A study on novel layered nanomaterials : synthesis, structural engineering and applications

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**A STUDY ON NOVEL LAYERED NANOMATERIALS:
SYNTHESIS, STRUCTURAL ENGINEERING AND
APPLICATIONS**

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**INTERDISCIPLINARY GRADUATE SCHOOL
ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)**

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SYNTHESIS, STRUCTURAL ENGINEERING AND
APPLICATIONS**

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Energy Research Institute @ NTU (ERI@N)**

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

2017

Statement of Originality

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

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Date

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Student Name

Abstract

Preparation of novel layered materials and engineering their composition and structure is fascinating to generate new functions for a diverse range of applications. In the light of this, the aim of this thesis is to synthesize novel layered materials and engineer their nanostructures through oxygen hybridization and size reduction, and then explore their potential applications in electronic devices such as light-emitting diodes (LEDs) and memory devices.

First, I demonstrated a facile method to oxidize the exfoliated MoS₂ nanosheets, forming MoS₂-MoO₃ hybrid nanomaterials. The oxidization process was realized through the in-situ oxidation process in air during the film preparation utilizing heat-assisted spray-coating process. After thermal annealing, the MoS₂-MoO₃ hybrid nanomaterials composed of (100)-dominated MoS₂ and (021)-dominated α -MoO₃ were formed. Importantly, the MoS₂-MoO₃ hybrid film can be formed on several solid substrates, such as SiC, Si, glass or quartz. Moreover, the obtained MoS₂-MoO₃ exhibited *p*-type conductivity. Then LEDs were fabricated by using the heterojunction composed of *p*-type MoS₂-MoO₃ (*p*-MoS₂-MoO₃) film and *n*-type 4H-SiC (*n*-SiC) substrate. The LEDs exhibited broad spectra with four sub-wavelength emissions. The electroluminescence mechanism was investigated through experiments and theoretical calculations.

Second, I decreased the lateral size of transition metal dichalcogenide (TMD) materials and prepared a series of TMD nanodots (NDs), including MoS₂, MoSe₂, WS₂, WSe₂, ReS₂, TaS₂, and NbSe₂. All these TMD NDs have a small size less than 10 nm and good dispersity in N-methyl-2-pyrrolidone (NMP) solution. Moreover, I also developed a method to isolate these NDs from the solvent of NMP, i.e., post-treatment of these NDs with hexane and chloroform. As a proof-of-concept application, the TMD NDs (e.g., MoSe₂, NbSe₂ or WS₂) were mixed with organic polymer (e.g., polyvinylpyrrolidone (PVP)) and used

as active layers for fabrication of memory devices. These devices display nonvolatile write-once-read-many (WORM) memory behavior with high ON/OFF current ratio and good stability. We believe that these TMD NDs can show more potential in optoelectronics, solar cells, catalysis, and biomedicine.

Then, I further extended the size reduction protocol to fabricate other novel layered NDs and prepared black phosphorus quantum dots (BPQDs) from the bulk black phosphorus crystal, which is an emerging layered material. The obtained BPQDs have a lateral size of 4.9 ± 1.6 nm and thickness of 1.9 ± 0.9 nm (ca. 4 ± 2 layers). As a proof of concept, a flexible memory device based on polyethylene terephthalate (PET) substrate, using BPQDs mixed with PVP as the active layer, have been successfully fabricated, which shows nonvolatile rewritable memory behavior with high ON/OFF current ratio of more than 6.0×10^4 and good stability.

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Abbreviations

0D	Zero-dimensional
2D	Two-dimensional
3D	Three-dimensional
AFM	Atomic Force Microscopy
BP	Black Phosphorus
BPQDs	Black Phosphorus Quantum Dots
CB	Conduction Band
CVD	Chemical Vapor Deposition
CMOS	Complementary Metal–oxide Semiconductor
DOS	Density of States
EDS	Energy Dispersive X-ray Spectroscopy
EL	Electroluminescence
EMSC	Effective Medium Semiconductor
FET	Field-effect Transistor
GQDs	Graphene Quantum Dots
HRTEM	High-resolution Transmission Electron Microscopy
HER	Hydrogen Evolution Reaction
HRS	High-resistance State
ITO	Indium Tin Oxide
LEDs	Light-emitting Diodes
LIBs	Li-ion Batteries
LRS	Low-resistance State
NAC	N-acetyl-L-cysteine
NDs	Nanodots
NIR	Near-infrared
NMP	N-methyl-pyrrolidone
PET	Polyethylene Terephthalate
PEN	Polyethylene Naphthalate

