar energy is to store the energy into molecular bonds. In this regard, water splitting into hydrogen and oxygen using semiconductor photocatalysts under light irradiation is the most promising approach.

Great efforts have been devoted to develop high efficient semiconductor photocatalyst for water splitting since the photoelectrochemical water-splitting over TiO_2 electrode was discovered by Fujisima in 1972. Although great progress have been achieved, the efficiency of photocatalytic water splitting is far from satisfied. Developing effective photocatalysts still remain challenge.

2.2 Basic Principles of Photocatalytic Hydrogen Evolution

2.2.1 Fundamental Mechanism of Water Splitting

The overall water splitting reaction includes two half-reactions, the hydrogen evolution reaction (Equation 2.1) and the oxygen evolution reaction (Equation 2.2).^[1, 2] The standard Gibbs free energy and redox potential of the multi-electron water splitting were shown in Equation 2.3. The split of water into hydrogen and oxygen is an uphill reaction since it needs a positive Gibbs free energy change of 237 kJ/mol.^[3]

Figure 2.1 Demonstration of photocatalytic water splitting on a semiconductor surface decorated with hydrogen and oxygen evolution co-catalysts. Reprinted with permission from ref. 4.

The fundamental principle of photocatalytic water splitting over a semiconductor photocatalyst surface under light irradiation was shown in Figure 2.1. To facilitate the two half reactions of water splitting by photo-generated charge carriers, the matching of the band structure and the position of the conduction band (CB) and the valence band (VB) are critical. Thermodynamically, both the oxidation and reduction potentials of H_2O should lie within the band gap of the semiconductor. The bottom level of the CB must be at more negative potential than the reduction potential of H^+ to H_2 (0 V vs normal hydrogen electrode (NHE) at pH = 0), and the top level of VB has to exceed the oxidation potential of H_2O to O_2 (1.23 V vs NHE). Therefore, for effective the water splitting, a semiconductor photocatalyst should have a minimum band gap energy (E_g) of 1.23 eV (<1000 nm). However, due to the energy losses, a much larger band gap is often required for appreciable water splitting reaction. The kinetic overpotentials associated with each electron transfer and gas evolution step are required to facilitate the HER and OER. Besides, the

semiconductor photocatalysts should have a small enough band gap to efficiently utilize the solar energy. Thus the E_g of a single semiconductor photocatalyst should lie in the range of 2.0 to 3 eV. [5-7]

2.2.2 Main Processes of Photocatalytic Hydrogen Evolution

Figure 2.2 shows the main processes in a photocatalytic HER reaction. These processes include absorption of photons by semiconductor, production of photo-excited electrons and holes (charge carriers), recombination of the photo-generated charge carriers, separation of excited charge carriers, transfer of the charge carriers, trap of the charge carriers, and transfer of photo-excited charge carriers to water and other molecules. The total efficiency of HER are affected by the above-mentioned processes.

Semiconductors have a band structure in which CB is separated from the VB by a band gap with certain energy, as shows in Figure 2.2.[8] When the semiconductor material absorbs a photon which energy is larger than that of the semiconductor's band gap, photo-excited electrons and holes are produced in CB and VB. The number of photo-generated electrons in the water/photocatalyst interface in reducing water is the determined factor of the final HER efficiency. Obviously, any process that involve in the photo-excited process should be taken into consideration to act positively to improve the activity of the HER in a photocatalyst system. And any other steps that consume photo-generated electrons must be avoided to improve the total efficiency. The width of band gap and the position of the VB and CB of a semiconductor are critical points, the semiconductor should have a small band gap to absorb as much solar energy as possible. And after excited by the photons, instead of generating heat, the semiconductor photocatalyst should possess the ability to generate excited charge carriers in high efficiency.

Charge recombination and separation/migration inside the semiconductor are two critical processes that greatly affect the total efficiency of the HER after photo-excited charge carriers are created. These two processes are competitive. The charge recombination process, including surface and bulk recombination, is classified as a deactivation process

that reduces the photo-excited charge carriers by emitting light or generating heat. On the other hand, charge separation and migration is an activation process, it's effective for HER. Only the charge migrate to the surface of semiconductor can be used for desired catalytic reaction. Effective charge separation and fast charge transportation are fundamentally important for photocatalytic HER. To design an effective photocatalyst, any method that improve the charge separation and transportation must be taken into consideration. The crystal structure, particle size and crystallinity of the photocatalysts can strong affect these two processes. Defects in materials act as trapping and recombination centers between photo-excited electrons and holes, resulting in an unsatisfied photocatalytic activity. If the particle size becomes small the recombination probability would be decreased due to the shortage of the charge diffusion pathway.

Figure 2.2 Processes in photocatalytic water splitting. Reprinted with permission from ref. 8.

The products of water splitting, H_2 and O_2 , can be easily recombined back to water, this phenomena is called “back reaction”, which is a negative process and should be avoided.^[9, 10] The back reaction can be suppressed by two main methods, the first one is adding sacrificial agents into the photocatalyst systems. The second approach is to create a separation of the photoactive sites for OER and HER on the surface of the photocatalysts.

Taking into consideration of the fundamental mechanism and main processes in photocatalytic HER, there are two key factors for design an efficient semiconductor photocatalyst for the photocatalytic HER under visible light irradiation: (1) a suitable band gap with proper band position. The band gap should neither too small no too large ($2.0 \text{ eV} < E_g < 3.0 \text{ eV}$) to both provide energetic electrons and harvest visible light. (2) Photo-generated charge carries in the semiconductor photocatalyst should be separated efficiently in order to decrease the possibility of charge recombination.

2.3 Co-catalysts in Photocatalytic Hydrogen Evolution

2.3.1 Heterostructure Photocatalysts

As discussed in section 2.2, to construct an efficient and stable photocatalyst for photocatalytic HER, the semiconductor photocatalyst should meet certain requirements. Firstly, the semiconductor should have a large enough band gap with proper band position to provide energetic electrons (theoretically $E_g > 1.23 \text{ eV}$, typically $E_g > 2.0 \text{ eV}$). Meanwhile, the semiconductor should possess a small band gap to efficient utilize the solar energy ($E_g < 3.0 \text{ eV}$). Secondly, the semiconductor should have the ability to efficiently separate the photo-generated charge carries. Furthermore, the semiconductor photocatalyst should have lots of active sites for desired catalytic reactions for efficient utilization of the photo-generated charge carriers. Lastly, for practical application, the long-term stability of photocatalyst is also very important. There should be a mechanism to protect the semiconductor from photo-corrosion. A single component photocatalyst is unlikely to satisfy all these requirements. Semiconductor heterostructure, which integrate distinct components with different functionalities into one system, can integrate the advantages of different components together and overcome the disadvantages of photocatalyst with single component.^[11-14] Thus the design of semiconductor heterostructure photocatalyst have become the focus of recent research.^[15-17]

Generally, semiconductor heterostructure photocatalyst can offer several potential benefits for enhancing the performance of photolytic HER, including (1) enhance the light

absorption, (2) promote the charge separation and transportation, (3) improve the stability and (4) act as co-catalyst. Taking the two-component heterostructure as example, the formed semiconductor heterostructures can be divided into three types, as shows in Figure 2.3.^[18] In type I heterostructure, the VB of component B is lower than that of component A, while the CB of component B is higher than that of component A. As electrons and holes obtain energy by moving down and up respectively, the photo-generated electrons are transfer from CB of component B (CB-B) to CB of component A (CB-A), while holes are also transfer from VB of component B (VB-B) to VB in component A (VB-A). Thus, all charge carriers are accumulated in component A, which results in the inefficient charge separation and thus do not improve the photocatalytic activity. The type II heterostructure is an idea model which have the optimal band positions for efficient charge separation and thus leads to enhanced photocatalytic activity. The photo-generated electros are transfer from CB-B to CB-A, and holes are transfer from VB-A to VB-B. In this case the photo-generated charge carriers are spatially separated from each other, which greatly reduce the recombination probability and increase the lifetime of electrons. Finally, the charge transfer in a type III heterostructure is the same with type II heterostructure, except the band positions are further set off.

Figure 2.3. Different types of heterostructures. Reprinted with permission form ref. 18.

The first-described and most studied semiconductor heterostructure is the CdS/TiO₂ system.^[19] TiO₂ is a very good photocatalyst due to the low coast and high chemical stability, which is the materials that Fujishima and Honda used to fist demonstration of photocatalytic water splitting.^[20] However, TiO₂ is a large band gap semiconductor ($E_g > 3.6$), it's only active under UV light irradiation. On the contrary, CdS is a promising semiconductor since it possesses an optimal band gap (around 2.4 eV) for effective

utilization of solar energy. The CdS/TiO₂ is a type II heterostructure, the photo-generated electrons are transfer from CB of CdS to TiO₂, and the holes are transfer from VB of TiO₂ to CdS, as shows in Figure 2.4. Under visible-light irradiation, only CdS are excited and produce electrons in CB, while no charge are generated in TiO₂. Thus photo-generated holes are only created in the VB of CdS nanocrystals (NCs), and accumulate at VB due to the higher VB positon of CdS than that of TiO₂. And the photo-generated electrons are transfer to CB of TiO₂, this kind of spatially separated electrons and holes reducing the recombination probability of photo-generated charge carriers. The charge transfer from CdS to TiO₂ is very fast, it was first reported to happen within 20 ps and now known to be completed in < 2 ps.^[21-23]

Figure 2.4 Charge transfer in CdS/TiO₂ heterostructure under visible-light irradiation.

Many other semiconductor heterostructures with improved photocatalytic activities have reported, including CdS-ZnO,^[24-27] CdS-K₄Nb₆O₁₇,^[28] CdS-AgI,^[23] Cd₃P₂-TiO₂/ZnO, CdS-CdSe^[29], CdSe-ZnS,^[30] ZnO/ZnS,^[31] ZnO-ZnSe^[32] and so on. A comprehensive study of multiple heterostructures (PbS, CdS, Ag₂S, Sb₂S₃, Bi₂S₃@ TiO₂, Ta₂O₅, Nb₂O₅, ZnO, SnO₂) was carried out by Weller et al.,^[33] in their study only PbS and CdS were found to be efficient.

The construction of a semiconductor heterostructure is not just mix different components together, a proper structure design is very important. For example, Amirav et al.^[34] reported a three-component heterostructure composed of a CdS nanorod with a Pt-tipped and an embedded CdSe seed, as shows in Figure 2.5a. In such structure, the photo-generated electrons are transferred to Pt tip, while the holes are three-dimensionally confined in the CdSe seed. Thus the electrons are spatially separated with the holes over

the three different components. By fine tuning the length of CdS nanorod and the size of CdSe seed, they were able to significantly increase the activity for HER compare with that of the unseeded rods, an apparent quantum yield of 20% at 450 nm was achieved (Figure 2.5b). And the stability was also improved compared to CdS rods without a CdSe seed.

Figure 2.5 (a). Schematic illustration and TEM images of the multicomponent heterostructure. Scale bar: 20 nm. (b) Relative quantum efficiency for HER using different samples. Reprinted with permission from ref. 34.

To summarize, construction of semiconductor heterostructure photocatalyst is a very promising way to improve the photocatalytic activity by enhanced light absorption, electron-hole separation. The stability can also be improved, it is possible to minimize the harmful side reactions that lead to decreased stability of semiconductor. Some semiconductors like MoS₂ can act as co-catalysts to improve the HER activity, which will be discussed in next session.

2.3.2 Roles of Co-catalysts in Photocatalytic Hydrogen Evolution

Co-catalysts play important roles in the photocatalytic HER process.^[9,35] Loading semiconductor photocatalysts with co-catalysts can provide active sites for photocatalytic process, improve the charge separation and the stability of photocatalysts.

Photocatalytic water splitting is a catalyst process. The activation energy or overpotential for hydrogen or oxygen evolution could be lowered by co-catalysts on the

surface of semiconductor photocatalyst, as shown in Figure 2.6. The procedure of O_2 evolution is a complex 4-electron transfer process together with the reduction of $4 H^+$ from H_2O molecules to form an O-O bond. Thus, the oxygen evolution reaction is considered as the most difficult step in a photocatalytic water splitting process. Therefore, the efficient of photocatalytic O_2 evolution reactions would be notably enhanced if co-catalysts with low O_2 evolution overpotential are loaded.

Figure 2.6 Roles of catalyst in a catalyst reaction.

What is more, the charge carrier recombination probability would be decreased since the co-catalyst/semiconductor interface could assist the electron-hole separation. The photo-generated electrons on CB of a semiconductor are transferred to the H_2 evolution active sites on co-catalysts and reduce protons to H_2 molecules, while photo-excited holes on VB of the semiconductor transfer to the O_2 evolution active sites on co-catalyst and oxidize H_2O to form O_2 . The formation of a suitable heterostructure between the co-catalyst and the semiconductor is critical for improving the electron-hole separation and migration from the semiconductor to the co-catalyst. Firstly, the relative energy level at the heterostructure interface dominate the charge carrier transport direction and separation efficiency. Secondly, the size of the heterostructure is also important, the charge transfer distance can be reduced with a short distance between the semiconductor and the co-catalyst, thus leads to the effective suppression of the bulk recombination and finally enhancing the overall efficiency.

The stability of semiconductor photocatalysts can be increased since co-catalysts could suppress the photo-corrosion. For example, many visible-light-responsive semiconductors, such as transition metal sulfides and nitrides are easy to be oxidized by photo-generated holes, resulting in the self-decomposition, which is also known as photo-corrosion. The loading of co-catalysts on these semiconductors surface could inhibit their photo-corrosion by extracting the photo-generated holes for O_2 evolution, therefore improve the durability of semiconductors.^[36-39]

Figure 2.7 The relationship between the loading amount of co-catalyst and the activity for photocatalyst process. Reprinted with permission from ref. 4.

There are many factor that affect the efficiency of using co-catalyst, such as loading amount, the size and nanostructure of the co-catalyst. Figure 2.7 illustrate the relationship between the efficiency of photocatalyst reaction and the loading amount of co-catalyst.^[4] Despite the synthesis method, the type of photocatalyst and co-catalyst, there is a volcano-type trend between them. At the first beginning, the photocatalytic activity was gradually enhanced by decorating co-catalyst on the surface of a semiconductor. This co-catalyst-semiconductor system achieved the highest activity when the loading amount of co-catalyst reaches the optimized value. However, the activity was then decrease with further increasing the loading amount. Several reasons may explain this phenomena. Firstly, the surface active sites for catalyst maybe covered when large amount of co-catalyst are loaded. And contact between semiconductor with sacrificial reagents or water molecules may be

hindered. Secondly, the incident light may be shielded by the thick coating of co-catalyst, results in the inefficient light absorption and thus reduce the photo-generated electrons inside the semiconductors. Thirdly, co-catalyst at high loading amount could act as recombination centers, thus decrease the catalytic activity.

The size of the co-catalyst is another important factor. Generally, at the same loading amount, co-catalyst with smaller size have a larger surface area and can provide more catalytic active sites, thus lead to the higher activity. What is more, the recombination of electrons and holes is more favorable in large particles of co-catalyst than in small ones. In some cases, small size of co-catalyst may benefit to the charge transfer between the semiconductor and the co-catalyst, for example, the electron-tunneling effect. Several studies demonstrated that the small size and high dispersion of the decorated co-catalyst can lead to the great improvement of the catalytic activity.^[40-44]

The interface structure between the semiconductor and the co-catalyst was found to have great influence to the charge transfer.^[45] Taking CdS-Pt heterostructure as an example, Pt acts as very good co-catalyst which promote a fast electron transfer from the CdS counterpart.^[36] However, the growth of Pt nanoparticle on CdS nanorod surface is non-epitaxial growth.^[46] The non-epitaxial nature between these two components gives rise to a large density of interfacial defects, which dissipate the excitation energy. Thus, engineering the interface structure via molecular epitaxy is the key to creating efficient semiconductor photocatalyst. However, most of the reported semiconductor heterostructures exhibit a random orientation between different components.^[47,48] Strategies to construction epitaxial heterostructures are urgent needed.

2.4 TMD as Co-catalysts in Photocatalytic Hydrogen Evolution

Most of the photocatalyst systems using precious metals, such as Pt,^[49-54] Ru,^[55] Pd,^[56,57] Rh^[58,59] and Au,^[40,60] as co-catalysts to achieve high activities. However, these metals are rare and expensive, which greatly limit their application. Thus it is urgent to develop an alternative co-catalyst with low price and high activity.^[61-63]

Transition metal dichalcogenides (TMDs) as typical graphite-like layered materials, have attracted tremendous interest due to their diversified components and remarkable optical and electronic properties.^[64] The TMD materials have a general formula of MX_2 , in which M represents transition metal atoms (group IV, V and IV), and X represents the chalcogen atoms (S, Se and Te). As shows in Figure 2.8, the crystal structure of TMD composed of sandwiched X-M-X layer held together by Van der Waals force. Most of the TMD materials, such as MoS_2 , MoSe_2 , WS_2 and WSe_2 , have different phases structures, i.e., 1T, 2H and 3R.^[67-71] The unit cell of 1T structure contains one layer MS_2 in tetragonal symmetry, octahedral coordination. And the 2H and 3R contain two and three layers per unit cell stack in the hexagonal symmetry with trigonal prismatic coordination and rhombohedral symmetry with trigonal prismatic coordination, respectively (as shows in Figure 2.8).

Figure 2.8 Crystal structure of transition metal dichalcogenides.

Figure 2.9 (a) STM image of MoS_2 NSs on gold [111]. (b) A schematic model of a NSs exposing both Mo and S edges from top and side view. Reprinted with permission from ref. 74.

MoS₂ and WS₂ are typical TMD materials. The use of MoS₂ as catalyst for electrochemical HER was started in the 1970s by Tribustsch.^[72] DFT studies^[73] shows that the edges of MoS₂ sheets are the active sites for hydrogen evolution, especially the [1 010] Mo-edges have the most advantageous hydrogen binding energy. This theoretical calculation indicates that the edges on MoS₂ are responsible for the activity, which was verified by Thomas and co-workers.^[74] In this study, MoS₂ single layer with a truncated triangular shape exposing [1 010] Mo-edges and [1 110] S-edges was deposited on Au [111] surface (Figure 2.9). The total edge length was quantified by STM, and electrochemical measurements showed that the edge length of MoS₂ catalyst was in linearly with the current density of electrocatalytic measurements for hydrogen evolution (Figure 2.10).

Figure 2.10 Plot of Exchange current density with the coverage area of MoS₂ (left) and (right) edge length of MoS₂. Reprinted with permission from ref. 74.