PL	Photoluminescence
PVDF	Poly(vinylidene fluoride)
PVP	Polyvinylpyrrolidone
rGO	Reduced Graphene Oxide
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
TED	Transmission Electron Detector
TEM	Transmission Electron Microscopy
THF	Tetrahydrofuran
TMDs	Transition Metal Dichalcogenides
UV-vis	Ultraviolet-visible
VASP	Vienna <i>ab Initio</i> Simulation Package
VB	Valence Band
VdW	Van der Waals
WORM	Write Once Read Many
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy

Chapter 1

Introduction

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

1.1 Hypothesis/Problem Statement

Two-dimensional (2D) layered materials have attracted considerable interest over the last decades.^[1-9] With the unique laminar structure, these materials have been exfoliated to nanosheets with single or few atomic layers, presenting intriguing physical, chemical or photoelectronic properties different from those of their bulk counterpart.^[1-9] To date, a great number of 2D ultrathin nanosheets, such as graphene, transition metal dichalcogenides (TMDs),^[1, 5, 6] black phosphorus (BP),^[10, 11] and MXenes (M is a transition metal, and X stands for C or N, such as Ti_2C , Nb_2C , Ti_3C_2 , V_2C , Ti_3CN , and Ta_4C_3),^[12] have been prepared and characterized for a wide range of applications in electronics, catalysis, sensing, and bio-applications.

TMDs and BP are two special types of layered materials, which have attracted great interest recently.^[1, 3, 13-17] The TMD materials represent a wide range of compounds with a generalized formula of MX_2 , where M stands for a transition metal from group IV (Ti, Zr, Hf), group V (V, Nb, Ta), and group VI (Mo, W), and X represents chalcogen atoms (S, Se, and Te).^[1, 6, 18, 19] The TMD materials show diverse physicochemical properties, which offer great opportunities for various applications, such as energy storage, catalysis, sensing and electronic devices like memory devices and field-effect transistors (FETs).^[14] BP is a conceptually new material with layered structure, which has sparked a recent resurgence of interest due to its unique structures as well as remarkable electronic and optical properties.^[20-22] Due to the similar layered structural feature with graphite and appealing tunable bandgap, BP shows great promise in filling the space between zero-gap graphene and large-gap TMDs, hence it is potentially promising for optical/electronic devices, catalysis and bio-application.^[20-22]

Despite that the search for new materials continues to be an attractive direction to pursue, developing methods to tune the structures and properties of existing materials in a wide range is equally promising, because a material with limited properties may not show versatile applications.^[14] Fortunately, the diversified layered materials provide a rich platform for engineering their structure and tuning their physical and chemical properties. Especially the successful exploration of graphene nanosheets provides valuable instructions for preparing of other novel layered materials through engineering their intrinsic structural feature. TMDs are particularly suitable candidates because they have diversified components, different structural polymorphs, and a wide range of electronic properties including superconductors, semiconductors, and metals, which offer great potential for engineering their structure to generate fascinating properties for many promising applications.^[1] For example, the crystal structure of MoS₂ can be transformed from hexagonal 2H-phase to tetragonal 1T-phase, resulting in the change of electronic property from semiconductors to metals, which provides great potential for electrocatalysis,^[23] supercapacitors,^[24] and electronics.^[25] So far, the structural engineering of layered TMD materials has been achieved through many protocols, such as (i) decrease of their size and thickness, (ii) phase engineering through intercalation of alkaline metal ions, and (iii) doping, alloying or hybridization.

Among the above-mentioned structural engineering protocols, the hybridization of layered TMD materials with other materials is extraordinarily attractive for generating new properties and optimizing their performance for specific applications. Because the chalcogen atoms at the surface of TMDs can be partially or fully replaced by oxygen atoms, forming oxygen-doped or oxidized TMD materials, the oxygen doping/oxidization is one of the most facial and straightforward processes to generate new structures with desired functions.^[3, 26] Furthermore, the ultrathin single- or few-layer metal chalcogenide nanosheets, especially those produced in solution, can be easily incorporated with oxygen

via morphology/topology transformation, which is promising for construction of novel nanostructures.^[27, 28] The hypothesis here is that the ultrathin TMD nanosheets, especially MoS₂, might be able to be oxidized through a facial oxidation process to generate MoS₂ based heterostructures, which may have potential in applications like electronic devices and photocatalysis. We believe that the structural engineering of layered materials offers great opportunities to optimize and improve their performance in practical applications.