WS₂ is also a layered material with a structure very similar with MoS₂, which also shows efficient catalytic activity towards HER.^[75-79] In electrocatalytic hydrogen evolution, the lowest Tafel slope of 1T WS₂ electrodes is about 60 mV per decade.^[80] For 1T MoS₂ electrodes, the Tafel slope is about 55 to 60 mV per decade. These values are quite comparable, indicating that the mechanisms responsible for H₂ production should be similar.

2.4.1 MoS₂ as Co-catalyst for Photocatalytic Hydrogen Evolution

MoS₂ is not a photocatalyst for hydrogen evolution reaction. However, in the presence of photosensitizers, they show activity for hydrogen evolution as co-catalysts.^[81-88] Poznan et al.^[89] synthesized SiO₂ supported MoS₂ (MoS₂/SiO₂) by decomposition of MoS₃/SiO₂ in argon and hydrogen at high temperature. MoS₂/SiO₂ did not manifest any photoresponse. However, in the presence of TiO₂ and CdS/SiO₂ as sensitizers, these samples produced hydrogen under light irradiation. Hydrogen evolution rates up to 15 mL H₂ per hour (1g catalyst) were reported. And compared with Pt/SiO₂, MoS₂/SiO₂ showed better hydrogen evolution activity and stability under the same condition. The affection of annealing temperature was also studied. It was found that the catalytic activity of MoS₂/SiO₂ decreased with the increased of calcination temperature. This is because MoS₂/SiO₂ sample obtained at low annealed temperature possesses more structural defects on the surface, which is also the active sites for hydrogen evolution. To date, many semiconductors, including CdS, ZnIn₂S₄, g-C₃N₄, TiO₂, ZnO, and SrTiO₃ *et. al.*, have been decorated with MoS₂ as co-catalyst for improving the H₂ evolution activity.

Figure 2.11 (a) TEM image of 1 wt% MoS₂/CdS obtained at 733 K and (b) the HR-TEM image took in the white square in image (a). Reprinted with permission from ref. 90.

Zong et al.^[90] directly deposited MoS₂ on the surface of photosensitizer CdS. The sample (MoS₂/CdS) was prepared by impregnating CdS into a water solution of

(NH_4) $_2\text{MoS}_4$, followed by a heat treatment process in the presence of H_2S at high temperature ranging from 443 to 773 K for 2 h. And the amount of MoS_2 loaded on CdS can be controlled. Figure 2.11 shows a HR-TEM image of 1 wt% MoS_2/CdS obtained at 773 K. It can be clearly observed that multi-layered MoS_2 with a layer space of about 0.61 nm were grown on the surface of CdS . The evaluation of photocatalytic activity toward hydrogen evolution was carried out with an aqueous suspension of MoS_2/CdS in 20% lactic acid solution. The highest rate of hydrogen production on MoS_2/CdS was recorded when loaded with only 0.2% wt of MoS_2 , which is nearly 36 times compare with that of pure CdS . A H_2 production of about $520 \mu\text{mol}\cdot\text{h}^{-1}$ was recorded when 0.1 g MoS_2/CdS was used. And the activity of 0.2 wt% MoS_2/CdS is even higher than CdS loaded with 0.2 wt% of different co-catalysts, which are MoS_2/Pt , MoS_2/Ru , MoS_2/Rh , MoS_2/Pd and MoS_2/Au , as showed in Figure 2.12.

Figure 2.12 Rate of photocatalytic HER rate on CdS decorated with 0.2 wt% of several types of co-catalysts. Reprinted with permission from ref. 90.

The amount of MoS_2 loaded on CdS is a critical point that affects the photocatalytic activity. The catalytic activity first increased and then decreased with the increased amount of MoS_2 decorated on CdS . There is an optimal loading amount, and further increase the amount of MoS_2 lead to decreased activity. This observation indicates that the contact between MoS_2 and CdS is critical for the interelectron transfer between these two

components. Therefore, the amount of MoS_2 should not be too thick or it will cover a large area of the surface of CdS .

Zong et al.^[91] also reported the use of colloidal MoS_2 nanoparticles as co-catalyst for visible light driven hydrogen evolution. Colloidal MoS_2 nanoparticles with diameters of less than 10 nm were prepared by solvothermal treatment of $(\text{NH}_4)_2\text{MoS}_4$ dissolved in methanol using PVP as protecting agent and N_2H_4 as a reductant. The as-prepared MoS_2 nanoparticles were amorphous as indicated by selected area electron diffraction. Different from the hydrogen evolution systems discussed above, the evaluation of HER activity were studied in a 2:1 acetonitrile-methanol solution instead of an aqueous solution. The reaction was carried out under visible light irradiation in a solution containing $\text{Ru}(\text{bpy})_3^{2+}$ as photosensitizer and ascorbic acid as sacrificial agent, as shows in Figure 2.13. When using colloidal MoS_2 prepared at 473 k, the highest turnover number for H_2 evolution was recorded to be 100 based on $\text{Ru}(\text{bpy})_3^{2+}$, which is much higher than traditional $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalyst.

Figure 2.13 Possible reaction mechanism for photocatalytic HER of the $\text{Ru}(\text{bpy})_3^{2+}$ - MoS_2 - H_2A system. Reprinted with permission from ref. 90.

As discussed above, forming a multiphase or multicomponent heterostructure usually increases the photocatalytic activity, but forming a p-n junction between p-type semiconductor and n-type semiconductor can further enhance the charge separation. Fanke et al.^[92] reported a nanoscale p-n junction of p-type MoS_2 / n-type nitrogen-doped reduced graphene oxide (n-rGO). In this work, p-type MoS_2 NSs with size of about 5-20 nm were

deposited on n-type n-rGO through a hydrothermal method. Free-standing MoS₂ and MoS₂ deposited on undoped r-GO were prepared by similar method. Photoelectrochemical measurement shows that p-MoS₂/n-rGO photocatalyst shows much higher photocatalytic activity than p-MoS₂/undoped-rGO composite. By N-doping, the rGO was transformed from a passive support to an active component of the heterostructure, and all three steps in photocatalysis were enhanced.

Jian et al.^[93] also reported a p-n junction formed between p-type MoS₂ and n-type CdS. 2D MoS₂/CdS sandwiched p-n heterostructures were prepared by growth of CdS on 2D layered MoS₂ NSs in a solvothermal reaction. To investigate the recombination of photo-generated electrons and holes, photoluminescence test was carried out. Results show that the photoluminescence intensity of MoS₂/CdS p-n junction decreased dramatically compared with pure MoS₂ and CdS under irradiation of a wavelength of 390 nm. This result proves that the formation of a p-n junction between p-type MoS₂ and n-type CdS facilitates the separation and transportation of photo-generated electrons and holes.

Figure 2.14 (a) Illustration of the charge transfer in the MoS₂/G-CdS heterostructure. (b) Amount of H₂ generation in 5 h. Reprinted with permission from ref. 94.

Recently, a heterostructure consisting of CdS nanocrystals (NCs) grown on the surface of a MoS₂/graphene composite was reported by Kun et al.^[94] Through the optimizing of each component proportion, a highest photocatalytic H₂ evolution activity of MoS₂/G-CdS was achieved when the content of the MoS₂/graphene co-catalyst is 2.0 wt %. A 1.8 mmol·h⁻¹ hydrogen evolution rate was recorded in lactic acid solution, which is not only

higher than MoS₂/G-CdS in Na₂S-Na₂SO₃ solution, but also much higher than that of using Pt as co-catalyst (Figure 2.14 (b)). Figure 2.14 (a) illustrates a possible mechanism for the high H₂ evolution rate of the MoS₂/G-CdS composite. The photo-excited electrons of CdS are generated and transferred to the surface under visible light irradiation. Some of the electrons transferred directly to the edges of MoS₂ and reacted with adsorbed H⁺ to produce H₂, the unsaturated active S atoms at the edge of MoS₂ are the active sites which can accept electrons and catalyze the H₂ generation. Other electrons on the MoS₂/graphene basal planes can be transferred to the edge of MoS₂ through the graphene sheets and then react with H⁺. Graphene here acts as a “highway” for electron transfer.

2.4.2 WS₂ as Co-catalyst for Photocatalytic Hydrogen Evolution

Although electrochemical studies show that the WS₂ possess similar activity towards HER with MoS₂, there are few reports about using WS₂ as co-catalysts in photocatalytic hydrogen evolution.^[95-99] Xu et al.^[89] reported the preparation of WS₂/CdS composite material for photocatalytic H₂ evolution under visible light irradiation. The preparation method is similar with that of MoS₂/CdS reported by the same group. By impregnating CdS with a water solution of (NH₄)₂WS₄, followed by a treatment in the presence of H₂S gas at high temperature, WS₂/CdS composites with different amount of WS₂ can be obtained. Photocatalytic H₂ evolution under visible light irradiation shows that the activity of WS₂/CdS composites increased up to 28 times when the CdS was loaded with only 1.0 wt% of WS₂ (Figure 2.15c). Electrochemical measurements indicates that the significantly improvement of H₂ evolution rate of WS₂/CdS composites mainly results from the heterojunction formed between WS₂ and CdS. As illustrated in Figure 2.15(d), the WS₂ co-catalyst is believed to enhance the charge separation, photo-generated electrons can transfer from CdS to the WS₂ sheets, and react with protons to form H₂.

Most of the attention has been focused on semiconducting WS₂ and MoS₂, which possess a prismatic coordination for metal atom (known as 2H structure). By using the lithium exfoliation method, it is possible to prepare a different structure with an octahedral coordination (known as 1T structure), which exhibits metallic properties. Recently, 1T WS₂ or MoS₂ was found to be more efficient towards hydrogen evolution reaction

compared with their 2H structures.^[68,80] Benoit et al.^[75] recently developed a wet chemical method to prepare monolayer WS₂ with controllable crystal phase, e.g. 1T or 2H structure. In this report, WCl₆ was used as tungsten source and was dissolved in a solution contain oleylamine and oleic acid. By injecting CS₂, which is the sulfide source, into the above solution at 320 degree, WS₂ with 1T phase can be obtained. 2H WS₂ can be prepared when hexamethyldisilazane (HMDS) was introduced in the reaction, as illustrated in Figure 2.16a. In order to compare the photocatalytic activity of semiconducting and metallic WS₂ nanostructure, TiO₂-WS₂ nanocomposites was prepared by using P25-TiO₂ as platform and loaded with 1T- or 2H- WS₂. TiO₂ acts as the light harvester in the case of TiO₂-1TWS₂ composite. Upon light irradiation, the photo-generated electron will be transferred to the 1T-WS₂ to react with proton to form H₂. On the other hand, 2H WS₂ acts as the light harvester in TiO₂-2HWS₂ composite. The photo-generated electron was transferred from 2H WS₂ to TiO₂ after absorption of a photon. The experimentally determined electronic band alignment between TiO₂, 1T WS₂ and 2H WS₂ was schematically illustrated in Figure 2.16b.

Figure 2.15 (a-b) TEM images of WS₂/CdS composite. (b) Photocatalytic activities of WS₂/CdS with different WS₂ loading amount. (c) Proposed Reaction Mechanism for Photocatalytic H₂ Production on WS₂/CdS Catalyst. Reprinted with permission from ref. 89.

Figure 2.16 (a) Schematically illustrated the preparation methods. (b) Band structure of TiO₂-WS₂. Reprinted with permission from ref. 75.

The photocatalytic activity of P25 TiO₂, TiO₂-1TWS₂ and TiO₂-2HWS₂ was conducted using methanol as sacrificial agent under illumination with a 300 W Xe source with an AM 1.5 filter. The produce of hydrogen gas at a rate of 700 μmol g⁻¹·h⁻¹ was record with using bare P25 TiO₂ as catalyst. Very impressively, the rate increased by more than 3-fold to 2570 umol g⁻¹·h⁻¹ when integrated with 1T-WS₂ NSs at an optimized loading of 1 wt%. However, the hydrogen evolution rate decreased to 225 μmol g⁻¹·h⁻¹ when the same P25 TiO₂ was loaded with 2H WS₂.

2.5 Questions to Answer Based on Literature

As discussed in the aforementioned literature review, great progress has been made in the synthesis of heterostructure photocatalysts using TMDs as co-catalysts. The photocatalytic activity has been greatly improved. Nevertheless, some questions are still need to be addressed.

Several reports have demonstrated that a p-n junction can be formed between CdS NCs and MoS₂ NSs, which results in great improvement of the activity towards the photocatalytic H₂ production. However, the used MoS₂ NSs often show a large lateral size and/or multilayered structure, which greatly limit their activity towards HER due to the low exposure of the active edge sites. Therefore, synthesis of photocatalysts containing layered MS₂ NSs with large number of active sites remains challenge.

What is more, previous works about prepare CdS-MoS₂ composite materials were realized through a high temperature treatment the presence of toxic H₂S gas using (NH₄)₂MoS₄ as a precursor. Multi-step experiments may needed. Thus, a relatively simple method to synthesis CdS-MoS₂ composites materials is highly desired.

2.6 PhD in Context of Literature

The focus of this thesis is synthesis of TMD based heterostructures for photocatalytic hydrogen evolution. The aforementioned questions were addressed by developing an easy method to fabricate CdS-MoS₂ and CdS-WS₂ heterostructures. The photocatalytic activity under visible light irradiation was evaluated. The contributions of this thesis to this research direction are described below.

First, a one-pot wet chemical method to synthesis CdS-MoS₂ and CdS-WS₂ heterostructure was developed. In the obtained heterostructure, single-layer MoS₂ and WS₂ NSs with size from 5-10 nm were selective grown on the Cd-rich (0001) surface of a hexagonal CdS NCs. The heterostructure showed improved photocatalytic activity towards H₂ production with excellent durability, arising from the abundant active sites of single-layer MoS₂ and WS₂ NSs and the inherent p-n heterojunction formed between MS₂ and CdS NCs. This method could be used for preparation of other CdS-TMD heterostructures for future clean energy applications.

Second, a wet-chemistry method was developed for synthesis of a new type of heterostructure, i.e. the TMD NSs including MoS₂ and MoSe₂ is vertically epitaxially grown on the longitudinal direction of 1D Cu_{2-x}S nanowires (NWs). The lateral size of TMD NSs can be tuned from less than 2 nm to ~10 nm by changing the amount of sulfur or selenide precursor. After cation exchange of Cu_{2-x}S to CdS NWs, the heterostructures of CdS-MoS₂ nanocomposites still remain. As a proof-of-concept, the obtained CdS-MoS₂ nanocomposites have been used for photocatalytic hydrogen evolution under the visible light irradiation (>420 nm). The obtained CdS-MoS₂ nanocomposites with 7.7 wt% of

MoS₂ can produce H₂ up to 4647 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is about 58 times that produced by pure CdS NWs.

References

- [1] X. Chen, S. Shen, L. Guo, S. S. Mao, *Chem. Rev.* **2010**, *110*, 6503-6570.
- [2] B. M. Hunter, H. B. Gray, A. M. Müller, *Chem. Rev.* **2016**, *116*, 14120-14136.
- [3] X. Li, J. Yu, J. Low, Y. Fang, J. Xiao, X. Chen, *J. Mater. Chem. A* **2015**, *3*, 2485-2534.
- [4] J. Ran, J. Zhang, J. Yu, M. Jaroniec, S. Z. Qiao, *Chem. Soc. Rev.* **2014**, *43*, 7787-7812.
- [5] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* **2010**, *110*, 6446-6473.
- [6] Z. Chen, T. F. Jaramillo, T. G. Deutsch, A. Kleiman-Shwarscstein, A. J. Forman, N. Gaillard, R. Garland, K. Takanabe, C. Heske, M. Sunkara, *J. Mater. Res.* **2010**, *25*, 3-16.
- [7] A. J. Bard, *J. Am. Chem. Soc.* **2010**, *132*, 7559-7567.
- [8] A. L. Linsebigler, G. Lu, J. T. Yates Jr, *Chem. Rev.* **1995**, *95*, 735-758.
- [9] A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253-278.
- [10] H. Kato, K. Asakura, A. Kudo, *J. Am. Chem. Soc.* **2003**, *125*, 3082-3089.
- [11] D. Geng, Y. Chen, Y. Chen, Y. Li, R. Li, X. Sun, S. Ye, S. Knights, *Energy. Environ. Sci.* **2011**, *4*, 760-764.
- [12] H. Zhou, Y. Qu, T. Zeid, X. Duan, *Energy. Environ. Sci.* **2012**, *5*, 6732-6743.
- [13] Z. Yang, J. Zhang, M. C. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, *Chem. Rev.* **2011**, *111*, 3577-3613.
- [14] Y. Qu, X. Duan, *Chem. Soc. Rev.* **2013**, *42*, 2568-2580.
- [15] J. S. Jang, H. G. Kim, J. S. Lee, *Catal. Today* **2012**, *185*, 270-277.
- [16] S. J. Moniz, S. A. Shevlin, D. J. Martin, Z.-X. Guo, J. Tang, *Energy. Environ. Sci.* **2015**, *8*, 731-759.
- [17] J. Su, L. Guo, N. Bao, C. A. Grimes, *Nano Lett* **2011**, *11*, 1928-1933.
- [18] R. Marschall, *Adv. Funct. Mater.* **2014**, *24*, 2421-2440.

- [19] N. Serpone, E. Borgarello, M. Grätzel, *Journal of the Chemical Society, Chemical Communications* **1984**, 342-344.
- [20] A. Fujishima, K. Honda, *Nature* **1972**, 238, 37-38.
- [21] J. Evans, K. Springer, J. Zhang, *J. Chem. Phys.* **1994**, 101, 6222-6225.
- [22] P. V. Kamat, *J. Phys. Chem. C* **2008**, 112, 18737-18753.
- [23] K. Gopidas, M. Bohorquez, P. V. Kamat, *J. Phys. Chem.* **1990**, 94, 6435-6440.
- [24] L. Spanhel, H. Weller, A. Henglein, *J. Am. Chem. Soc.* **1987**, 109, 6632-6635.
- [25] S. Hotchandani, P. V. Kamat, *J. Phys. Chem.* **1992**, 96, 6834-6839.
- [26] S. Kohtani, A. Kudo, T. Sakata, *Chem. Phys. Lett.* **1993**, 206, 166-170.
- [27] S. Hotchandani, P. V. Kamat, *Chem. Phys. Lett.* **1992**, 191, 320-326.
- [28] J. Yoshimura, A. Kudo, A. Tanaka, K. Domen, K.-i. Maruya, T. Onishi, *Chem. Phys. Lett.* **1988**, 147, 401-404.
- [29] Y. Tian, T. Newton, N. A. Kotov, D. M. Guldi, J. H. Fendler, *J. Phys. Chem.* **1996**, 100, 8927-8939.
- [30] A. Kortan, R. Hull, R. L. Opila, M. G. Bawendi, M. L. Steigerwald, P. Carroll, L. E. Brus, *J. Am. Chem. Soc.* **1990**, 112, 1327-1332.
- [31] J. Rabani, *J. Phys. Chem.* **1989**, 93, 7707-7713.
- [32] P. V. Kamat, B. Patrick, *J. Phys. Chem.* **1992**, 96, 6829-6834.
- [33] R. Vogel, P. Hoyer, H. Weller, *J. Phys. Chem.* **1994**, 98, 3183-3188.
- [34] L. Amirav, A. P. Alivisatos, *J. Phys. Chem. Lett.* **2010**, 1, 1051-1054.
- [35] P. Du, R. Eisenberg, *Energy. Environ. Sci.* **2012**, 5, 6012-6021.
- [36] N. Bao, L. Shen, T. Takata, K. Domen, *Chem. Mater.* **2007**, 20, 110-117.
- [37] T. Takahashi, A. Kudo, S. Kuwabata, A. Ishikawa, H. Ishihara, Y. Tsuboi, T. Torimoto, *J. Phys. Chem. C* **2012**, 117, 2511-2520.
- [38] J. Yu, J. Zhang, M. Jaroniec, *Green. Chem.* **2010**, 12, 1611-1614.
- [39] Q. Li, H. Meng, P. Zhou, Y. Zheng, J. Wang, J. Yu, J. Gong, *ACS Catalysis* **2013**, 3, 882-889.
- [40] H.-Y. Lin, H.-C. Yang, W.-L. Wang, *Catal. Today* **2011**, 174, 106-113.
- [41] J. Yu, J. Ran, *Energy. Environ. Sci.* **2011**, 4, 1364-1371.
- [42] J. Yu, Y. Hai, B. Cheng, *J. Phys. Chem. C* **2011**, 115, 4953-4958.

- [43] S. W. Seo, S. Park, H.-Y. Jeong, S. H. Kim, U. Sim, C. W. Lee, K. T. Nam, K. S. Hong, *Chem. Commun.* **2012**, 48, 10452-10454.
- [44] Y. Hou, A. B. Laursen, J. Zhang, G. Zhang, Y. Zhu, X. Wang, S. Dahl, I. Chorkendorff, *Angew. Chem. Int. Ed.* **2013**, 52, 3621-3625.
- [45] N. Razgoniaeva, P. Moroz, S. Lambright, M. Zamkov, *J. Phys. Chem. Lett.* **2015**, 6, 4352-4359.
- [46] E. Khon, A. Mereshchenko, A. N. Tarnovsky, K. Acharya, A. Klinkova, N. N. Hewa-Kasakarage, I. Nemitz, M. Zamkov, *Nano Lett* **2011**, 11, 1792-1799.
- [47] W. Zhou, Z. Yin, Y. Du, X. Huang, Z. Zeng, Z. Fan, H. Liu, J. Wang, H. Zhang, *Small* **2013**, 9, 140-147.
- [48] J. Liu, J. Jiang, C. Cheng, H. Li, J. Zhang, H. Gong, H. J. Fan, *Adv. Mater.* **2011**, 23, 2076-2081.
- [49] H. Yan, J. Yang, G. Ma, G. Wu, X. Zong, Z. Lei, J. Shi, C. Li, *J. Catal.* **2009**, 266, 165-168.
- [50] K. Wu, H. Zhu, Z. Liu, W. Rodríguez-Córdoba, T. Lian, *J. Am. Chem. Soc.* **2012**, 134, 10337-10340.
- [51] S. Lingampalli, U. K. Gautam, C. Rao, *Energy. Environ. Sci.* **2013**, 6, 3589-3594.
- [52] Q. Li, B. Guo, J. Yu, J. Ran, B. Zhang, H. Yan, J. R. Gong, *J. Am. Chem. Soc.* **2011**, 133, 10878-10884.
- [53] J. Yu, L. Qi, M. Jaroniec, *J. Phys. Chem. C* **2010**, 114, 13118-13125.
- [54] Q. Xiang, J. Yu, M. Jaroniec, *J. Phys. Chem. C* **2011**, 115, 7355-7363.
- [55] I. Tsuji, H. Kato, A. Kudo, *Angew. Chem. Int. Ed.* **2005**, 44, 3565-3568.
- [56] M. Hara, J. Nunoshige, T. Takata, J. N. Kondo, K. Domen, *Chem. Commun.* **2003**, 3000-3001.
- [57] F. N. Sayed, O. Jayakumar, R. Sasikala, R. Kadam, S. R. Bharadwaj, L. Kienle, U. Schürmann, S. r. Kaps, R. Adelung, J. Mittal, *J. Phys. Chem. C* **2012**, 116, 12462-12467.
- [58] Y. Sasaki, A. Iwase, H. Kato, A. Kudo, *J. Catal.* **2008**, 259, 133-137.
- [59] K. Maeda, N. Sakamoto, T. Ikeda, H. Ohtsuka, A. Xiong, D. Lu, M. Kanehara, T. Teranishi, K. Domen, *Chem. Eur. J.* **2010**, 16, 7750-7759.

- [60] M. Murdoch, G. Waterhouse, M. Nadeem, J. Metson, M. Keane, R. Howe, J. Llorca, H. Idriss, *Nat. Chem.* **2011**, *3*, 489-492.
- [61] Y. Qu, X. Zhong, Y. Li, L. Liao, Y. Huang, X. Duan, *J. Mater. Chem.* **2010**, *20*, 3590-3594.
- [62] H. Park, W. Choi, M. R. Hoffmann, *J. Mater. Chem.* **2008**, *18*, 2379-2385.
- [63] X. Ma, K. Zhao, H. Tang, Y. Chen, C. Lu, W. Liu, Y. Gao, H. Zhao, Z. Tang, *Small* **2014**, *10*, 4664-4670.
- [64] C. Tan, X. Cao, X.-J. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han, G.-H. Nam, *Chem. Rev.* **2017**, *117*, 6225-6331.
- [65] A. Beal, J. Knights, W. Liang, *J. Phys. C: Solid State Phys.* **1972**, *5*, 3540.
- [66] A. N. Enyashin, L. Yadgarov, L. Houben, I. Popov, M. Weidenbach, R. Tenne, M. Bar-Sadan, G. Seifert, *J. Phys. Chem. C* **2011**, *115*, 24586-24591.
- [67] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, H. Zhang, *Nat. Chem.* **2013**, *5*, 263-275.
- [68] D. Voiry, M. Salehi, R. Silva, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda, M. Chhowalla, *Nano Lett* **2013**, *13*, 6222-6227.
- [69] G. Eda, T. Fujita, H. Yamaguchi, D. Voiry, M. Chen, M. Chhowalla, *ACS Nano* **2012**, *6*, 7311-7317.
- [70] D. Voiry, A. Mohite, M. Chhowalla, *Chem. Soc. Rev.* **2015**, *44*, 2702-2712.
- [71] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, M. Chhowalla, *Nano Lett* **2011**, *11*, 5111-5116.
- [72] K. Kam, B. Parkinson, *J. Phys. Chem.* **1982**, *86*, 463-467.
- [73] B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Horch, I. Chorkendorff, J. K. Nørskov, *J. Am. Chem. Soc.* **2005**, *127*, 5308-5309.
- [74] T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch, I. Chorkendorff, *Science* **2007**, *317*, 100-102.
- [75] B. Mahler, V. Hoepfner, K. Liao, G. A. Ozin, *J. Am. Chem. Soc.* **2014**, *136*, 14121-14127.
- [76] J. Duan, S. Chen, B. A. Chambers, G. G. Andersson, S. Z. Qiao, *Adv. Mater.* **2015**, *27*, 4234-4241.

- [77] K. Xu, F. Wang, Z. Wang, X. Zhan, Q. Wang, Z. Cheng, M. Safdar, J. He, *ACS Nano* **2014**, 8, 8468-8476.
- [78] S. Xu, D. Li, P. Wu, *Adv. Funct. Mater.* **2015**, 25, 1127-1136.
- [79] L. Cheng, W. Huang, Q. Gong, C. Liu, Z. Liu, Y. Li, H. Dai, *Angew. Chem. Int. Ed.* **2014**, 53, 7860-7863.
- [80] D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. Alves, T. Fujita, M. Chen, T. Asefa, V. Shenoy, G. Eda, *arXiv preprint arXiv:1212.1513* 2012.
- [81] Y. Tian, L. Ge, K. Wang, Y. Chai, *Mater. Charact.* **2014**, 87, 70-73.
- [82] J. Di, J. Xia, Y. Ge, L. Xu, H. Xu, J. Chen, M. He, H. Li, *Dalton. Trans.* **2014**, 43, 15429-15438.
- [83] Y. Min, G. He, Q. Xu, Y. Chen, *J. Mater. Chem. A* **2014**, 2, 2578-2584
- [84] Y. Chen, G. Tian, Y. Shi, Y. Xiao, H. Fu, *Appl. Catal. B: Environ.* **2015**, 164, 40-47.
- [85] H. Fu, K. Yu, H. Li, J. Li, B. Guo, Y. Tan, C. Song, Z. Zhu, *Dalton. Trans.* **2015**, 44, 1664-1672.
- [86] W. Gao, M. Wang, C. Ran, L. Li, *Chem. Commun.* **2015**, 51, 1709-1712.
- [87] H. Li, K. Yu, X. Lei, B. Guo, H. Fu, Z. Zhu, *J. Phys. Chem. C* **2015**, 119, 22681-22689.
- [88] B. Weng, X. Zhang, N. Zhang, Z.-R. Tang, Y.-J. Xu, *Langmuir* **2015**, 31, 4314-4322.
- [89] A. Sobczynski, A. Yildiz, A. J. Bard, A. Campion, M. A. Fox, T. Mallouk, S. E. Webber, J. M. White, *J. Phys. Chem.* **1988**, 92, 2311-2315.
- [90] X. Zong, H. Yan, G. Wu, G. Ma, F. Wen, L. Wang, C. Li, *J. Am. Chem. Soc.* **2008**, 130, 7176-7177.
- [91] X. Zong, Y. Na, F. Wen, G. Ma, J. Yang, D. Wang, Y. Ma, M. Wang, L. Sun, C. Li, *Chem. Commun.* **2009**, 4536-4538.
- [92] F. Meng, J. Li, S. K. Cushing, M. Zhi, N. Wu, *J. Am. Chem. Soc.* **2013**, 135, 10286-10289.
- [93] J. Zhang, Z. Zhu, X. Feng, *Chem. Eur. J.* **2014**, 20, 10632-10635.
- [94] K. Chang, Z. Mei, T. Wang, Q. Kang, S. Ouyang, J. Ye, *ACS Nano* **2014**, 8, 7078-7087.
- [95] Q. Xiang, F. Cheng, D. Lang, *ChemSusChem* **2016**, 9, 996-1002.

- [96] D. Chu, C. Zhang, P. Yang, Y. Du, C. Lu, *Catalysts* **2016**, 6, 136.
- [97] M. S. Akple, J. Low, S. Wageh, A. A. Al-Ghamdi, J. Yu, J. Zhang, *Appl. Surf. Sci.* **2015**, 358, 196-203.
- [98] J.-P. Zou, J. Ma, J.-M. Luo, J. Yu, J. He, Y. Meng, Z. Luo, S.-K. Bao, H.-L. Liu, S.-L. Luo, *Appl. Catal. B: Environ.* **2015**, 179, 220-228.
- [99] D. Jing, L. Guo, *Catal. Commun.* **2007**, 8, 795-799.
- [100] F. Xiong, H. Wang, X. Liu, J. Sun, M. Brongersma, E. Pop, Y. Cui, *Nano Lett* **2015**, 15, 6777-6784.
- [101] D. Kong, H. Wang, J. J. Cha, M. Pasta, K. J. Koski, J. Yao, Y. Cui, *Nano Lett* **2013**, 13, 1341-1347.
- [102] J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. W. D. Lou, Y. Xie, *Adv. Mater.* **2013**, 25, 5807-5813.
- [103] J. Chen, X. J. Wu, L. Yin, B. Li, X. Hong, Z. Fan, B. Chen, C. Xue, H. Zhang, *Angew. Chem. Int. Ed.* **2015**, 54, 1210-1214.
- [104] J. Chen, X.-J. Wu, Y. Gong, Y. Zhu, Z. Yang, B. Li, Q. Lu, Y. Yu, S. Han, Z. Zhang, *J. Am. Chem. Soc.* **2017**, 139, 8653–8660.

Chapter 3

Experimental Methodology

The principles underlying the selection of materials and techniques are discussed in this chapter. An effective photocatalyst for hydrogen evolution reaction consists of two components, a light harvesting semiconductor and a redox co-catalyst. CdS has a band-gap energy of 2.4 eV, which fits very well with the solar spectrum. What is more, the synthesis of CdS nanostructure has been extensively studied in past decades. The morphologies of the CdS nanostructures can be well controlled. Thus in this thesis, CdS was selected as a light harvesting antenna for solar energy absorption. Instead of noble-metal co-catalysts that are mostly used in the hydrogen evolution reaction systems, this thesis uses transition metal dichalcogenides (TMDs) as co-catalysts due to their highly active chalcogenide atoms on the edges towards hydrogen evolution reaction. The synthetic methods to construct CdS-TMD heterostructures together with the characterization methods will be introduced in detail in this chapter.

3.1 Rationale for Material and Method Selection

Generally, an effective photocatalyst for hydrogen evolution reaction consists of two components, a light harvesting semiconductor and a redox co-catalyst. In this thesis, the layered transition metal dichalcogenides (TMDs), including MoS₂, WS₂ and MoSe₂, were selected as the co-catalysts for photocatalyst hydrogen evolution reaction (HER). And CdS was selected as a light harvesting antenna for solar energy absorption. CdS has a band-gap energy of 2.4 eV, which fits very well with the solar spectrum. What is more, the synthesis of CdS nanostructures have been extensively studied in past decades. The morphologies of CdS nanostructures can be well controlled from nanoparticle, nanorod to very complex three dimensional architectures. Thus the selection of CdS as light harvesting antenna provides a lot of opportunities to construct complex heterostructures to improve the efficiency for HER.

Noble-metals are the most used co-catalysts in photocatalyst systems to achieve high photocatalytic activity. Noble metals, including Pt, Au, Pd, Ru and Rh, have been reported to be very effective for improving the activity of CdS photocatalysis.^[2-13] However, the above mentioned noble-metals are too scarce and very expensive, thus greatly limit the large-scale energy production. Therefore, find an earth abundant co-catalyst with high efficiency and low cost is highly desired. TMD is considered as one of the most promising candidates for noble metal co-catalysts due to their highly active chalcogenide atoms on the edges towards HER. For example, the CdS-MoS₂ composite shows higher activity than CdS-Pt towards photocatalytic hydrogen evolution. Thus the focus of this thesis is to develop highly active CdS-TMD heterostructures for photocatalytic HER.

3.2 Chemicals and Synthesis Process

3.2.1 Chemicals

Cadmium oxide (CdO, 99.99%, Puratrem), Cadmium acetate dihydrate [Cd(Ac)₂·2H₂O, 98%, Alfa Aesar], bis(acetylacetonato)dioxomolybdenum(VI) [MoO₂(acac)₂, Sigma-

Aldrich], copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ACS reagent, >99.0%, Sigma-Aldrich), ammonium tetrathiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$, 99.97%, Sigma-Aldrich), ammonium tetrathiotungstate ($(\text{NH}_4)_2\text{WS}_4$, 99.9%, Sigma-Aldrich), oleylamine (OM, technical grade, 70%, Sigma-Aldrich), ethylenediamine (absolute, >99.5%, Sigma-Aldrich), diphenyl diselenide (PDSe, 98%, Sigma-Aldrich), sulfur powder (−100 mesh, refined, Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), tert-Dodecylmercaptan (t-DDT, 98%, Sigma-Aldrich), Trioctylphosphine (TOP, 97%, Sigma-Aldrich), ammonium sulfide solution [$(\text{NH}_4)_2\text{S}$, 20% in water, Sigma-Aldrich], 3-mercaptopropionic acid (MPA, 99%, Sigma-Aldrich), triethanolamine (TEA, 98%, Sigma-Aldrich), acetone (technical grade), 1-octadecene (ODE, technical grade, 90%, Sigma-Aldrich), methanol (AR) and toluene (99.8%, Sigma-Aldrich) were used as received without further purification. Deionized water (18 $\text{k}\Omega \cdot \text{cm}$, Milli-Q System, Millipore, Billerica) was used in the photocatalytic HER experiments.

3.2.2 Synthesis of CdS-WS₂ Heterostructures

0.3 mmol of CdO was added into the solvent composed of 9 mL ODE, 3 mL OM and 3 mL OA in a three-necked flask (100 mL) at room temperature. The mixture was heated to 120 °C to remove H_2O and O_2 under vacuum for 15 min in a heating mantle with stirring. The mixture was then purged with nitrogen and heat up to 300 °C, and then 2 mL of 0.05 M $(\text{NH}_4)_2\text{WS}_4$ OM stock solution was quickly inject into the resulting solution. The temperature of was quickly dropped to ~280 °C and was allowed to recover to 300 °C and maintained at this temperature for 2 hours. After that, the mixture was cooled to room temperature, the heterostructures were precipitated by adding acetone and collected by centrifugation, and then washed by the mixture of toluene and acetone for 3 times.

The 0.05 M $(\text{NH}_4)_2\text{WS}_4$ oleylamine stock solution was prepared by combining 174 mg $(\text{NH}_4)_2\text{WS}_4$ (0.5 mmol) and 10 mL oleylamine in a 25 mL bottle and heated to 80 °C for 5 hours.

3.2.3 Synthesis of CdS-MoS₂ Heterostructures

The synthetic processes for the preparation of CdS-MoS₂ heterostructures are similar with that for preparation of CdS-WS₂ heterostructures. A 0.05 M (NH₄)₂MoS₄:OM stock solution was prepared by combining 0.5 mmol (NH₄)₂MoS₄ and 10 mL OM in a 25 mL bottle and heated to 80 °C for 5 hours. 0.3 mmol of CdO was added into the solvent composed of 3 mL OA, 3 mL OM and 9 mL ODE in a three-necked flask (100 mL) at room temperature. The mixture was heated to 120 °C to remove H₂O and O₂ under vacuum for 15 min in a heating mantle with stirring. The mixture was then purged with nitrogen and heat up to 280 °C, and then 2 mL of 0.05 M (NH₄)₂MoS₄:OM stock solution was quickly inject into the resulting solution. The temperature of was quickly dropped to ~280 °C and was allowed to recover to 300 °C and maintained at this temperature for 2 hours. After that, the mixture was cooled to room temperature, the heterostructures were precipitated by adding acetone and collected by centrifugation, and then washed by the mixture of toluene and acetone for 3 times. The collection and wash steps are the same with that of CdS-WS₂ heterostructures.