In addition of the structural engineering of TMD materials by oxygen doping or hybridization, exploration of novel structures/morphologies by decreasing their lateral sizes is also scientifically meaningful. Besides the layered flakes or nanosheets, zero-dimensional (0D) ultra-small nanodots (NDs) are another form of 2D structures, as their properties can be distinctive from their bulk counterpart.^[29-31] The earlier attempts of graphene quantum dots (GQDs) have proved their potential with appealing properties and applications.^[29-31] Therefore, the structural engineering of other layered structures by reducing the dimension along the in-plane direction is potentially valuable to generate new properties for potential applications. For one thing, the tunable bandgap as a function of the size of TMDs provides great opportunities for optical electronics and bio-imaging. From another point of view, when the size of TMD materials is reduced to nanoscale, a large portion of edge atoms with unsaturated coordination are exposed and the edge effect will also significantly affect the properties and applications of nanomaterials. It has been reported that the unsaturated coordination edges of TMD materials, especially MoS₂ NDs, show metallic state and catalytic activity for hydrogen evolution, which is in sharp contrast to the inert in-plane sites with weak activity.^[5, 32] Moreover, the TMD NDs are able to inherit some of the properties from their 2D counterpart, and meanwhile show different properties due to the size effect and edge coordination.^[14, 32-35] Therefore, the hypothesis here is to decrease the lateral size of a series of novel layered materials, especially those with semiconductor

properties such as MoS₂, WS₂, MoSe₂, WSe₂, ZrS₂, and BP, and explore their potential applications in electronic devices. We believe that the structural engineering of layered materials offers great opportunities to optimize and improve their performance for practical applications.

1.2 Objectives and Scope

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

First, the MoS₂ nanosheets with atomic thickness will be prepared by the electrochemical Li intercalation/exfoliation method, and then used as backbone to produce MoS₂-MoO₃ hybrid nanomaterials via in-situ oxidation process. The oxidized MoS₂ nanosheets will be characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area electron diffraction (SAED), and X-ray photoelectron spectroscopy (XPS). Then the physical properties, e.g., conductivity type, will be tested. Then the MoS₂-MoO₃ hybrid materials will be used for fabrication of electronic devices, e.g., light-emitting diodes (LEDs). The hybridization of MoS₂ and MoO₃ provides opportunities to broaden the applications of MoS₂.

Second, the lateral size of TMD materials will be reduced and TMD NDs will be prepared by combining mechanical grinding and sonication process in solution. These NDs will be characterized by TEM, HRTEM, SAED, AFM, XPS, Raman, and UV-vis absorption spectroscopy. Moreover, the solution-processed NDs will be hybridized with organic polymer and the potential application for fabrication of data storage devices (e.g., memory devices) will be explored.

Third, the size reduction process will be extended to prepare other novel layered materials, i.e., BP quantum dots (BPQDs). The bulk BP crystals will be prepared from red phosphorus at high pressure and high temperature, which will be used as starting materials for preparation of BPQDs. The obtained materials will be characterized using TEM, HRTEM, SAED, AFM, XPS, Raman, and UV-vis absorption spectroscopy. The potential application for fabrication of flexible memory devices will be investigated.

1.3 Dissertation Overview

This thesis demonstrates the synthesis of novel layered structures by engineering their intrinsic structure features, including forming heterostructures and decreasing the lateral size, to optimize and improve their performance for applications in electronics. The potential of the novel structure in electronic devices like LEDs and non-resistive memory devices will be demonstrated.

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

Chapter 2 reviews the literature concerning the current research progress on the structure engineering of layered materials, especially graphene, TMD, and BP materials.

Chapter 3 discusses the rationale analysis for material selection, the detailed synthetic procedure, characterization techniques as well as the potential applications for layered NDs.

Chapter 4 elaborates the oxidation of MoS₂ nanosheets, the synthesis of MoS₂-MoO₃ hybrid materials, and the utilization of these materials for fabrication of LEDs.