3.2.4 Synthesis of CdS NWs

0.3 mmol of Cd(Ac)₂·2H₂O and 1 mmol sulfur powder were added into 9 mL ethylenediamine and stirred for 20 min to form a yellow dispersion. Then it was transferred to a 23 mL autoclave and heated at 200 °C and keep at 200 °C for 3 hrs. After cooling down to room temperature naturally, the CdS NWs was collected by centrifugation. The product was then washed with ethanol for several times and re-dispersed in 6 mL OM.

3.2.5 Synthesis of Cu_{2-x}S NWs by Cation Exchange of CdS NWs

1 mmol of CuCl₂·2H₂O was added to 10 mL OM in a 100 mL three-necked flask at room temperature. The mixture was heated to 120 °C to remove H₂O and O₂ under vacuum for 30 min in a heating mantle with stirring. After that, it was purged with N₂ and heated to 150 °C to produce a clear, yellow solution. 0.1 mmol CdS dispersion in 2 mL OM was

quickly inject into the abovementioned solution. The temperature was dropped to 140 °C within 10 seconds, and it is allowed to maintain at 140 °C for 10 min. After that the mixture was cooled down to room temperature, and the Cu_{2-x}S nanowires were collect by centrifugation at 6,000 r.p.m for 3 min, and then washed by toluene for three times.

3.2.6 Synthesis of Cu_{2-x}S-MoSe₂ Heterostructures

0.1 mmol of Cu_{2-x}S NWs and 0.1 mmol of MoO₂(acac)₂ were added to 15 mL OM in a 100 mL three-necked flask at room temperature. The mixture was heated to 120 °C to remove H₂O and O₂ under vacuum for 30 min in a heating mantle with stirring. After the mixture was purged with N₂ for another 30 min, it was heated to 200 °C. Subsequently, 1.75 mL of 0.05 M PDSe-OM stock solution was pumped into the mixture at a speed of 0.5 mL/h. After all of the stock solution was introduced, the system was cooled down to room temperature. The Cu_{2-x}S NWs was collected by centrifugation at 6,000 r.p.m for 5 min, and then washed by toluene for three times. The obtained product can be dispersed in toluene.

The 0.05 M PDSe-OM stock solution was prepared by dissolving 0.5 mmol of PDSe in 10 mL OM in a 20 mL bottle, which was then purged with nitrogen for 30 min and sealed for future use.

3.2.7 Synthesis of Cu_{2-x}S-MoS₂ Heterostructures

The procedures for synthesis of Cu_{2-x}S-MoS₂ heterostructures were similar with those for synthesis of Cu_{2-x}S-MoSe₂ heterostructures. 0.1 mmol of Cu_{2-x}S nanowires and 0.1 mmol of MoO₂(acac)₂ were added to 15 mL OM in a 100 mL three-necked flask at room temperature. The mixture was heated to 120 °C to remove H₂O and O₂ under vacuum for 30 min in a heating mantle with stirring. After the mixture was purged with nitrogen for another 30 min, it was heated to 200 °C. Subsequently, 2 mL tDDT-OM stock solution was pumped into the mixture at a speed of 0.25 mL/h. After all of the stock solution was introduced, the system was cooled down to room temperature. The heterostructures were

collected by centrifugation at 6,000 r.p.m for 5 min, and then washed by toluene for three times.

The tDDT-OM stock solution was prepared by mixing 235 μL tDDT in 2.265 mL OM in a 10 mL bottle, which was then purged with nitrogen for 30 min and sealed for future use.

3.2.8 Synthesis of CdS-MoS₂ Heterostructures by Cation Exchange of Cu_{2-x}S-MoS₂ Heterostructures

1 mmol of CdO was added to a solvent of 4 mL OA and 6 mL ODE in a 100 mL three-necked flask. The mixture was heated to 120 °C to remove H₂O and O₂ under vacuum for 30 min in a heating mantle with stirring. The mixture was then heated to 230 °C to produce a clean, colorless solution. Then the solution was cooled down to 190 °C. Subsequently, 0.1 mmol of Cu_{2-x}S-MoS₂ dispersed in 2 mL TOP was quickly injected to the abovementioned solution. After the resulting solution was kept at 190 °C for 60 mins, it was cooled down to room temperature. The CdS-MoS₂ heterostructures was collect by centrifugation at 6,000 r.p.m for 3 min, and then washed by toluene for three times.

3.2.9 Preparation of the Water-soluble CdS-MoS₂ Heterostructures.

The obtained CdS-MoS₂ heterostructures in toluene were transferred to water phase by (NH₄)₂S-assisted transfer method. 20 mg CdS-MoS₂ heterostructures in 5 ml toluene were added into a 20 mL glass bottle, 0.5 mL of 10% (NH₄)₂S water solution together with 0.5 mL of methanol were added into it under stirring. After 5 mins, the CdS-MoS₂ was transferred to water phase. The water soluble CdS-MoS₂ were collected by centrifugation at 10,000 r.p.m for 10 min and washed three times with methanol to remove excess (NH₄)₂S.

3.2.10 Photocatalytic Hydrogen Evolution

The photocatalytic activity was evaluated using water soluble CdS-MoS₂

heterostructures as photocatalysts, 5 mg of CdS-MoS₂ photocatalysts were dispersed in 10 mL H₂O containing 10% of TEA (used as sacrificial agent). The mixture was sealed in a 25 mL quartz vessel and purged with Argon for 15 min to remove O₂. A 300 W Xenon lamp (MAX-302, Asahi Spectra Company, Led.) was used as light source. To evaluate the photocatalytic activity, the vessel was then exposed under the light coupled with a UV cutoff filter (>420 nm). The H₂ product was analyzed by periodically injecting 500 μ L gas into a gas chromatograph (GC, Agilent 7890A).

3.3 Characterization

After various heterostructures are obtained, proper techniques are required to characterize their structure features, such as the morphology, crystal structure and composition. With the advancement of manufacturing technology, various characterization techniques have been well developed. For example, HR-TEM and STEM with atomic resolution can provide useful information to reveal the detail interfacial crystal structures of the heterojunctions. To better utilize each characterization technology, one should familiar with their principles. Thus in this section, the basic principles of TEM, XRD and XPS will be briefly introduced.

3.3.1 Transmission Electron Microscopy

TEM is a microscopy technique for obtaining high-resolution images of nanomaterials.^[14,15] When high energy electron beam passes through a thin sample, the interaction between the electrons and the material atoms can be used to observe the structure feature of nanomaterial. Currently, TEM technique is one of the most common and powerful tools to provide the detailed information of nanomaterials, such as crystallinity, lateral size, grain boundaries, structure dislocations, interlayer distance, and elemental composition. Typically, the lateral size of NSs or NCs can be directly and precisely measured through low magnification TEM images.

The high-resolution TEM images (HR-TEM) and SAED patterns are widely used to

investigate the crystal structure, structure dislocations, crystal orientation and exposed crystal facets of NSs and NCs. It can also be used for particle counting and size determination. The crystal lattice is the intrinsic feature of crystals and can be used to confirm the crystal structure by measuring the distance of crystal lattice fringes. Moreover, the HR-TEM can also be used to determine the crystallinity of materials, for example, NCs normally give clear crystal lattice fringes, while amorphous materials do not show any crystal lattices in HR-TEM images. Furthermore, the crystallinity, e.g., single-crystalline, polycrystalline and amorphous structure of a material, can be studied by the SAED pattern. Single-crystalline materials give clear bright dot patterns in the SAED pattern images, polycrystalline materials display ring-like pattern, and amorphous materials do not show any SAED patterns. In most cases, the size of NCs is so small that the diffraction area of SAED can include more than one single particle. In this case, due to the different orientations of individual crystals, the diffraction pattern of NCs, sometimes, shows ring-like pattern, similar to that of polycrystalline materials. Furthermore, the EDS spectra and corresponding elemental mapping from TEM equipment can also be used to confirm the elemental compositions and distribution, and roughly determine the relative ratio (mass ratio and molar ratio) for each element.

3.3.2 X-ray Diffraction

X-ray diffraction (XRD) is a non-destructive analytical technique used to analyze the crystallographic information of a crystalline materials.^[16-17] XRD technique is based on the constructive interference of monochromatic X-ray with a crystalline material. When the incident angel of X-ray satisfy the Bragg's Law (Equation 3.1), the interaction of the X-ray with the crystalline material will generate constructive interference.

$$n\lambda = 2d\sin\theta \quad (3.1)$$

Equation 3.1 shows the Bragg's Law, in which λ is the wavelength of X-ray, θ is the incident angle, and d is the lattice distance of a crystalline material, as shows in Figure 3.1. The Bragg's law links the electromagnetic radiation wavelength (λ), the diffraction angle

(θ) and the lattice distance (d) together. By scanning the crystalline materials through a range of 2θ degree, all diffraction directions of the crystal should be recorded due to the random orientation of the powdered material. Conversion of the diffraction peaks to d -spacings allows identification of the crystalline material because each crystalline material has a set of unique d -spacings. Typically, this is achieved by comparison of d -spacings with standard reference patterns.

Figure 3.1 Schematic illustration of the Bragg diffraction.

In the thesis, the XRD characterization was used to identify the crystal structure of the CdS-WS₂, CdS-MoS₂, Cu_{2-x}S-MoSe₂ and Cu_{2-x}S-MoS₂ heterostructures.

3.3.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) measurement was carried out by using Kratos Axis-ULTRA XPS instrument equipped with a monochromatic Al K α (1486.7 eV) X-ray source with emission of 10 mA and anode HT of 15 kV. The sample analysis chamber pressure was $\sim 10^{-9}$ torr during spectrum acquisition. All the samples were measured with an area of $400 \times 400 \mu\text{m}^2$. All the spectra were calibrated by using the C1s peak (284.6 eV) as the reference. For preparation of XPS samples, a drop of solution containing the prepared heterostructures was drop-casted on a clean Si substrate and then naturally dried in air, which then can be used for XPS measurement.

XPS is a surface-sensitive technique which is used to measure the binding energies of element at the surface of a material, and can be used to analyze the chemical composition, oxidation state, and electronic state of elements in a compound.^[18] Typically, an XPS spectrum represents the number of detected electrons as a function of the binding energy of the detected electrons within a material when it is exposed to an X-ray beam. Normally, the XPS spectrum includes XPS survey spectrum and high-resolution XPS spectrum. The XPS survey spectrum can be used to qualitatively determine the chemical composition in materials and provide the rough binding energy of element in a compound. By deconvolution of the XPS high-resolution spectrum, the electronic states of elements, which contain more precise information about the compositional and structural features of the studied materials, can be quantitatively determined from the binding energy.

References

- [1] Y. Qu, X. Duan, *Chem Soc Rev* **2013**, 42, 2568-2580.
- [2] H. Yan, J. Yang, G. Ma, G. Wu, X. Zong, Z. Lei, J. Shi, C. Li, *J. Catal.* **2009**, 266, 165-168.
- [3] K. Wu, H. Zhu, Z. Liu, W. Rodríguez-Córdoba, T. Lian, *J. Am. Chem. Soc.* **2012**, 134, 10337-10340.
- [4] S. Lingampalli, U. K. Gautam, C. Rao, *Energy. Environ. Sci.* **2013**, 6, 3589-3594.
- [5] Q. Li, B. Guo, J. Yu, J. Ran, B. Zhang, H. Yan, J. R. Gong, *J. Am. Chem. Soc.* **2011**, 133, 10878-10884.
- [6] J. Yu, L. Qi, M. Jaroniec, *J. Phys. Chem. C* **2010**, 114, 13118-13125.
- [7] Q. Xiang, J. Yu, M. Jaroniec, *J. Phys. Chem. C* **2011**, 115, 7355-7363.
- [8] I. Tsuji, H. Kato, A. Kudo, *Angew. Chem. Int. Ed.* **2005**, 44, 3565-3568.
- [9] M. Hara, J. Nunoshige, T. Takata, J. N. Kondo, K. Domen, *Chem. Commun.* **2003**, 3000-3001.
- [10] F. N. Sayed, O. Jayakumar, R. Sasikala, R. Kadam, S. R. Bharadwaj, L. Kienle, U. Schürmann, S. r. Kaps, R. Adelung, J. Mittal, *J. Phys. Chem. C* **2012**, 116, 12462-12467.
- [11] Y. Sasaki, A. Iwase, H. Kato, A. Kudo, *J. Catal.* **2008**, 259, 133-137.

- [12] K. Maeda, N. Sakamoto, T. Ikeda, H. Ohtsuka, A. Xiong, D. Lu, M. Kanehara, T. Teranishi, K. Domen, *Chem. Eur. J.* **2010**, *16*, 7750-7759.
- [13] M. Murdoch, G. Waterhouse, M. Nadeem, J. Metson, M. Keane, R. Howe, J. Llorca, H. Idriss, *Nat. Chem.* **2011**, *3*, 489-492.
- [14] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano. *Nat. Nanotechnol.* **2012**, *7*, 699-712.
- [15] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A. K. Geim. *Proc. Natl. Acad. Sci.* **2005**, *102*, 10451-10453.
- [16] H. Li, G. Lu, Z. Yin, Q. He, H. Li, Q. Zhang, H. Zhang. *Small.* **2012**, *8*, 682-686.
- [17] J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuwissen, D. W. McComb, P. D. Nellist, V. Nicolosi. *Science.* **2011**, *331*, 568-571.
- [18] Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, F. Boey, H. Zhang. *Angew. Chem. Int. Ed.* **2011**, *50*, 11093-11097.

Chapter 4*

CdS-MoS₂ and CdS-WS₂ Heterostructures for Photocatalytic Hydrogen Evolution

Exploiting effective photocatalysts with low cost and high abundance is of great interest for solar photocatalytic water splitting. Transition Metal Dichalcogenides (TMDs) already show excellent performance as co-catalysts for hydrogen evolution reaction (HER). However, designing TMD nanostructures with abundant active sites for HER still remains urgent. Herein, a one-pot wet chemical method was developed to fabricate CdS-MS₂ (M=W or Mo) heterojunctions that expose large amount of active edge sites for HER. Single layer MS₂ with a lateral size around 5-10 nm were selectively grown on the (111) surface of zinc blende CdS nanocrystals (NCs). The photocatalytic activity of CdS-WS₂ and CdS- MoS₂ heterojunctions towards HER under visible light irradiation is about 18 and 13 times of that of pure CdS, respectively. It is believed that these Cd- MS₂ heterojunctions would have great potential application in the photocatalytic HER.

* The content in this chapter has been published in Angewandte Chemie-International Edition (Angew. Chem. Int. Ed. 2015, 54, 1210-1214).

4.1 Introduction

The conversion of solar energy into chemical fuels by photocatalytic hydrogen evolution reaction (HER) using semiconductors as catalysts is recognized as one of the most promising way to meet the future energy demand and solve global environmental problems.^[1] Since the first use of TiO₂ as photocatalyst for photoinduced water splitting in 1972,^[2] numerous semiconductor materials have been developed and demonstrated to be able to produce H₂ under photo-irradiation.^[3-5] Among various candidates, CdS has attracted lots of attention due to its narrow band gap (~2.4 eV) for effective absorption of solar energy, relatively simple fabrication method and proper conduction band for HER.^[6-8] However, CdS alone shows extremely low photocatalytic hydrogen production activity and poor durability due to the electrons-holes recombination and photocorrosion.^[9]

To inhibit the charge carrier recombination, decorating semiconductor photocatalysts with co-catalysts is an effective way.^[9] Several CdS-based composites have been developed and show promising results, such as CdS-Pt,^[10] CdS-NiO,^[11] CdS-Cu₂S,^[12] etc., which have already shown promising results. Transition metal dichalcogenide (TMD) nanosheets (NSs), such as MS₂ (M = W or Mo),^[13] a typical layered materials, show very good activity towards electrocatalytic H₂ evolution.^[14,15] It has been proved that the edge sites of TMD NSs are the active sites for HER.^[16-18] Thus, engineering TMD to preferentially expose active edge sites can great enhance their activity towards photocatalytic HER.^[19,20] Up to now, several reports have demonstrated that a p-n junction can be formed by integrating of CdS NCs with MoS₂ NSs, which great enhances the performance towards the photocatalytic HER.^[21-24] However, the used MoS₂ NSs with large lateral sizes or/and multilayered structures leads to the low exposure of the active edge site, which greatly limit their activity towards HER. Therefore, synthesis of photocatalysts containing layered MS₂ NSs with abundant of active sites remains challenge.

4.2 Results and Discussion

4.2.1 Synthesis and Characterization of CdS-WS₂ heterostructures

The heterostructures were synthesized through a hot-injection method and the preparation of CdS-WS₂ heterostructure is detailed as a representative. An oleylamine (OM) stock solution containing 0.1 mmol of (NH₄)₂WS₄ was injected into an OM and ODE mixed solution contains 0.3 mmol Cd(oleate)₂ at 290. The temperature was dropped to ~280 °C and was allowed to recover to 300 °C and maintained at this temperature for 2 hours.

The TEM image indicates that the CdS-WS₂ heterostructures are very uniform nanoparticles with the size of 4–10 nm (shows in Figure 4.1a). Surprisingly, several single nanoparticles show obvious optical contrast at HR-TEM image (Figure 4.1b), just like a single layered nanomaterials (indicated by arrows) selectively grown on one side of the CdS NCs. These single layered nanomaterials are confirmed to be WS₂. An analysis of the powder X-ray diffraction (XRD) patterns revealed the wurtzite phase of CdS NCs. All diffraction peaks can be assigned to hexagonal CdS (Figure 4.2). However, the WS₂ do not show any obvious peaks in the XRD pattern which results from its single layered structure. The measured lattice distances are 0.33 nm and 0.35 nm, which can be assigned to the adjacent {0002} and {10 1 0} planes of wurtzite CdS (Figure 4.1c, d), respectively. Importantly, HR-TEM image viewed perpendicular to *c* axes further reveal that single layer WS₂ with a thickness of 0.4 nm was grown on the (111) surface of CdS (Figure 4.1c), which is consistent with distance between two S layers in WS₂.^[46] Because of this unique morphology, we try to figure out its detailed structure. It has been proved that the CdS with hexagonal crystal contains alternating cadmium and sulfur atoms layers along the [0001] direction. In this case, the exposed {0001} facets are end with either cadmium-rich (0001) surface or sulfur -rich (0001) surface. It has been reported that anionic sulfur donors, such as MoS₄²⁻ or Et₂NCS₂, favorited to adsorb on the cadmium -rich surface.^[47] Thus, it is reasonable to deduce that the monolayer WS₂ should selectively grows on the cadmium-rich (0001) surface of CdS NCs. The cadmium-rich surface has strong interaction with the sulfur layer in the WS₂. A representative sketch picture of this unique structure is given in

the inset of Figure 4.1c. Given that, the WS₂ layer *c* cannot be observed if HR-TEM image was taken with electron beam parallel to *c* axes of CdS because of its ultrathin characteristic (Figure 4.1d).

Figure 4.1 TEM images and EDS mapping of CdS-WS₂ heterostructures. (a, b) TEM images of CdS-WS₂. Single-layer WS₂ NSs was indicated by arrows, which grew on the Cd-rich (0001) surface of CdS NCs. (c, d) Representative high-resolution TEM images of CdS-WS₂ viewed perpendicular and parallel to *c* axes, correspondingly. (e) DF-STEM image and EDS mapping of CdS-WS₂ heterostructures (scale bar = 100 nm)

Furthermore, STEM-EDS analysis was performed to confirm the composition of the heterostructures. The dark-field image shows CdS-WS₂ heterostructures are uniformly distributed on the copper grid, and the uniform distribution of Cd, S and W elements was revealed by the corresponding EDS elemental mapping, as shows in Figure 4.1e. And based on the EDS analysis, the molar ratio of W to Cd was determined to be 11:100, as shows in Figure 4.3.

Figure 4.2 XRD pattern of CdS-WS₂.

Figure 4.3 EDS spectrum of CdS-WS₂ heterostructures deposited on Si/SiO₂ copper grid. The Cu signal is from the copper grid substrate.

4.2.2 Formation process of CdS-WS₂ Heterostructures

To study the formation process of such unique heterostructures, by taking the aliquots at different reaction time intervals, a series of samples at different evolution stages have been taken out and investigated. It should be noted that the thermal decomposition of (NH₄)₂WS₄ involve two different steps. WS₃ was formed in the first step and H₂S molecule was released (equation 4.1); and in the second step the as-formed WS₃ further decomposed into WS₂ and S (equation 4.2).^[48]

Figure 4.4 TEM images of CdS-WS₂ heterostructures obtained at different reaction time. The reaction time is (a) 5 min, (b) 30 min, (c) 60 min. (d) Schematic illustration of the shape evolution of CdS-WS₂ heterostructures.

The first decomposition step is much easier to proceed, since it takes place at a relatively low temperature (about 180 °C) compared with the second decomposition step. Taking into consideration that there is no additional S source adopted in the synthesis, (NH₄)₂WS₄ not only serves as the precursor decomposed to form WS₂, but also provides S source for the nucleation and growth of CdS nanocrystal.

Figure 4.5 TEM images of the product of decomposition of (NH₄)₂WS₄ (a,b) in the absence of TOP (c,d) in the presence of TOP at 5 min.

Figure 4.4a-c demonstrate the typical TEM images of the products at different reaction time. At the beginning, only small WS₂ clusters (~1 nm) grown on the surface of CdS NCs was observed at the reaction time of 5 min (Figure 4.4a). However, the thermal decomposition of sole (NH₄)₂WS₄ at 300 °C in solution (the same procedures as the preparing of CdS-WS₂, except without adding CdO) is a rapid process, resulting in the formation of large aggregations of WS₂ NSs just at the time of 5 min (Figure 4.5a, b). Compared both experiments, it can be seen that the decomposition process of (NH₄)₂WS₄ slows down in the presence of Cd²⁺. It should be noted that the H₂S generated at the first

decomposition step can be rapidly consumed in the presence of Cd²⁺ to form CdS nanoparticles. At the first glance, this reaction will accelerate the first decomposition step and further the second decomposition process, which goes against the observed results. The explanation is that the H₂S formed at the first decomposition step is a very reactive agent and it can attack the WS₃ again and further accelerate the second decomposition process to form WS₂. This hypothesis can be verified by the experiment of decomposition of (NH₄)₂WS₄ in the presence of TOP, which can strongly coordinated with H₂S to form TOP=S, dramatically reducing its reactivity. Not surprisingly, only very small WS₂ NSs (~10 nm) were obtained even after 60 min reaction (Figure 4.5c, d).

As the reaction proceeds, WS₃ continuously decomposes to release WS₂. The small WS₂ clusters observed at reaction time of 5 min look like growing and fusing together, resulting in the formation of discontinuous single layer WS₂ (Figure 4.4b). After ageing for 1 hours, the discontinuous WS₂ NSs further evolved into a smooth, continuous single layer WS₂, which selectively grown on the (0001) surface of CdS nanocrystal (Figure 4.4c). It can be seen that Ostwald ripening or/and oriented attachment processes should play an very important role in the whole evolution process.^[49]

Figure 4.6 TEM image of the CdS-MoS₂ when 0.3 mmol of (NH₄)₂WS₄ was injected.

In our experiment the ratio between (NH₄)₂WS₄ and Cd(oleate)₂ was very important for controlling the structure of obtained CdS-WS₂. For example, when 0.3 mmol of

(NH₄)₂WS₄ was injected into the reaction solution, WS₂ with very large lateral size random cover on the CdS surface was obtained, as shows in Fig 4.6.

4.2.3 Synthesis and Characterization of CdS-MoS₂ Heterostructures

Impressively, the method can also be extended to synthesize CdS-MoS₂ heterostructure through using (NH₄)₂MoS₄ to replace the (NH₄)₂WS₄. The heterostructure is also characteristic with single layer MoS₂ selectively growth on the (0001) surface of CdS NCs. Low-resolution TEM image shows large scale of CdS-MoS₂ heterostructure with size of 6–11 nm (Figure 4.7a). MoS₂ with single layer structure can also be clearly observed in the HR-TEM image (Figure 4.7b, indicated by white arrows). HR-TEM (Figure 4.7c) just given four representative heterostructures viewed perpendicular to c axes, and each of them have a clear single layer of MoS₂ with the thickness of about 0.4 nm. The observed inter-plane distance between the lattice fringes is ~0.33nm, which can be assigned to the {0001} planes of hexagonal CdS. The hexagonal wurtzite CdS was further confirmed by XRD characterization (Figure 4.8). And the EDS analysis shows the molar ratio of Mo to Cd was about 7:100 (Figure 4.8), which shows quite similar value with that of CdS-WS₂ heterostructures. The binding energies of the elements in CdS-MoS₂ heterostructures were further characterized by XPS analysis (Figure 4.10). The oxidation states of Mo, S and Cd was examined by the high-resolution spectra of Mo 3d, S 2p, and Cd 3d. The peaks of Mo 3d appear at binding energy of 228.9 eV (Mo 3d_{5/2}) and 232.1eV (Mo 3d_{3/2}), which indicates that Mo⁴⁺ is the dominant oxidation states. Also, the presence of S in the heterostructure was confirmed by the two peaks of S 2p that are located at 161.9 eV and 163.1 eV, respectively. The binding energies of Mo and S are accord with reported value, confirmed the presence of MoS₂.^[50] The high resolution Cd 3d spectra contain two peaks centered at 405.7 eV (Cd 3d_{5/2}) and 412.5 eV (Cd 3d_{3/2}), indicate the typical divalent source of Cd from the CdS.^[51]

Figure 4.7 TEM images of CdS- MoS₂ heterostructures. (a, b) TEM images of CdS-MoS₂ heterostructures. (c) HR-TEM images of CdS-MoS₂ heterostructures viewed perpendicularly to the c axis of CdS NCs. MoS₂ with single-layer are indicated with arrows in b and c, which attached on the Cd-rich (0001) surface of CdS NCs.

Figure 4.8 XRD pattern of CdS-MoS₂ heterostructure.

Figure 4.9 EDS spectrum of CdS-MoS₂ heterostructures deposited on Si/SiO₂ substrate. The Si signal is from the Si/SiO₂ substrate.

Figure 4.10 XPS survey spectrum (a) and high-resolution XPS spectra of MoS₂-CdS heterostructures: (b) Mo 3d, (c) S 2p, (d) Cd 3d.

Figure 4.11 Photocatalytic activity of CdS-MS₂ heterostructures for HER. (a) Time-dependent photocatalytic H₂ production for CdS-WS₂, CdS-MoS₂ and pure CdS, respectively. (b) Comparison of the H₂-production rate under the light irradiation for CdS-WS₂, CdS-MoS₂ and pure CdS. (c) Cycling test of photocatalytic HER for CdS-WS₂. (d) Illustration of the photocatalytic process in CdS-MoS₂ heterostructures.

4.2.4 Photocatalytic activity of CdS-WS₂ and CdS-MoS₂ Heterostructures

As the lateral size of the single layer TMD growth on CdS NCs is typically less than 10 nm and such a structure could lead to the exposure of large amount of active edge sites. What is more, the diameters of the CdS-MS₂ heterostructures are very small (from 4–11 nm), which means that the diffusion pathway of the charge carriers is reduced, thus the recombination probability can be decreased. Meanwhile, the adjacent single layer TMD and CdS will form p-n junction, which accelerates the electron–hole pair separation. Therefore, enhanced photocatalytic activity can be expected for these unique heterostructures. Photocatalytic hydrogen production activities of as prepared CdS-WS₂ and CdS-MoS₂ heterostructures were evaluated under visible light irradiation ($\lambda > 420$ nm). Figure 4.11a–b summarize the hydrogen evolution rate by pure CdS, and CdS-WS₂, CdS-MoS₂ heterostructures, respectively. Under irradiation, the amounts of hydrogen evolution steadily increase with the time for pure CdS and both heterostructures (Figure 4.11a).

However, the pure CdS shows the lowest photocatalytic activity, while both heterostructures show enhanced activities, which the performance of CdS-WS₂ heterostructures is superior to CdS-MoS₂ heterostructures. The CdS-WS₂ heterostructures exhibit a hydrogen evolution rate of 1984 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which nearly equal to 16 times activity compare with that of pure CdS. Also, CdS-MoS₂ heterostructures show a hydrogen evolution rate of 1472 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is also about 12-fold increase than that of pure CdS (Figure 4.11b). To study the durability of CdS-WS₂ heterostructures, four photocatalytic reactions were performed with each irradiation of 4 h. The hydrogen evolution amount increased steadily with irradiation time in every turn, however, the photocatalytic activity slightly decrease after 16 hours of irradiation (Figure 4.11c). It should be noted that 70% of activity still be remained even after four consecutive rounds. The gradual deterioration of the activity of the heterostructures should mainly result from the photocorrosion of CdS NCs during the photocatalytic hydrogen reaction. Figure 4.11d shows the scheme of the photocatalytic process of the heterostructures. Upon photoexcitation, the electron-hole will be generated in CdS nanoparticles and the electrons can transfer to the single layer MS₂ NSs because of the formed p-n junction, and react with H⁺ in solution to produce H₂ at edge of MS₂. Meanwhile, the hole will be consumed by the sacrificial agent (lactic acid) to form CO₂.

4.3 Conclusion

In summary, a facile one-pot method was developed to fabricate CdS-WS₂ and CdS-MoS₂ heterostructures by using (NH₄)₂MS₄ (M=W or Mo) as both metal and sulfur source. The characterizations demonstrate that single layer MS₂ nanosheets are selectively grown on the (002) surface of wurtzite CdS nanocrystals. A possible mechanism is proposed to explain the formation process of these fancy heterostructures. The interaction between the Cd-rich surface of CdS nanocrystals and MS₄²⁻ is critical for the formation of such structure. CdS-MS₂ heterostructures materials shown excellent catalytic activity towards photocatalytic HER due to the plenty amount of active site for HER results from the small lateral size of MS₂ layers and the heterojunction formed between MS₂ and CdS.

References

- [1] N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729-15735.
- [2] A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37-38.
- [3] A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253-278.
- [4] F. E. Osterloh, *Chem. Mater.* **2008**, *20*, 35-54.
- [5] X. Chen, S. Shen, L. Guo, S. S. Mao, *Chem. Rev.* **2010**, *110*, 6503-6570.
- [6] Y. Li, L. Tang, S. Peng, Z. Li, G. Lu, *CrystEngComm* **2012**, *14*, 6974-6982.
- [7] T. Peng, K. Li, P. Zeng, Q. Zhang, X. Zhang, *J. Phys. Chem. C* **2012**, *116*, 22720-22726.
- [8] C. Nasr, S. Hotchandani, W. Y. Kim, R. H. Schmehl, P. V. Kamat, *J. Phys. Chem. B* **1997**, *101*, 7480-7487.
- [9] R. Marschall, *Adv. Funct. Mater.* **2014**, *24*, 2421-2440.
- [10] H. Park, W. Choi, M. R. Hoffmann, *J. Mater. Chem.* **2008**, *18*, 2379-2385.
- [11] Z. Khan, M. Khannam, N. Vinothkumar, M. De, M. Qureshi, *J. Mater. Chem.* **2012**, *22*, 12090-12095.
- [12] M. Sam, M. Bayati, M. Mojtahedi, K. Janghorban, *Appl. Surf. Sci.* **2010**, *257*, 1449-1453.
- [13] Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, F. Boey, H. Zhang, *Angew. Chem. Int. Ed.* **2011**, *50*, 11093-11097.
- [14] X. Huang, Z. Zeng, S. Bao, M. Wang, X. Qi, Z. Fan, H. Zhang, *Nat. Commun.* **2013**, *4*, 1444.
- [15] D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. Alves, T. Fujita, M. Chen, T. Asefa, V. Shenoy, G. Eda, *arXiv preprint arXiv:1212.1513* **2012**.
- [16] X. Zong, H. Yan, G. Wu, G. Ma, F. Wen, L. Wang, C. Li, *J. Am. Chem. Soc.* **2008**, *130*, 7176-7177.
- [17] J. Kibsgaard, Z. Chen, B. N. Reinecke, T. F. Jaramillo, *Nat. Mater.* **2012**, *11*, 963.
- [18] T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch, I. Chorkendorff, *Science* **2007**, *317*, 100-102.
- [19] H. I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J. R. Long, C. J. Chang, *Science* **2012**, *335*, 698-702.

- [20] J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. W. D. Lou, Y. Xie, *Adv. Mater.* **2013**, 25, 5807-5813.
- [21] K. Chang, Z. Mei, T. Wang, Q. Kang, S. Ouyang, J. Ye, *ACS Nano* **2014**, 8, 7078-7087.
- [22] J. Zhang, Z. Zhu, X. Feng, *Chem. Eur. J.* **2014**, 20, 10632-10635.
- [23] X. Zong, J. Han, G. Ma, H. Yan, G. Wu, C. Li, *J. Phys. Chem. C* **2011**, 115, 12202-12208.
- [24] M.-Q. Yang, C. Han, Y.-J. Xu, *J. Phys. Chem. C* **2015**, 119, 27234-27246.

Chapter 5*

Edge Epitaxy of Two-dimensional MoS₂ and MoSe₂ Nanosheets on One-dimensional Nanowires

Rational design and synthesis of epitaxial heterostructures based on transition metal dichalcogenides (TMDs), such as MoS₂ and MoSe₂, have attracted considerable interest because of their wide application in electronics, optoelectronics, thermoelectronics and catalysis. However, the construction of epitaxial heterostructures interfaced at the edge of TMD nanosheets (NSs) is still remains a great challenge. Here, a wet-chemistry method were reported for synthesis of a new type of heterostructure featured that the edge of TMD NSs, e.g., MoS₂ and MoSe₂, vertically epitaxially grown on the longitudinal direction of 1D Cu_{2-x}S nanowires. The as-obtained Cu_{2-x}S-MoS₂ heterostructures could enhance their catalytic performance due to the large amount of the catalytically active edge sites that are exposed. After cation exchange of Cu_{2-x}S to CdS nanowires, the CdS-MoS₂ heterostructures still remain. Compared to the pure CdS nanowires, the CdS-MoS₂ heterostructures with 7.7 wt% of MoS₂ show better photocatalytic hydrogen evolution reaction performance. The photocatalytic H₂ production rate up to 4647 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ is about 58 times that of using pure CdS nanowires as photocatalyst. This synthetic strategy opens up a new way for the controlled synthesis of TMD-based epitaxial heterostructures which could exhibit promising catalytic applications.

* The content in this chapter has been published in Journal of the American Chemical Society (J. Am. Chem. Soc. 2017, 139, 8653–8660).

5.1 Introduction

Heterostructures of nanocomposites, which integrate distinct components with different functionalities into one system, have attracted tremendous attention due to their fascinating properties and the accompanied synergistic coupling effects for various promising applications.^[1-5] As known, the epitaxial growth^[6] is one kind of valid methods to prepare novel heterostructures with low density of defects at interfaces, exhibiting unique physicochemical properties and thus greatly enhancing their promising applications in electronics,^[7-9] optoelectronics,^[10-12] thermoelectronics^[13, 14] and catalysis.^[15, 16]

Transition metal dichalcogenides are one class of layered materials, in which the atomic layers are weakly bonded by the van der Waals interaction.^[17] Thus they can be easily exfoliated into single or multiple layers with no dangling bonds on their basal planes.^[18, 19] This unique feature facilitates their integration with other layered materials via staking to form van der Waals heterostructures.^[20] Furthermore, they also can serve as excellent platform to produce epitaxial heterostructures with different nanomaterials without the limitation of the lattice matching.^[21-24] However, the epitaxial heterostructures grown laterally from the edges of TDMs remains a great challenge, because there is lack of materials with compatible chemical bonding and lattice matching with the edges of TMDs. Until now, the reported lateral heterostructures are only limited to the growth of a similar layered nanomaterial in the edge of the other, such as MoS₂-MoSe₂,^[25] MoS₂-WS₂,^[26, 27] MoSe₂-WS₂,^[28] MoSe₂-WSe₂,^[29] and WS₂-WSe₂.^[25] There is no report on the preparation of epitaxial heterostructures via the TMD edges interfaced with other non-layered semiconducting materials. Although this type of heterostructures may possess tremendous potential applications due to the anisotropic properties of TMD, for example, the in-plane conductivity of MoSe₂ is ~1500 times that of the cross-plane conductivity.^[30]

Here a wet-chemistry method was developed for synthesis of a new type of heterostructure, i.e. the TMD NSs including MoS₂ and MoSe₂ is vertically epitaxially grown on the longitudinal direction of 1D Cu_{2-x}S nanowires. The lateral size of TMD NSs can be tuned from less than 2 nm to ~10 nm by changing the amount of sulfur or selenide

precursor. After cation exchange of Cu_{2-x}S to CdS NWs, the heterostructures of CdS-MoS₂ nanocomposites still remain. As a proof-of-concept, the obtained CdS-MoS₂ nanocomposites have been used for photocatalytic hydrogen evolution under the visible light irradiation (>420 nm). The obtained CdS-MoS₂ nanocomposites with 7.7 wt% of MoS₂ can produce H₂ up to 4647 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is about 58 times that produced by pure CdS NWs.