Chapter 5 elaborates the synthesis and characterization of TMD NDs, including MoS₂, MoSe₂, WS₂, WSe₂, ReS₂, TaS₂, and NbSe₂, and the utilization of these NDs as active layers for fabrication of non-resistive memory diodes.

Chapter 6 elaborates the preparation and characterization of BPQDs, and demonstrates the potential application for fabrication of flexible memory devices.

Chapter 7 concludes the whole thesis and elaborates the reconnaissance studies which could be conducted in the near future.

1.4 Findings and Outcomes/Originality

This research leads to several novel outcomes:

1. First, a facile oxidation process has been established to partially oxidize the exfoliated MoS₂ nanosheets, and prepare MoS₂-MoO₃ hybrid nanomaterials. The oxidization was realized by in-situ oxidization of MoS₂ nanosheets during the film preparation using heat-assisted spray-coating method, followed by the annealing-driven crystallization. The oxidization process can be processed on any solid substrates, such as SiC, Si, glass or quartz. The as-formed MoS₂-MoO₃ hybrid nanomaterials are composed of (100)-dominated MoS₂ and (021)-dominated-MoO₃. Importantly, the obtained MoS₂-MoO₃ exhibits *p*-type conductivity. Moreover, LED devices have been fabricated by using the *p-n* heterojunction composed of the as-formed *p*-type MoS₂-MoO₃ film (*p*-MoS₂-MoO₃) and *n*-type 4H-SiC (*n*-SiC) substrate with the configuration of Au/Ti/*n*-SiC/*p*-MoS₂-MoO₃/ITO/glass. The LEDs show multi-wavelength light emission. In addition, the electroluminescent mechanism has been investigated. It is suggested that the radiative recombination of electrons and holes, i.e., electrons

from conduction band (CB) and holes from valence band (VB) of MoS₂, and electrons from CB and holes from VB of MoO₃, are accounted for two peaks in EL spectrum. The other two peaks, revealed by theoretical calculation, are originated from the defective levels in MoO₃.

2. A series of TMD NDs, a new type of layered materials, including MoS₂, MoSe₂, WS₂, WSe₂, ReS₂, TaS₂, and NbSe₂ NDs, have been fabricated from their bulk crystal counterpart by combination of grinding and sonication techniques. All these TMD NDs have size less than 10 nm and show high dispersity in NMP. Moreover, we demonstrate a facial process to separate these NDs from the NMP solvent by post-treating these NDs with hexane and then chloroform. Furthermore, as a proof-of-concept application, the TMD NDs (e.g., MoSe₂, WS₂ or NbSe₂) are hybridized with polyvinylpyrrolidone (PVP) for fabrication of memory devices as active layers, which exhibit nonvolatile write-once-read-many (WORM) memory effect. We believe that these TMD NDs should have diverse applications in catalysis, optoelectronics, solar cells, and bio-imaging.

3. As an emerging 2D nanomaterial, layered BP has shown promising applications in electronics. Here, we further extend the previous size reduction process to the preparation of BPQDs. The lateral size of the obtained BPQDs is 4.9 ± 1.6 nm and thickness is 1.9 ± 0.9 nm, corresponding to 4 ± 2 layers. Moreover, the solution-processed BPQDs can be hybridized with PVP and are promising for being the active layer of flexible memory device. The memory device based on BPQDs exhibits a nonvolatile rewritable memory behavior with a high ON/OFF current ratio of more than 6.0×10^4 and shows good stability.

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Chapter 2

Literature Review

This chapter gives the literature review on the recent progress of the structure tuning process of layered materials, especially for TMDs and BP. The crystal structure of TMDs and BP are first introduced. Then the methods for effectively tuning the structure and properties of TMD and BP materials are described, including phase engineering through intercalation, heterostructure formation through oxidation, and size reduction by preparation of layered nanodots. Finally, the questions related to the thesis based on literature are also discussed.

2.1 Overview

Layered materials, in which the individual layers are stacked together through Van der Waals (VdW) interactions, have been discovered and studied over several decades.^[1, 2] Due to their unique laminar structures, these materials exhibit fascinating properties and applications. For instance, graphite and MoS₂ powder/crystals have been traditionally utilized as dry lubricants. Moreover, due to the weak interlayer VdW interaction, these materials can be exfoliated to ultrathin single- or few-layer nanosheets, generating unique properties which are distinct from their bulk counterpart. The typical example is graphite, and the corresponding atomic nanosheets, i.e., graphene nanosheets, have been isolated, showing fascinating electronic/photoelectronic properties.^[3-8] After that, intensive studies have been devoted to the exploration of graphene-analogous materials. In 2004, following the same mechanical exfoliation methodology originally used in graphite, Novoselov et al. successfully isolated a great number of single-layer two-dimensional (2D) nanosheets, including h-BN, transition metal dichalcogenides (TMDs) (such as MoS₂ and NbSe₂) and complex oxides (such as Ba₂CaCu₂O_x and Sr₂CaCu₂O_x).^[9] Later on, a wide range of layered materials, ranging from black phosphorus (BP), silicone,^[10] arsenene,^[11] to more exotic examples such as inorganic layered clays,^[12] MXene (transition metal carbides and nitrides, such as Ti₃C₂ and Ti₂C),^[13] and coordination polymers^[14, 15] have been prepared and characterized. Due to the unique layered structure with ultrathin thickness, these materials display many intriguing optical, electronic, mechanical, and chemical properties, and show promising potential for various applications in electronic devices, sensing, energy storage and conversion, and bio-applications.^[16-20]

TMDs, one special type of “graphene-analogous materials”, have attracted particular interest due to their diversified chemical compositions, unique crystal structures, and a wide range of physicochemical properties as well as great

potential applications.^[16-23] Especially the inherently tunable bandgap of TMDs offers properties that are complementary to zero bandgap of graphene.^[22-26] Due to the weak interlayer interaction, these layered materials can be well isolated into individual layers, exhibiting layer-dependent physical/chemical behaviors, which provide pathways for tuning their properties such as conductivity and optical properties to realize better performances for diversified applications.^[22, 23] For example, bulk MoS₂ is a semiconductor with a narrow indirect bandgap of 1.29 eV, while isolated monolayer MoS₂ is a direct bandgap semiconductor with a larger gap of 1.8 eV as evidenced by the emergence of photoluminescence (PL).^[27] Importantly, the PL quantum yield in monolayer MoS₂ is much higher than that of few-layer MoS₂, which opens the possibility of electronic, optoelectronic and sensing applications.^[27] The transition from indirect bandgap to direct bandgap resulted from decreasing thickness from bulk to monolayer also appears in other TMDs such as MoTe₂ and MoSe₂.^[23] Owing to the interesting tunable bandgap, the development of optical/electronic devices based on TMDs is accelerated, and other applications of TMDs, such as catalysis, sensing, and bioimaging, are also extensively explored.^[16-20] Currently, the reliable single- and few-layer TMD nanosheets have been prepared through top-down methods, e.g., mechanical exfoliation,^[9] liquid phase exfoliation,^[28] Li-ion intercalation and exfoliation,^[29-33] and laser thinning technique,^[34] as well as bottom-up methods like chemical vapor deposition (CVD) growth^[35] and wet chemical synthesis method,^[36] etc.

BP, the bulk counterpart of phosphorene, is the most stable allotrope of phosphorus at room temperature that was first prepared in 1914 from red phosphorus at high temperature and high pressure.^[37] Since its discovery, this material was greatly ignored in materials science due to its strong toxicity and structural instability. Recently, the tremendous interest in layered materials has sparked a resurgence of interest in BP as a new layered 2D material.^[38-44] Especially in 2012, the successful fabrication of the BP nanosheet-based field-

effect-transistors (FETs) with outstanding performance prompted an intense exploration of the structure and properties of BP.^[45] Currently, many synthetic methods have been reported for preparation of BP nanosheets, and diverse applications have been studied, such as catalysis, photothermal therapy, photovoltaic applications, and electronics.^[38, 39]

The explosive development of layered materials provides a great platform for tuning their intrinsic properties towards desired functions, which further draws tremendous attention and offers a lot of opportunities for various applications. Especially the earlier works on graphene provide valuable instruction for structure tuning of graphene analogue materials.^[46-49] For example, the bandgap of graphene can be effectively tuned by decreasing its lateral size through fabrication of graphene nanodots (NDs) or graphene nanoribbon.^[47, 49] Similarly, the properties of other layered materials, especially TMDs and BP, can also be tuned due to their high anisotropic structure as well as the layer-dependent electronic and optical properties.²³ To date, various chemical methodologies have been developed to effectively tune the structure and properties of TMDs (e.g., MoS₂) in a wide regime including: (i) decrease of the size and thickness,^[50, 51] (ii) phase engineering through intercalation of alkaline metal ions,^[52, 53] and (iii) doping, alloying or hybridization.^[54] Note that the aforementioned structural engineering is potentially able to alter the intrinsic properties of materials,^[55] leading to the enhanced performance for some specific applications, e.g., electrochemical hydrogen evolution reaction (HER). Among these methods, the size reduction and formation of heterostructures are two facial processes for tuning the properties of TMD and BP materials due to their easy operation and high production yield for practical applications.