Figure 5.1 (a) XRD pattern of CdS NWs. The standard diffraction pattern of wurtzite CdS (JCPDS No. 41-1049) is used as reference. (b) Low magnification TEM image of CdS NWs with diameter of 30–50 nm and lengths up to 3 μm . (c) TEM image and (d) corresponding SAED pattern of a typical CdS NW. Inset in (c): HR-TEM image of the CdS NW showing the well crystalline structure. The measured lattice fringe of 0.33 nm is ascribed to (002) plane of wurtzite CdS, indicating that the CdS NW grew along the *c* direction.

5.2 Results and Discussion

5.2.1 Synthesis of CdS Nanowires and Their Cation Exchange to Cu_{2-x}S

The CdS NWs were synthesized according to a reported solvothermal method with slight modification.^[31] The as-prepared hexagonal CdS NWs have a diameter of 30-50 nm and length of 1-3 μm , as shown in Figure 5.1. The Cu_{2-x}S NWs was transformed from the CdS NWs via well-known cation exchange method. After cation exchange, the obtained Cu_{2-x}S NWs are well kept 1D shape and the successful transformation was confirmed by the XRD characterization, as shown in Figure 5.2.

Figure 5.2 (a) XRD pattern of the Cu_{2-x}S NWs. The standard diffraction pattern of djurleite Cu_{2-x}S (JCPDS No. 20-0365) is used as reference. (b) Low magnification TEM image of Cu_{2-x}S NWs. It is found that the size and shape of obtained Cu_{2-x}S NWs are well maintained compared to the original CdS NWs. (c) TEM image and (d) the corresponding SAED pattern of a typical Cu_{2-x}S NW, proving its well crystalline structure.

Figure 5.3 (a) Schematic illustration of the synthesis of $\text{Cu}_{2-x}\text{S-MoX}_2$ ($\text{X}=\text{S}$ or Se) heterostructure. (b) HAADF-STEM image of a typical $\text{Cu}_{2-x}\text{S-MoSe}_2$ heterostructure. (c) TEM image of $\text{Cu}_{2-x}\text{S-MoSe}_2$ heterostructure. The circles indicate the $\text{Cu}_{1.94}\text{S}$, component i and Cu_2S , component ii. The black arrows indicate the MoSe_2 , component iii. Inset: corresponding FFT pattern of the $\text{Cu}_{2-x}\text{S-MoSe}_2$. (d) HR-TEM image of $\text{Cu}_{2-x}\text{S-MoSe}_2$ taken in the square in (c). (e-g) Bragg-filtered image derived by inverse FFT in component i, ii and iii. The Bragg-filtered images are derived by using the (080) reflection of component i (e), the (110) reflection of component ii (f) and the (002) reflection of component iii (g). The images were then processed with a Sobel filter to enhance their boundaries. (h) Overlap of the Bragg-filtered images of the three components.

Figure 5.4 (a, b) Low magnification TEM images of Cu_{2-x}S-MoSe₂ heterostructures. (c, d) TEM images of Cu_{2-x}S-MoSe₂ heterostructures. High-density MoSe₂ NSs grown on the tip (c) and body (d) of Cu_{2-x}S NWs are clearly observed.

5.2.2 Synthesis of Cu_{2-x}S-MoSe₂ Heterostructure Nanowires

To fulfill the directional growth of the TMD NSs on the 1D Cu_{2-x}S NWs, the sulfur/selenium precursor solution was slowly injected into the mixture composed of 1D Cu_{2-x}S nanowire seeds and molybdenum precursor in oleylamine at 200 °C by syringe pump to minimize the homogenous nucleation. Figure 5.3b shows a typical high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the as-obtained Cu_{2-x}S-MoSe₂ heterostructure NWs, in which high density of multilayer MoSe₂ NSs are observed to vertically grow on the longitudinal direction of 1D Cu_{2-x}S NWs. Figure 5.4a shows the low magnification TEM images, from which large scale

heterostructure nanowires can be observed. The length and diameter of the Cu_{2-x}S NWs in Cu_{2-x}S-MoSe₂ heterostructures are well maintained as compared to the original Cu_{2-x}S NWs. And the XRD result shows that the Cu_{2-x}S-MoSe₂ has the same crystal structure with Cu_{2-x}S NWs, as shown in Figure 5.5.

It is worth mention that the reaction temperature is very important for the construction of this kind of heterostructure. Fig. 5.6 gives the TEM images of Cu_{2-x}S-MoSe₂ composites obtained at reaction temperature of 260 °C. Instead of vertically grow, the MoSe₂ just cover on the Cu_{2-x}S NW surface at high reaction temperature.

Figure 5.5 XRD pattern of Cu_{2-x}S-MoSe₂ heterostructures. The standard diffraction pattern of djurleite Cu_{2-x}S (JCPDS No. 20-0365) is used as reference. Not obvious peaks from MoSe₂ are detected.

Further high-resolution transmission electron microscopy (HR-TEM) image (Figure 5.3c) clearly displays that the as-prepared Cu_{2-x}S-MoSe₂ heterostructure NWs are actually consisted of three compositional parts, that is, the 1D Cu_{2-x}S NWs are indeed composed of djurleite Cu_{1.94}S - high chalcocite Cu₂S core-shell structure and the MoSe₂ NSs are grown vertically on the longitudinal direction of the high chalcocite shell. These three compositional parts can be identified from the corresponding fast Fourier transformation

(FFT) pattern (the inset of Figure 5.3c). The selected area electron diffraction (SAED) pattern of the Cu_{2-x}S-MoSe₂ heterostructure NWs indicate that the major component is djurleite Cu_{1.94}S, which is accord with the simulate electron diffraction pattern (Figure 5.7). The FFT patterns taken at black circle area I, II and blue square area III can be indexed to djurleite Cu_{1.94}S (Figure 5.8a), high chalcocite Cu₂S (Figure 5.8b) and MoSe₂ (Figure 5.8c), respectively. Noted that the djurleite and high chalcocite copper sulfides have almost the same lattice fringes, and the lattice mismatch between (080) planes of djurleite phase (1.97 nm) and (110) planes of high chalcocite phase (2.02 nm) is only 2.5 % (Figure 5.9).

Figure 5.6 TEM image of Cu_{2-x}S-MoSe₂ composites obtained at 260 °C.

Figure 5.7 (a) Experimental electron diffraction pattern of Cu_{2-x}S-MoSe₂ heterostructures. (b) Simulated electron diffraction pattern (Kinematical) of djurleite (Cu_{1.94}S). The SAED pattern of the Cu_{2-x}S-MoSe₂ heterostructures (a) indicates the major component of the Cu_{2-x}S-MoSe₂ heterostructures is djurleite Cu_{1.94}S, which is well accord with the simulate electron diffraction pattern (b).

Figure 5.8 (a) The FFT pattern taken at the circle (i) in Figure 5.3c, indicating the major component of Cu_{2-x}S-MoSe₂ heterostructures is the djurleite Cu_{1.94}S. (b) FFT pattern of Cu₂S, component ii. (c) FFT pattern of MoSe₂, component iii.

Figure 5.9 FFT pattern of Cu_{2-x}S-MoSe₂ heterostructure. The enlarged image (right) indicates the difference between the (080) reflection of djurleite Cu_{1.94}S (i) and the (110) reflection of high chalcocite Cu₂S (ii). The djurleite Cu_{1.94}S (i) and high chalcocite Cu₂S (ii) almost have the same lattice fringes, and the lattice mismatch between the (080) planes of djurleite phase (1.97 nm) and the (110) planes of high chalcocite phase (2.02 nm) is only about 2.5%.

Figure 5.10 (a) HR-TEM image taken at the tip of Cu_{2-x}S-MoSe₂ heterostructure. Few-layer MoSe₂ NSs grown on the tip of Cu_{2-x}S NW are observed. (b) Bragg-filtered image from the (080) reflection of djurleite Cu_{1.94}S. The yellow area clearly indicates the presence of djurleite Cu_{1.94}S (i). (c) Bragg-filtered image from the (110) reflection of high chalcocite Cu₂S. The green area indicates the presence of high chalcocite Cu₂S (ii). (d) Bragg-filtered image from the (002) reflection of MoSe₂. The location of MoSe₂ (iii) is indicated by the red area in the tip of NW. (e) Overlap of the Bragg-filtered images (b-d).

To visualize the high chalcocite Cu₂S shell, a Bragg-filtered image from (110) reflection of high chalcocite phase is shown in Figure 5.3f and the yellow area clearly indicates the presence of the high chalcocite shell. A HR-TEM image taken from the blue square III was shown in Figure 5.3d, in which the (002) plane of MoSe₂ can be clearly observed. Bragg-filtered image from (002) reflection of MoSe₂ is also used to visualize the MoSe₂ phase (Figure 5.3h), which is indicated by the yellow area in the heterostructure NWs. Moreover, HR-TEM images taken from the end of the NWs shows quite similar results, several MoSe₂ layers cover on the end of the Cu_{2-x}S NW can be observed (Figure 5.10).

The successful synthesis of Cu_{2-x}S-MoSe₂ heterostructure was further confirmed by XPS, as shown in Figure 5.11. The peaks observed at 931.7 and 951.8 eV can be ascribed to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively. The peaks of Mo 3d appear at binding energy of 228.5 eV (Mo3d_{5/2}) and 231.6 eV (Mo3d_{3/2}), indicating that Mo⁴⁺ is the dominant oxidation

states. From the high resolution XPS spectra of Se 3d, the two peaks located at around 53.8 and 54.8 eV are indexed to Se 3d_{5/2} and Se 3d_{3/2}, respectively, indicating the Se²⁻ oxidation state in MoSe₂.

Figure 5.11 (a) High-resolution XPS spectra of Cu 2p. (b) High resolution XPS spectra of Mo 3d. (c) High resolution XPS spectra of S 2p. The two peaks located at 161.9 eV and 163.1 eV can be assigned to the presence of S. (d) High resolution XPS spectra of Se 3d.

To reveal the detailed interface structure between the high chalcocite Cu₂S shell and the grown MoSe₂ NSs, and establish a deep understanding of the 1D/2D interface at atomic level, a series of STEM characterization were performed (Figure 5.12). The HAADF-STEM images taken from the center and end of the NWs are shown in Figure 5.12a and 5.12b, respectively. It can be seen that MoSe₂ are close contacted with the high chalcocite Cu₂S shell and there is smooth transition cross the interface which indicates the epitaxial growth between these two materials. Furthermore, the measured lattice fringes of the Cu₂S shells are well matched with the ones in MoSe₂ NSs along the longitudinal direction, that is 0.33 nm for (002) planes of chalcocite Cu₂S and 0.66 nm for (002) planes of MoSe₂ (noted that the lattice fringe of (002)_{Cu₂S} is just one half of the lattice fringe of (002)_{MoSe₂}). The measured lattice fringes of 0.19 nm and 0.16 nm can be assigned to the (1 20) planes

of Cu₂S and MoSe₂, respectively. It can be deduced that the epitaxial relationship between the Cu₂S shells and MoSe₂ NSs is (002)_{Cu₂S} $\parallel$ (002)_{MoSe₂} and (1 20)_{Cu₂S} $\parallel$ (1 20)_{MoSe₂}.

Figure 5.12 TEM analyses and crystal model of Cu_{2-x}S-MoSe₂ heterostructure NWs. (a, b) HAADF-STEM image of Cu_{2-x}S-MoSe₂ taken at the centre (a) and the end (b) of Cu_{2-x}S-MoSe₂ heterostructure NWs, the white triangles indicate the position of MoSe₂ NSs. (c) HAADF-STEM (left) and ABF-STEM image (right) of Cu_{2-x}S-MoSe₂ heterostructure NW. (d) Schematic illustration of the crystal structure of Cu_{2-x}S-MoSe₂ at the interface of Cu₂S and MoSe₂.

Figure 5.13 (a-c) TEM images of the Cu_{2-x}S-MoSe₂ heterostructures obtained at different injection volume of Se precursor solution: (a) 0.5 mL, (b) 1 mL and (c) 1.75 mL. (d) The plot of the weight percentage (wt%) of MoSe₂ in Cu_{2-x}S-MoSe₂ heterostructures, measured by ICP-OES, versus the volume of Se precursor solution.

Figure 5.12c gives a comparative combination of a HAADF-STEM image (left) and an annular bright field STEM (ABF-STEM) image (right) taken at the same area. In the HAADF-STEM image, three bright rows of Mo atoms (indicate by three dashed arrows) can be clear observed because of its larger atomic number than selenium, which further extended into the high chalcocite Cu₂S shell. While in ABF-STEM image, these rows of Mo atoms can be detected as dark lines, which located in between the dark rows

distinguished in high chalcocite Cu₂S. Noted that the high chalcocite Cu₂S has a structure consist of alternating layers of mixed Cu-S and pure Cu layer along c axis, as shown in Figure 5.12d.^[32] Therefore, the detected dark rows should be ascribed to the pure Cu layers. From this detailed structure, it can be deduced that the Mo layers of MoSe₂ are located between two Cu layers (indicate by the solid lines in Figure 5.12c, ABF-STEM image) of Cu₂S, which means that the Mo layers in MoSe₂ NSs are selectively contacted with the Cu-S layers in the high chalcocite Cu₂S (Figure 5.12d). It should be noted that the lattice fringes of (002) planes of MoSe₂ (0.66 nm) is well accorded with the value of (001) planes of Cu₂S (0.66 nm), which ensures the perfect match of the surface dangling bonds between the MoSe₂ and Cu₂S.

Table 5.1 The amount of MoSe₂ and MoS₂ in Cu_{2-x}S-MoSe₂, Cu_{2-x}S-MoS₂ and CdS-MoS₂ heterostructures determined by ICP-OES.

Adding volume of the chalcogen precursors	MoSe ₂ in Cu _{2-x} S- MoSe ₂ (wt%)	MoS ₂ in Cu _{2-x} S- MoS ₂ (wt%)	MoS ₂ in CdS- MoS ₂ (wt%)
0.25 mL of Se precursor	3.8 %	--	--
0.5 mL of Se precursor	4.8 %	--	--
1 mL of Se precursor	8.4 %	--	--
1.5 mL of Se precursor	10.5 %	--	--
1.75 mL of Se precursor	13.6 %	--	--
0.5 mL of S precursor	--	1.1 %	1.3 %
1 mL of S precursor	--	4.4 %	4.6 %
1.5 mL of S precursor	--	7.6 %	7.7 %
2 mL of S precursor	--	9.3 %	9.4 %

In the experiment, the chalcogenide precursor solution was injected into the mixture solution by syringe pump, so the density and lateral size of MoSe₂ can be easily controlled by tuning the addition amount of the precursors. Figure 5.13a-c illustrate the typical TEM images of the Cu_{2-x}S-MoSe₂ heterostructure NWs obtained at different addition amount of Se precursor stock solution. When only 0.5mL of Se precursor solution was used, few MoSe₂ NSs with a lateral size of 1-2 nm can be observed on Cu_{2-x}S NWs (Figure 5.13a). High-density of MoSe₂ NSs with a lateral size of about 5 nm can be detected on Cu_{2-x}S

NWs when 1 mL Se precursor was introduced (Figure 5.13b). Further increasing the addition amount of Se precursor to 1.75 mL, the MoSe₂ NSs can be growth up to 10 nm (Figure 5.13c). Accordingly, the loading amount of MoSe₂ NSs on Cu_{2-x}S NWs continuously increases with the addition amount of Se precursor (Figure 5.13d). The loading weight percentage of MoSe₂ NSs on Cu_{2-x}S NWs can be tuned from 3.8% to 13.6%, as determined by ICP-OES characterization (Table 5.1).

5.2.3 Synthesis of Cu_{2-x}S-MoS₂ Heterostructure Nanowires

Impressively, the method can also be used to synthesize Cu_{2-x}S-MoS₂ heterostructures by simply changing the Se precursor to S precursor. Figure 5.14a shows a typical TEM image of the obtained Cu_{2-x}S-MoS₂ heterostructures, in which MoS₂ NSs are grown vertically along the longitudinal direction of Cu_{2-x}S NWs (see XPS and XRD patterns in Figure 5.15 and Figure 5.16, respectively). The continuous lattice fringes across the interface between MoS₂ and Cu₂S can be observed in the HAADF-STEM images taken at the tip (Figure 5.14b) and body (Figure 5.14c) of Cu_{2-x}S-MoS₂ heterostructures, indicating the epitaxial growth of MoS₂ on Cu₂S. In Figure 5.14c, the measured lattice fringes are 0.64 nm and 0.33 nm, assignable to the (002) planes of MoS₂ and Cu₂S, respectively. More importantly, the Mo layer in MoS₂ (indicated by white dashed arrows) are also located between two pure Cu layers in Cu₂S (indicate by white dashed lines), confirming its same structure as the Cu_{2-x}S-MoSe₂ heterostructures. The HAADF-STEM image of a typical Cu_{2-x}S-MoS₂ heterostructure and the corresponding STEM-EDS elemental maps indicate the existence of Cu, S and Mo elements (Figure 5.17), and the uniform growth of MoS₂ NSs on Cu_{2-x}S NWs.

The density and lateral size of the MoS₂ on Cu_{2-x}S NWs also can be systematically controlled by tuning the addition amount of the sulfur precursor solution (Figure 5.14 d-g). Figure 5.14d-f illustrate the typical TEM images of Cu_{2-x}S-MoS₂ heterostructures obtained at different injection volume of S precursor solution. Noted that quite thick layers of MoS₂ NSs covered the entire surface of Cu_{2-x}S NWs can be obtained after 2 mL of sulfur precursor solution was injected (Figure 5.14f). Similarly, the loading amount of MoS₂ NSs

on Cu_{2-x}S NWs also continuously increase with the injection amount of S precursor solution. As shows in Fig. 4g, the loading amount of MoS₂ can be reached at 9.3% after 2 mL of sulfur precursor solution were added.

Figure 5.14 (a) TEM image of a typical Cu_{2-x}S-MoS₂ heterostructure, obtained by using 1.5 mL of S precursor solution. (b, c) HAADF-STEM images of Cu_{2-x}S-MoS₂ heterostructures taken at the tip (b) and the body (c) parts. The red triangles indicate the position of MoS₂ NSs. (d-f) TEM images of the Cu_{2-x}S-MoS₂ heterostructures obtained by using different injection volume of S precursor solution: (d) 0.5, (e) 1.0, and (f) 2 mL. (g) The plot of the weight percentage (wt%) of MoS₂ in Cu_{2-x}S-MoS₂ heterostructures, measured by ICP-OES, versus the volume of S precursor solution.

Figure 5.15 (a) High-resolution XPS spectra of Cu 2p. (b) High resolution XPS spectra of Mo 3d. The peaks of Mo 3d appear at binding energy of 228.4 eV (Mo3d_{5/2}) and 231.8 eV (Mo3d_{3/2}), indicating that Mo⁴⁺ is the dominant oxidation state. (c) High resolution XPS spectra of S 2p. The two peaks located at 161.6 eV and 162.6 eV can be assigned to the presence of S²⁻.

Figure 5.16 XRD pattern of Cu_{2-x}S-MoS₂ heterostructures. The standard diffraction pattern of djurleite Cu_{2-x}S (JCPDS No. 20-0365) is used as reference. The experimental XRD pattern matches well with the standard one. No obvious peaks from MoS₂ were detected.

Figure 5.17 (a) HAADF-STEM and (b-d) the corresponding STEM-EDS images of (b) Cu, (c) Mo and (d) S in the Cu_{2-x}S-MoS₂ heterostructures, indicating the existence of Cu, S and Mo, and suggesting the uniform growth of MoS₂ NSs on Cu_{2-x}S NWs.

The aforementioned results demonstrate the successful construction of epitaxial heterostructure consists of 2D MoS₂ and MoSe₂ NSs and 1D Cu_{2-x}S NWs, which is different from reported 2D/1D heterostructures with a random orientation of their 2D units.^[33, 34] The epitaxial growth of 2D MoS₂ and MoSe₂ NSs through its edge dangling bonds onto 1D Cu_{2-x}S NWs ensure the direct contact between MoS₂/MoSe₂ and Cu_{2-x}S, and create a 2D/1D interface with low interfacial defects, which benefits the charge transportation. More importantly, the vertical alignment of 2D TMD layers on a 1D NWs can expose its edge sites, which possess great potential in catalysis application.

Figure 5.18 (a) High-resolution XPS spectra of Cd 3d. (b) High resolution XPS spectra of Mo 3d. (c) High resolution XPS spectra of S 2p.

5.2.4 Photocatalytic Activity of CdS-MoS₂ Heterostructure Nanowires

Recent studies proved that MoS₂ is a promising co-catalyst alternative to platinum for the photocatalytic hydrogen evolution reaction, owing to its relatively low cost, earth abundance and high catalytic activity.^[35-37] In this work, by using the cation exchange method, the Cu_{2-x}S-MoS₂ heterostructures with different loading amount of MoS₂ NSs were transformed to CdS-MoS₂ heterostructures. The vertical alignment architecture of MoS₂ on Cu_{2-x}S were well preserved in the obtained CdS-MoS₂ heterostructures, as show in Figure 5.20a-c. The successful transformation of Cu_{2-x}S-MoS₂ to CdS-MoS₂ heterostructures was further confirmed by XPS, EDS mapping and XRD (Figure 5.18-5.20). The peaks located at 405.1 and 411.9 eV can be ascribed to Cd 3d_{5/2} and Cd 3d_{3/2}, respectively. In the High resolution XPS spectra of Mo 3d, the peaks of Mo 3d appear at binding energy of 228.8 eV (Mo3d_{5/2}) and 232 eV (Mo3d_{3/2}), indicating that Mo⁴⁺ is the dominant oxidation state. Two peaks located at 161.6 and 162.6 eV can be assigned to the presence of S²⁻. Note that the aforementioned CdS-MoS₂ heterostructures cannot be directly synthesized by using CdS NWs as seeds. As a proof-of-concept application, the

CdS-MoS₂ heterostructure was used as photocatalyst for HER under visible light irradiation ($\lambda > 420$ nm).

Figure 5.19 (a) HAADF-STEM and (b-d) the corresponding STEM-EDS images of (b) Cd, (c) S and (d) Mo in CdS-MoS₂ heterostructures, indicating the existence of Cd, S and Mo, and suggesting the successful transformation of Cu_{2-x}S-MoS₂ to CdS-MoS₂ heterostructures.

Figure 5.20 XRD pattern of CdS-MoS₂ heterostructures. The standard diffraction pattern of wurtzite CdS (JCPDS No. 41-1049) is used as reference. Experimental XRD pattern matches well with the standard one, indicating the successful cation exchange from Cu_{2-x}S-MoS₂ to CdS-MoS₂ heterostructures.

Figure 5.21 (a) TEM image of CdS-MoS₂ heterostructures. (b) HAADF-STEM and (c) ABF-STEM images of the tip area of CdS-MoS₂ heterostructures. The red triangles indicate the position of MoS₂ NSs. (d) Comparison of H₂ production activities using CdS NW and CdS-MoS₂ heterostructures with different loading amount of MoS₂ NSs as catalysts. (e) Produced H₂ amount after 5 h photocatalytic HERs using CdS NW and CdS-MoS₂ heterostructures with different loading amount of MoS₂ NSs as catalysts. (f) Cycling test of photocatalytic H₂ evolution using CdS-MoS₂ heterostructures with 7.7 wt% MoS₂ NSs as catalyst.

Figure 5.21d compares the rate of H₂ evolution by using the original CdS NWs and CdS-MoS₂ heterostructures with different loading amounts of MoS₂ NSs as catalysts. Obviously, pure CdS NWs exhibit negligible catalytic activity (H₂ evolution rate of 79.3 μmol·h⁻¹·g⁻¹) because of the fast recombination of electron-hole pairs in CdS.^[38] In contrast, the CdS-MoS₂ heterostructures show enhanced photocatalytic H₂ production activity due to the recombination delay of electron-hole pairs by MoS₂ NSs. Especially, the CdS-MoS₂ heterostructures with 7.7 wt% of MoS₂ NSs give the highest H₂ production rate of 4,647 μmol·h⁻¹·g⁻¹, which is about 58 times that catalyzed with pure CdS NWs, and total 114.1 μmol of H₂ were produced after 5 h of reaction (Figure 5.21e). Further increasing the

loaded MoS₂ cocatalyst, e.g. 9.4 wt%, results in the decrease of the H₂ evolution rate. This might attribute to the high-density MoS₂ layers which could block the light absorption of CdS NWs. Moreover, the photocatalytic stability of CdS-MoS₂ heterostructures with 7.7 wt% of MoS₂ NSs was tested and repeated four times (total 20 h), as shown in Figure. 5.21f. After four cycles, it does not show significant loss of activity, indicating its good stability for photocatalytic H₂ evolution.

5.3 Conclusion

In summary, a unique type of 1D/2D epitaxial heterostructure was successfully synthesized, in which the TMD NSs vertically grown along the longitudinal direction of 1D Cu_{2-x}S NWs in an epitaxial manner. The well matched crystal structures between the TMD and Cu₂S are critical for the successful construction of epitaxial heterostructures. The epitaxial growth of TMD NSs on NWs can facilitate the charge transfer between 2D TMD NSs and 1D NWs, and thus enhance their catalytic performance. Taking the as-obtained CdS-MoS₂ heterostructures as example, they indeed exhibit enhanced photocatalytic activity toward HER under visible light irradiation compared to the pure CdS NWs. The strategy for the rational design and synthesis of epitaxial heterostructure in this work offers a new approach for the construction of other TMD-based epitaxial heterostructures, which might have various promising applications.

References

- [1] P. D. Cozzoli, T. Pellegrino and L. Manna, *Chem. Soc. Rev.* **2006**, 35, 1195-1208.
- [2] R. Costi, A. E. Saunders and U. Banin, *Angew. Chem. Int. Ed.* **2010**, 49, 4878-4897.
- [3] Z.-c. Zhang, B. Xu and X. Wang, *Chem. Soc. Rev.* **2014**, 43, 7870-7886.
- [4] C. L. Choi and A. P. Alivisatos, *Annu. Rev. Phys. Chem.* **2010**, 61, 369-389.
- [5] L. Manna, D. J. Milliron, A. Meisel, E. C. Scher and A. P. Alivisatos, *Nat. Mater.* **2003**, 2, 382-385.
- [6] J. Matthews, *Epitaxial growth*, Elsevier, **2012**.

- [7] H. T. Ng, J. Li, M. K. Smith, P. Nguyen, A. Cassell, J. Han and M. Meyyappan, *Science* **2003**, *300*, 1249-1249.
- [8] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi and B. H. Hong, *Nature* **2009**, *457*, 706-710.
- [9] E. P. Bakkers, J. A. Van Dam, S. De Franceschi, L. P. Kouwenhoven, M. Kaiser, M. Verheijen, H. Wondergem and P. van der Sluis, *Nat. Mater.* **2004**, *3*, 769-773.
- [10] O. Chen, J. Zhao, V. P. Chauhan, J. Cui, C. Wong, D. K. Harris, H. Wei, H.-S. Han, D. Fukumura and R. K. Jain, *Nat. Mater.* **2013**, *12*, 445-451.
- [11] Y. Ma, W. Li, E. C. Cho, Z. Li, T. Yu, J. Zeng, Z. Xie and Y. Xia, *ACS Nano* **2010**, *4*, 6725-6734.
- [12] D. J. Milliron, S. M. Hughes, Y. Cui, L. Manna, J. Li, L.-W. Wang and A. P. Alivisatos, *Nature* **2004**, *430*, 190-195.
- [13] G. Zhang, Q. Yu, W. Wang and X. Li, *Adv. Mater.* **2010**, *22*, 1959-1962.
- [14] G. J. Snyder and E. S. Toberer, *Nat. Mater.* **2008**, *7*, 105-114.
- [15] B. Lim, M. Jiang, P. H. Camargo, E. C. Cho, J. Tao, X. Lu, Y. Zhu and Y. Xia, *Science* **2009**, *324*, 1302-1305.
- [16] H. Lee, S. E. Habas, G. A. Somorjai and P. Yang, *J. Am. Chem. Soc.* **2008**, *130*, 5406-5407.
- [17] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh and H. Zhang, *Nat. Chem.* **2013**, *5*, 263-275.
- [18] J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De and R. J. Smith, *Science* **2011**, *331*, 568-571.
- [19] Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, F. Boey and H. Zhang, *Angew. Chem. Int. Ed.* **2011**, *50*, 11093-11097.
- [20] A. K. Geim and I. V. Grigorieva, *Nature* **2013**, *499*, 419-425.
- [21] A. Koma, *Thin Solid Films* **1992**, *216*, 72-76.
- [22] X. Huang, Z. Zeng, S. Bao, M. Wang, X. Qi, Z. Fan and H. Zhang, *Nat. Commun.* **2013**, *4*, 1444.
- [23] J. Schornbaum, B. Winter, S. P. Schießl, F. Gannott, G. Katsukis, D. M. Guldi, E. Spiecker and J. Zaumseil, *Adv. Funct. Mater.* **2014**, *24*, 5798-5806.

- [24] C. Tan, Z. Zeng, X. Huang, X. Rui, X. J. Wu, B. Li, Z. Luo, J. Chen, B. Chen and Q. Yan, *Angew. Chem. Int. Ed.* **2015**, *54*, 1841-1845.
- [25] X. Duan, C. Wang, J. C. Shaw, R. Cheng, Y. Chen, H. Li, X. Wu, Y. Tang, Q. Zhang and A. Pan, *Nat. Nanotechnol.* **2014**, *9*, 1024-1030.
- [26] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai and B. I. Yakobson, *Nat. Mater.* **2014**, *13*, 1135-1142.
- [27] H. Heo, J. H. Sung, G. Jin, J. H. Ahn, K. Kim, M. J. Lee, S. Cha, H. Choi and M. H. Jo, *Adv. Mater.* **2015**, *27*, 3803-3810.
- [28] M.-Y. Li, Y. Shi, C.-C. Cheng, L.-S. Lu, Y.-C. Lin, H.-L. Tang, M.-L. Tsai, C.-W. Chu, K.-H. Wei and J.-H. He, *Science* **2015**, *349*, 524-528.
- [29] C. Huang, S. Wu, A. M. Sanchez, J. J. Peters, R. Beanland, J. S. Ross, P. Rivera, W. Yao, D. H. Cobden and X. Xu, *Nat. Mater.* **2014**, *13*, 1096-1101.
- [30] T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch and I. Chorkendorff, *Science* **2007**, *317*, 100-102.
- [31] D. Zhang, A. B. Wong, Y. Yu, S. Brittman, J. Sun, A. Fu, B. Beberwyck, A. P. Alivisatos and P. Yang, *J. Am. Chem. Soc.* **2014**, *136*, 17430-17433.
- [32] P. Lukashev, W. R. Lambrecht, T. Kotani and M. van Schilfgaarde, *Phys. Rev. B* **2007**, *76*, 195202.
- [33] B. Xu, P. He, H. Liu, P. Wang, G. Zhou and X. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 2339-2343.
- [34] J. Liu, J. Jiang, C. Cheng, H. Li, J. Zhang, H. Gong and H. J. Fan, *Adv. Mater.* **2011**, *23*, 2076-2081.
- [35] W. Zhou, Z. Yin, Y. Du, X. Huang, Z. Zeng, Z. Fan, H. Liu, J. Wang and H. Zhang, *Small* **2013**, *9*, 140-147.
- [36] X. Zong, H. Yan, G. Wu, G. Ma, F. Wen, L. Wang and C. Li, *J. Am. Chem. Soc.* **2008**, *130*, 7176-7177.
- [37] J. Chen, X. J. Wu, L. Yin, B. Li, X. Hong, Z. Fan, B. Chen, C. Xue and H. Zhang, *Angew. Chem. Int. Ed.* **2015**, *54*, 1210-1214.
- [38] K. Chang, Z. Mei, T. Wang, Q. Kang, S. Ouyang and J. Ye, *ACS Nano*, **2014**, *8*, 7078-7087.

Chapter 6

Discussion and Future Work

This chapter gives a general discussion to conclude the whole thesis and discusses the originality of the research works in this thesis. First, a facile one-pot wet chemical method was developed to fabricate CdS-MS₂ (M = W or Mo) heterostructures, characterized with a single layer of MS₂ with lateral size about 4–10 nm selectively grown on the (0001) surface of wurtzite CdS nanocrystals (NCs). Detailed experiments have been performed to study the shape evolution of the heterostructures. These heterostructures possess a large number of edge sites in the MS₂ layers, which are also the active sites for hydrogen evolution reaction (HER). These CdS-MS₂ show excellent photocatalytic activity towards HER with quite good stability. Second, a new type of epitaxial heterostructure consisting of two dimensional (2D) transition metal dichalcogenide nanosheets (TMD NSs, i.e., MoSe₂ and MoS₂) and one dimensional (1D) non-layered Cu_{2-x}S nanowires have been synthesized. The 2D TMD NSs are vertically grown along the longitudinal direction of 1D Cu_{2-x}S nanowire in an epitaxial manner. The architectures of the heterostructures can be well maintained even if the composition and crystal structure of the original Cu_{2-x}S nanowires are transformed to CdS nanowires by the well-known cation exchange method. Based on the current research status, some works that can be focused on in the near future is also discussed.

6.1 General Discussion

This thesis focuses on the design and synthesis novel TMD based semiconductor heterostructures, i.e., preparation of CdS-MoS₂, CdS-WS₂, Cu_{2-x}S-MoS₂ and Cu_{2-x}S-MoSe₂. The formation mechanism and detail structure are investigated. Moreover, their photocatalytic activities towards photocatalytic hydrogen evolution under visible light irradiation were also studied.

6.1.1 Discussion on the preparation of CdS-MoS₂ and CdS-WS₂ heterostructures for HER.

In this part, a facile one-pot wet chemical method was developed to fabricate CdS-MS₂ (M = W or Mo) heterostructures. The heterostructures are quite uniform nanoparticles with the size of 4–11 nm, characteristic with single layer MS₂ with lateral size about 4–10 nm selectively grown on the (0001) surface of wurtzite CdS NCs. A detailed experiment has been performed to study the shape evolution of the heterostructures. These heterostructures possess large number of edge sites in the MS₂ layers, which are also active sites for hydrogen evolution reaction, and show excellent photocatalytic activity towards HER with quite good stability. These heterostructures would have great potential application in photocatalytic water splitting.

The novelties and significances of this work are listed below:

(1) Transition metal dichalcogenides such as WS₂ and MoS₂ have exhibited excellent performance towards electrocatalytic hydrogen evolution and are considered as promising alternatives for platinum. Several works have been reported that a p-n junction can be formed by integrating the CdS nanomaterials with TMD NSs, which could lead to outstanding performance towards photocatalytic hydrogen production. However, in all of these reports, all TMD NSs exhibit large lateral size or multilayered structure, which greatly limit their activity towards HER owing to the low exposure of the active edge sites. Therefore, in this thesis, a facile one-pot wet chemical method was developed to fabricate

CdS-MS₂ (M = W or Mo) heterostructures, which characteristic with single layer TMD NSs selectively grown on the Cd-rich (0001) surface of hexagonal CdS NCs. The lateral size of single layer TMD is only 4–10 nm, which indicates that these TMD NSs expose lots of active edge sites.

(2) Previous works about prepare CdS-MS₂ composite materials were realized through a high temperature treatment process, using (NH₄)₂MS₄ as a precursor in the presence of toxic H₂S gas, or involve multi-step experiments. In comparison with the previous reported methods, the approach in this work is a one-pot wet-chemical synthesis, using (NH₄)₂MS₄ as both metal and sulfur source, which is easy to scale up and offers more opportunities to design the structure.

(3) As the lateral size of the single layer TMD decorated on CdS NCs is typically less than 10 nm and such a structure could significantly increase the exposed area of active edge sites. Meanwhile, the diameters of the CdS-MS₂ heterostructures are very small (from 4–11 nm), in this case, the diffusion pathway of the charge carriers could be decreased, thus reduces the recombination probability. Furthermore, the adjacent single layer TMD and CdS will form a p-n junction, which accelerates the electron-hole separation. Therefore, the CdS-WS₂ and CdS-MoS₂ heterostructures show excellent photocatalytic performance towards HER under visible light irradiation, which are about 16 and 12 times of that of pure CdS, respectively. The heterostructures also show very good durability after long-time test.