2.2 The Crystal Structure of Transition Metal Dichalcogenides and Black Phosphorus

2.2.1 The crystal structure of transition metal dichalcogenides

The layered materials provide rich sources for material engineering to enrich their physical and chemical properties and optimize the performance for specific applications. Beyond the intensively studied graphene, the TMDs, which crystallize in a graphite-like layered structure, have sparked a recent resurgence of interest for their diversified components and remarkable optical and electronic properties.^[18, 56] The TMD materials are usually denoted by a general formula of MX_2 , where M represents transition metal atoms in group IV, V and IV (such as Ti, Zr, Hf, V, Nb, Ta, Mo, and W), and X represents the chalcogen atoms (S, Se, and Te).^[57, 58] As depicted in Figure 2.1, each individual layer of TMDs is formed by triplet-layer atoms containing a six-fold-bonded transition metal layer (M) sandwiched between two layers of three-fold-bonded chalcogen atoms (X). The intralayer M–X bonds are predominantly covalent in nature, whereas the interlayers are coupled through weak VdW interaction. The in-plane lattice constants of TMD materials vary from 3.1 Å (VS_2) to 3.6 Å (TiTe_2), while the distance between the nearest bottom and top chalcogen layers is approximately the same (3.6 Å).^[59] Each single-layer nanosheet typically has a thickness of about 6~7 Å. Depending on the different coordination between the central transition metal atoms (M) and chalcogen atoms (X), most of the TMD materials, such as MoS_2 , WS_2 , MoSe_2 , WSe_2 and MoTe_2 , have different types of polymorph structures such as 1T phase (one layer per repeat unit, tetragonal symmetry, octahedral coordination), 2H phase (two layers per repeat unit, hexagonal symmetry, trigonal prismatic coordination), and 3R phase (three layers per repeat unit, rhombohedral symmetry, trigonal prismatic coordination) (Figure 2.1).^[20, 21, 30, 53, 59, 60] In these abbreviations of the phases, the digital numbers represent the unit number in the cell and the letters stand for the trigonal (T), hexagonal (H), and rhombohedral (R), respectively. For a particular TMD material, different phases have different stabilities. Taking MoS_2 as an example, the 2H phase dominates in nature and is

the most stable one. These different configurations can be transformed under external forces, e.g., the 2H phase MoS₂ can be transformed to 1T phase after Li-intercalation, while 1T and 3R phase can be converted to 2H phase upon heating.^[20, 21, 30, 53, 59, 60] Different configurations generate different properties and applications of these materials. The detailed description of the phase transformation of TMD materials will be introduced in the section of 2.2.1 in this chapter.

Figure 2. 1 Schematics of TMD materials with different structural polytypes. The yellow sphere represents the chalcogen atoms (X) and the grey one stands for the metal atoms (M).^[23]

2.2.2 The crystal structure of black phosphorus

The crystal structure of BP is similar to that of graphene, which has a layered crystal structure, and the individual layers interact with each other through VdW force. The BP has orthorhombic crystal structure with the space group of *Cmca*.^[38, 39, 43] The representative structural characteristic of BP is shown in Figure 2.2. Each layer is composed of a puckered honeycomb structure and each phosphorus atom bonds with three adjacent atoms. Two of the atoms are

located at the same plane while the other one is out of the plane, and these two planes are parallel, forming single-layer BP. Due to the weak VdW force interaction, the BP can be isolated to single- or few-layer nanosheets. Similar to graphene and TMDs, the BP nanosheets also present tunable electronic properties with respect to the number of layers. For example, it has been predicted that the bandgap of BP can be increased from 0.3 eV to 0.8-1.5 eV as the thickness decreases from bulk to monolayer.^[61] Intriguingly, the appealing sizable bandgap of BP is able to fill the space between zero-gap graphene and large-gap TMDs. As a result, nearly the entire range from 0 to 2 eV can be provided by layered materials.^[38, 39, 43, 44] Furthermore, the tunable bandgap and high hole mobility of BP show distinct advantages over graphene and TMDs for applications for electronic devices such as FETs. To date, diverse methods have been developed for fabrication of layered BP nanosheets, including mechanical exfoliation method, CVD method, and liquid exfoliation method.^[40] Among these synthetic methods, the solution-based processes show great advantages in terms of mass production at a relatively low cost, which are essential for practical applications.

Figure 2.2 The atomic crystal structure of BP with (a) 3D representation, (b) lateral view, and (c) top view.^[62]

2.3 Structure Tuning of Transition Metal Dichalcogenides and Black Phosphorus

2.3.1 Phase engineering through intercalation

Intercalation of metal ions into layered materials has been widely used for exfoliation of nanosheets over the past decades. During the intercalation process, the intercalated metal ions are able to change the optical, electronic, and chemical properties of host materials, thus giving rise to new functions for some applications.^[63, 64] In the case of TMDs, alkali metals (Li, Na, K) are the most common intercalants.^[20, 21, 30, 53] During intercalation, the electrons or charges can be transferred from alkali metal to the chalcogenide layers, giving rise to intriguing electronic properties, e.g., the increased carrier density and Fermi energy of TMD materials.^[20, 21, 30, 53]

Figure 2.3 (a) Crystal structure of 2H-phase MoS₂. (b) Schematic of the lithium intercalation process using battery testing system. The MoS₂ nanofilms with layers perpendicular to the substrate are used as cathode, and the Li foils are used as anode. (c) Galvanostatic discharge curve and structure transformation scheme of MoS₂ from 2H phase to 1T phase.^[65]

Intriguingly, the crystal structure of TMDs can be transformed from 2H stacking structure into 1T stacking structure upon alkali metal intercalation.^[30, 31, 53] As introduced in section 2.2.1, the TMD materials crystallized in different structure configurations, i.e., trigonal prismatic phase (2H), octahedral phase (1T) and trigonal prismatic phase (3R). It has been known that the crystal structures in single-layer TMDs are greatly dependent on their d orbital electron density of the metal, which can be engineered by electron donating.^[20, 53] The alkali metal intercalation, which can donate electrons to TMD materials (such as MoS₂, WS₂, and MoSe₂), is one of the most widely used methods for preparation of metallic 1T metallic chalcogenide nanosheets from the bulk 2H phase crystals. Actually, as an early attempt in 1983, Py and coworkers have demonstrated that the electron transfer from the lithium atoms to the metal chalcogenide can increase the electron density in the d orbital of Mo atoms, thus inducing the phase transformation of MoS₂ from 2H to 1T phase.^[66] Recently, our group has demonstrated a controllable lithium intercalation process for fabrication of single-layer TMD materials by using battery testing system. Later, by using a vertically grown MoS₂ film as raw materials, Cui's group reported that such intercalation process can also realize the phase transformation of MoS₂ from 2H to 1T phase (Figure 2.3).^[65] Due to the lithium intercalation, the exfoliated TMD nanosheets (such as MoS₂, WS₂, and MoSe₂) with metallic 1T phase usually have negatively charged surface, which makes them easily dispersed in polar solvents such as water.^[20, 53] In addition to the alkali metal intercalation process, other methods such as the electron beam irradiation^[67] and laser irradiation^[68], have also been developed for engineering the phase of TMDs for specific applications.

Different structure features lead to different properties, thus presenting different applications. For example, the 2H phase MoS₂ show semiconductive properties, while the 1T phase MoS₂ is metallic with the conductivity comparable with

rGO electrode, which is $\sim 10^7$ times higher than that of 2H phase MoS₂.^[69, 70] Moreover, the 1T phase MoS₂ is active for electrocatalytic hydrogen evolution, while 2H phase MoS₂ shows negligible catalytic activity towards HER. Also, it was found the electrode using 1T phase MoS₂ nanosheets shows much larger capacitance than that based on 2H phase MoS₂.^[31] Currently, MoS₂ nanosheets with high concentration of 1T phase has shown greatly improved performance in applications like low-resistance contact transistors,^[71] electrocatalysis,^[72] and electrochemical supercapacitors.^[21] For example, Chhawalla and coworkers demonstrated high proportion of strain and enhanced conductivity enabled by the metallic 1T' phase greatly improve the activity toward electrocatalytic HER.^[72] The same group also demonstrated that the electrochemically exfoliated MoS₂ nanosheets with high concentration of metallic 1T phase are promising electrochemical electrode for high-performance supercapacitors.^[21]