6.1.2 Discussion on the Edge Epitaxy of 2D MoS₂ and MoSe₂ on 1D NWs

Epitaxial heterostructures, integrating distinct components with different functionalities into one system with precisely controlled composition and electronic modulation, are of critical importance for various applications, including electronics, optoelectronics, thermoelectric and catalysis. Two-dimensional (2D) transition metal dichalcogenide (TMD) NSs, one type of appealing layered materials, have been widely

used as a platform for construction of heterostructures through the vertically or laterally epitaxial growth of other materials.

However, the epitaxial growth of lateral heterostructures at the edges of TMD NSs still remains a great challenge, which mainly originates from the lack of materials with crystal symmetries and lattice parameters matching with the edges of TMDs. Until now, only a few lateral heterostructures have been reported, such as $\text{MoS}_2\text{--MoSe}_2$,^[1] $\text{MoS}_2\text{--WS}_2$,^[2] $\text{MoSe}_2\text{--WS}_2$,^[3] $\text{MoSe}_2\text{--WSe}_2$ ^[4] and $\text{WS}_2\text{--WSe}_2$.^[1] However, both components in the aforementioned lateral heterostructures are limited to the TMD NSs, which strongly limit their applications. There is no report on the preparation of epitaxial heterostructures based on TMDs with other non-layered materials interfaced at the edges of TMDs.

In this section, for the first time, the controlled synthesis of a new type of heterostructure was reported, in which TMD NSs (i.e., MoS_2 and MoSe_2) vertically grown along the longitudinal direction of one-dimensional Cu_{2-x}S nanowire in an epitaxial manner. The heterostructures were systematically characterized by the high-angle annular dark (bright)-field scanning transmission electron microscopy, which demonstrated the well match of crystal symmetries and lattice fringes between the TMD and Cu_2S is critical for the construction of the epitaxial heterostructures. The architectures of the heterostructures can be well maintained after the composition and crystal structure of the original Cu_{2-x}S nanowires are transformed by the well-known cation exchange method (e.g., Cu_{2-x}S to CdS). As a proof-of-concept application, the as-obtained CdS--MoS_2 heterostructures with different loading amount of MoS_2 are used as photocatalyst for photocatalytic hydrogen evolution reaction, exhibiting enhanced photocatalytic activity toward HER under visible light irradiation as compared to the pure CdS nanowires. This synthetic strategy opens up a new way for the controlled synthesis of TMD-based heterostructures which could have various promising applications.

The novelty and significance of this work are listed below:

(1) For the first time, a new type of epitaxial heterostructures consisting of 2D TMD NSs (i.e., MoSe₂ and MoS₂) and 1D non-layered Cu_{2-x}S nanowire have been synthesized. The 2D TMD NSs are vertically grown along the longitudinal direction of 1D Cu_{2-x}S nanowire in an epitaxial manner. The loading amount and lateral size of TMD NSs can be well tuned by the consecutive growth of TMD NSs on Cu_{2-x}S nanowire through the gradually injection method.

(2) The detailed interface structure between the high chalcocite Cu₂S and the grown MoSe₂ NSs in Cu_{2-x}S-MoSe₂ heterostructures has been revealed by a series of scanning transmission electron microscopy characterization. It is confirmed that the Se layers in MoSe₂ closely contacted the pure Cu layers in the high chalcocite Cu₂S, demonstrating that the well match of crystal symmetries and lattice fringes between TMD and Cu₂S is critical for the construction of epitaxial heterostructures.

(3) The architectures of the heterostructures can be well maintained even if the composition and crystal structure of the original Cu_{2-x}S nanowires are transformed to CdS nanowires by the well-known cation exchange method. The vertical alignment of MoS₂ on nanowire can be well preserved in the obtained CdS-MoS₂ heterostructures, which cannot be directly synthesized by using CdS nanowires as seeds. As a proof-of-concept application, compared to the pure CdS nanowires, the CdS-MoS₂ heterostructures with 7.7 wt% loading of MoS₂ NSs exhibit the best performance in the photocatalytic hydrogen evolution reaction with the H₂ production rate up to 4,647 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, about 58 times that catalyzed with pure CdS nanowires.

6.2 Reconnaissance

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

6.2.1 Synthesis of $\text{CdS}_x\text{Se}_{1-x}\text{-MoS}_2$ Epitaxial Heterostructures for Photocatalytic Hydrogen Evolution

Band gap engineering is critical for semiconductor photocatalyst to maximally utilize the solar energy.^[5,6] Also, the size and morphology control is very important for improving the activity of photocatalysts. In chapter 5, MoS_2 NSs were successfully grown vertically to the longitudinal direction of CdS nanowire, which shows great improvement toward photocatalytic HER compare with pure CdS nanowire. However, the size of obtained CdS- MoS_2 heterostructure is too large (length in micrometer), thus greatly limit its activity. $\text{CdS}_x\text{Se}_{1-x}\text{-MoS}_2$ with different S/Se ratio were fabricated. By controlling the chalcogen ratio, the energy bandgaps can be tuned. Figure 6.1 a-b show typical TEM images of $\text{CdS}_x\text{Se}_{1-x}\text{-MoS}_2$, from which MoS_2 vertically grown on $\text{CdS}_z\text{Se}_{1-z}$ nanoparticles can be observed. The as-synthesized $\text{CdS}_x\text{Se}_{1-x}\text{-MoS}_2$ are quite uniform tetradecahedron structure with size of 15-20 nm. A FFT pattern from (002) surface shows in the inset of Figure 6.1 b, in which two set of diffraction pattern can be observed, indicates that the epitaxial growth of MoS_2 on $\text{CdS}_x\text{Se}_{1-x}$ surface. The top-view and side-view HR-TEM images are shown in Figure 6.1c-d, the measured lattice distances are 0.33 and 0.35 nm, which can be assigned to the adjacent {0002} and (1010) planes of hexagonal $\text{CdS}_x\text{Se}_{1-x}$, respectively. Elemental quantification excluded the presence of a mixture of CdSe and CdS NCs and confirmed instead the presence of alloy $\text{CdS}_x\text{Se}_{1-x}$. Figure 6.1e displays the XRD pattern for a series of Cd-based heterostructure. The diffraction data suggests that all the samples have a hexagonal structure. From the amplified (110) diffraction peaks of the samples, it can be seen that the peaks successively shift to higher degrees with the decrease of Se in the samples. This shift could be attributed to a decrease in the size of the crystallographic unit cell due to the incorporation of more S which has a smaller atomic than Se. Next, $\text{CdS}_x\text{Se}_{1-x}\text{-MoS}_2$ heterostructures with different chalcogen ratio and different loadings of MoS_2 will be used for the photocatalytic hydrogen evolution reaction under the visible light irradiation (>420 nm).

6.2.2 Preparation of Other TMD-Based Heterostructures

As a kind of layered materials, TMDs are excellent platform to construct heterostructures.^[7] The hexagonal lattice of these TMD semiconductors may allow for an epitaxial growth onto chalcogenide semiconductors. In this thesis, a series of heterostructures based on MoS₂ and WS₂ have been constructed. Other TMD materials, such as ReS₂, TaS₂^[8] and TiS₂,^[9] have shown promising applications in catalysis and energy storage.

Figure 6.1 Synthesis and characterization of CdS_xSe_{1-x}-MoS₂ heterostructure. (a, b) TEM image of CdS_xSe_{1-x}-MoS₂ heterostructures. (c) A typical side view HR-TEM image of CdS_xSe_{1-x}-MoS₂ heterostructure. (d) A typical top view HR-TEM image of CdS_xSe_{1-x}-MoS₂ heterostructure. (e) Dark-field STEM image and corresponding EDS mapping images of CdS_xSe_{1-x}-MoS₂ heterostructures. (f-g) XRD pattern of CdS_xSe_{1-x}-MoS₂ heterostructure with different S/Se ratio.

Therefore, it is interesting to prepare other TMD based heterostructures and used as catalysts for photo/electro-water splitting, energy storage and so on. Among available TMD materials, VS_2 is predicted to be the beset for the HER, a ranking of different type of monolayer TMD being $\text{VS}_2 > \text{MoS}_2 > \text{WS}_2$.^[10] And VS_2 is predicted to be on par with or even exceed that of Pt. These theoretical calculation calls for additional experimental studies. Thus, synthesis of TMD based heterostructures, especially VS_2 -based heterostructure is of great importance.

6.2.3 Preparation of 1 T TMD Based Heterostructures

As introduced in the Literature Review in Chapter 3, TMD materials have several different phases. It has been known that the 2H phase MoS_2 or WS_2 can be transform to 1T phase upon lithium intercalation, and the metallic 1T phase TMD NSs have shown great potential in electronics, electrocatalysis and electrochemical supercapacitors.^[11-12] For example, the catalytic activity of 1T MoS_2 is much higher than 2H MoS_2 . Although a lot of works about the construction 1T phase TMD have been reported, there are very few reports about construction of 1T phase TMD based heterostructure due to the instability of 1T phase. In this thesis, several kinds of 2H TMD based heterostructures have been successfully synthesized. Based on these heterostructures, it is possible to use the lithium intercalation method to transform the 2H phase to 1 T phase. The 1T TMD based heterostructures may show some interesting properties or enhanced catalytic activity.

References

- [1] X. Duan, C. Wang, J. C. Shaw, R. Cheng, Y. Chen, H. Li, X. Wu, Y. Tang, Q. Zhang, A. Pan, *Nat. Nanotech.* **2014**, 9, 1024-1030.
- [2] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai, B. I. Yakobson, *Nat. Mater.* **2014**, 13, 1135-1142.
- [3] M.-Y. Li, Y. Shi, C.-C. Cheng, L.-S. Lu, Y.-C. Lin, H.-L. Tang, M.-L. Tsai, C.-W. Chu, K.-H. Wei, J.-H. He, *Science* **2015**, 349, 524-528.

- [4] C. Huang, S. Wu, A. M. Sanchez, J. J. P. Peters, R. Beanland, J. S. Ross, P. Rivera, W. Yao, D. H. Cobden, X. Xu, *Nat. Mater.* **2014**, *13*, 1096-1101.
- [5] J. Zhang, J. Sun, K. Maeda, K. Domen, P. Liu, M. Antonietti, X. Fu, X. Wang, *Energy & Environmental Science* **2011**, *4*, 675-678.
- [6] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* **2001**, *293*, 269-271.
- [7] C.-H. Lee, G.-H. Lee, A. M. Van Der Zande, W. Chen, Y. Li, M. Han, X. Cui, G. Arefe, C. Nuckolls, T. F. Heinz, *Nat. Nanotech.* **2014**, *9*, 676-681.
- [8] S. Tongay, H. Sahin, C. Ko, A. Luce, W. Fan, K. Liu, J. Zhou, Y.-S. Huang, C.-H. Ho, J. Yan, *Nat. commun.* **2014**, *5*, 3252.
- [9] H. Li, G. Lu, Y. Wang, Z. Yin, C. Cong, Q. He, L. Wang, F. Ding, T. Yu, H. Zhang, *Small* **2013**, *9*, 1974-1981.
- [10] X. Fan, S. Wang, Y. An, W. Lau, *J. Phys. Chem. C* **2016**, *120*, 1623-1632.
- [11] K. Chang, X. Hai, H. Pang, H. Zhang, L. Shi, G. Liu, H. Liu, G. Zhao, M. Li, J. Ye, *Adv. Mater.* **2016**, *28*, 10033-10041.
- [12] B. Mahler, V. Hoepfner, K. Liao, G. A. Ozin, *J. Am. Chem. Soc.* **2014**, *136*, 14121-14127.

Publication List

- [1] **J. Chen**, X.-J. Wu, Y. Gong, Y. Zhu, Z. Yang, B. Li, Q. Lu, Y. Yu, S. Han, Z. Zhang, Z. Yun, Y. Han, G. Lin, H. Zhang, *J. Am. Chem. Soc.* **2017**, *139*, 8653–8660.
- [2] **J. Chen**, X. J. Wu, L. Yin, B. Li, X. Hong, Z. Fan, B. Chen, C. Xue, H. Zhang, *Angew. Chem., Int. Ed.* **2015**, *54*, 1210-1214.
- [3] X.-J. Wu, **J. Chen**, C. Tan, Y. Zhu, Y. Han, H. Zhang, *Nat. Chem.* **2016**, *8*, 470-475.
- [4] N. Yang, Z. Zhang, B. Chen, Y. Huang, **J. Chen**, Z. Lai, Y. Chen, M. Sindoro, A. L. Wang, H. Cheng, Z. Fan, Z. Liu, B. Li, Y. Zong, L. Gu, H. Zhang, *Adv. Mater.* DOI: 10.1002/adma.201700769.
- [5] C. Tan, X. Cao, X.-J. Wu, Q. He, J. Yang, X. Zhang, **J. Chen**, W. Zhao, S. Han, G.-H. Nam, M. Sindoro, H. Zhang, *Chem. Rev.* **2017**, *117*, 6225-6331.
- [6] S. Han, X. Yang, Y. Zhu, C. Tan, X. Zhang, **J. Chen**, Y. Huang, B. Chen, Z. Luo, Q. Ma, M. Sindoro, H. Zhang, X. Qi, H. Li, X. Huang, W. Huang, X. Sun, Y. Han, H. Zhang, *Angew. Chem., Int. Ed.* DOI: 10.1002/anie.201705617.
- [7] Q. Ma, H. Cheng, Y. Yu, Y. Huang, Q. Lu, S. Han, **J. Chen**, R. Wang, A. G. Fane, H. Zhang, *Small* DOI: 10.1002/smll.201700391.
- [8] Y. Yu, X. J. Wu, M. Zhao, Q. Ma, **J. Chen**, B. Chen, M. Sindoro, J. Yang, S. Han, Q. Lu, H. Zhang, *Angew. Chem., Int. Ed.* **2017**, *56*, 578-581.
- [9] Z. Luo, C. Tan, X. Zhang, **J. Chen**, X. Cao, B. Li, Y. Zong, L. Huang, X. Huang, L. Wang, W. Huang, H. Zhang, *Small* **2016**, *12*, 5920-5926.
- [10] Z. Zhang, Z. Luo, B. Chen, C. Wei, J. Zhao, **J. Chen**, X. Zhang, Z. Lai, Z. Fan, C. Tan, M. Zhao, Q. Lu, B. Li, Y. Zong, C. Yan, G. Wang, Z. Xu, H. Zhang *Adv. Mater.* **2016**, *28*, 8712-8717.
- [11] Q. Lu, M. Zhao, **J. Chen**, B. Chen, C. Tan, X. Zhang, Y. Huang, J. Yang, F. Cao, Y. Yu, J. Ping, Z. Zhang, X. J. Wu, H. Zhang *Small* **2016**, *12*, 4669-4674.
- [12] J. Ping, Y. Wang, Q. Lu, B. Chen, **J. Chen**, Y. Huang, Q. Ma, C. Tan, J. Yang, X. Cao, Z. Wang, J. Wu, Y. Ying, H. Zhang, *Adv. Mater.* **2016**, *28*, 7640-7645.

- [13] Y. Wang, M. Zhao, J. Ping, B. Chen, X. Cao, Y. Huang, C. Tan, Q. Ma, S. Wu, Y. Yu, Q. Lu, **J. Chen**, W. Zhao, Y. Yi, H. Zhang, *Adv. Mater.* **2016**, 28, 4149-4155.
- [14] C. Tan, W. Zhao, A. Chaturvedi, Z. Fei, Z. Zeng, **J. Chen**, Y. Huang, P. Ercius, Z. Luo, X. Qi, B. Chen, Z. Lai, B. Li, X. Zhang, J. Yang, Y. Zong, C. Jin, H. Zheng, C. Kloc, H. Zhang, *Small* **2016**, 12, 1866-1874.
- [15] J. Chen, H. B. Yang, H. B. Tao, L. Zhang, J. Miao, H. Y. Wang, **J. Chen**, H. Zhang, B. Liu, *Adv. Funct. Mater.* **2016**, 26, 456-465.
- [16] C. Tan, P. Yu, Y. Hu, **J. Chen**, Y. Huang, Y. Cai, Z. Luo, B. Li, Q. Lu, L. Wang, Z. Liu, H. Zhang, *J. Am. Chem. Soc.* **2015**, 137, 10430-10436.
- [17] X. Hong, C. Tan, J. Liu, J. Yang, X.-J. Wu, Z. Fan, Z. Luo, **J. Chen**, X. Zhang, B. Chen, H. Zhang, *J. Am. Chem. Soc.* **2015**, 137, 1444-1447.
- [18] C. Tan, Z. Zeng, X. Huang, X. Rui, X. J. Wu, B. Li, Z. Luo, **J. Chen**, B. Chen, Q. Yan, H. Zhang, *Angew. Chem., Int. Ed.* **2015**, 54, 1841-1845.
- [19] Y. Zhang, B. Zheng, C. Zhu, X. Zhang, C. Tan, H. Li, B. Chen, J. Yang, **J. Chen**, Y. Huang, L. Wang, H. Zhang, *Adv. Mater.* **2015**, 27, 935-939.
- [20] X. Hong, C. Tan, **J. Chen**, Z. Xu, H. Zhang, *Nano Research* **2015**, 8, 40-55.
- [21] X. Huang, B. Zheng, Z. Liu, C. Tan, J. Liu, B. Chen, H. Li, **J. Chen**, X. Zhang, Z. Fan, W. Zhang, Z. Guo, F. Huo, Y. Yang, L. H. Xie, W. Huang, H. Zhang, *ACS Nano* **2014**, 8, 8695-8701.
- [22] X. Hong, J. Liu, B. Zheng, X. Huang, X. Zhang, C. Tan, **J. Chen**, Z. Fan, H. Zhang, *Adv. Mater.* **2014**, 26, 6250-6254.
- [23] Z. Yin, X. Zhang, Y. Cai, **J. Chen**, J. I. Wong, Y. Y. Tay, J. Chai, J. Wu, Z. Zeng, B. Zheng, H. Yang, H. Zhang, *Angew. Chem., Int. Ed.* **2014**, 53, 12560-12565.
- [24] Z. Yin, B. Chen, M. Bosman, X. Cao, **J. Chen**, B. Zheng, H. Zhang, *Small* **2014**, 10, 3537-3543.
- [25] X. Hong, Z. Yin, Z. Fan, Y. Y. Tay, **J. Chen**, Y. Du, C. Xue, H. Chen, H. Zhang, *Small* **2014**, 10, 479-482.
- [26] Y. Huang, M. Zhao, S. Han, Z. Lai, J. Yang, C. Tan, Q. Ma, Q. Lu, **J. Chen**, X. Zhang, Z. Zhang, B. Li, B. Chen, Y. Zong, H. Zhang, *Adv. Mater.* DOI: 10.1002/adma.201700102.