Even though the metallic 1T phase TMDs (e.g., MoS₂, WS₂, and MoSe₂) show a lot of promising applications, the transformation from 2H phase to 1T phase is detrimental to their semiconducting properties since it gives rise to the metastable structures and degrades their electronic behaviors and device functionalization. Therefore, the transformation from the metallic structure to semiconductive structure is equally desired, as their semiconductive properties are especially important for electronics and photoelectronics, such as FETs and light emitting diodes (LEDs). Currently, the heat treatment of metallic 1T phase MoS₂ under moderate temperature (e.g., 300 °C) is one of the most popular methods to generate 2H phase from 1T phase.^[21, 30, 53] In most cases, the 2H MoS₂ converted from 1T phase by heat treatment is used as reference for comparing the performance of 2H and 1T phase.

2.3.2 Heterostructure formation through oxidation

Practical applications require the materials have a broad range of functions and properties, which are difficult to realize in one single material without any modifications. Engineering the intrinsic properties of layered materials by hybridization with other materials is particularly attractive to overcome the shortcomings of individual counterparts and improve their performance or even generate new functions for practical applications.^[18, 73-76] In the past several years, great progress has been made in constructing functional hybrid nanostructures based on TMD nanosheets to tune their physicochemical properties, thus enhancing their performance for various kinds of applications.^[18,74,75] For example, the vertically arranged layered heterostructures like graphene/WS₂/graphene^[77] and graphene/BN/graphene^[78] prepared by dry-transfer method, which exhibit field-effect vertical-tunneling features, offer great opportunities to integrate different advantages of materials. Till now, a number of nanomaterials have been hybridized with TMD nanosheets through different protocols, such as vertical assembly of the mechanical exfoliated nanosheets into *p-n* heterostructures,^[73, 77, 79] growth of lateral *p-n* heterostructures,^[80, 81] oxidation of TMDs,^[82] decoration of noble metals^[83, 84] and metal chalcogenides.^[85, 86] Among these above-mentioned methods, the oxidation of TMD materials is especially easy for tuning the properties of 2D materials.

It is noteworthy that TMD nanosheets, especially those with atomic thickness, are not stable in air, and the sulfide atoms at the TMD surface can be replaced by oxygen, allowing the formation of oxygen doped or partially oxidized metal sulfide-metal oxide heterostructures. Compared with the vertical assembly and the lateral growth of *p-n* junction, the oxygen incorporation is more straightforward and effective for engineering the structure and properties of TMDs as well as generating novel properties and functions for specific applications. The simulation works have revealed that oxygen molecules could physically or chemically adsorb on the surface of TMDs.^[87] Particularly, when

there are S vacancies on the surface of TMD nanosheets, oxygen molecules could occupy the S vacancy of TMD with a strong binding energy (~ 2.395 eV for MoS_2), thus influencing the properties and performance of MoS_2 nanosheets.^[88] For example, the chemical oxygen adsorption on MoS_2 nanosheets gives rise to heavy p doping, while the pristine MoS_2 nanosheets show n -type semiconductor properties.^[88] Recently, Ni and coworkers reported that the PL intensity of MoS_2 nanosheets can be greatly enhanced by at least thousands of times through bonding oxygen on the defect sites of monolayer MoS_2 .^[88] In addition to the oxygen bonded on the defect sites of MoS_2 nanosheets, Khondaker and coworkers demonstrated that the oxidation of MoS_2 nanosheets can be achieved through a controllable oxygen plasma (an O_2 -Ar mixture at a ratio of 20:80) treatment for different exposure durations, and the electrical properties of the single-layer MoS_2 based FETs can be continuously tuned from semiconducting to insulating.^[89] When exposed to oxygen plasma, the MoS_2 nanosheets can interact with the energetic oxygen molecules and create MoO_3 -rich defect regions. The coverage of the defect regions can be increased by prolonging the exposure time. The as-formed heterostructure can be regarded as an effective medium semiconductor (EMSC), i.e., MoS_2 containing insulating MoO_3 -rich defect domains acted as a tunnel barrier for the injected conduction electrons. Consequently, as the plasma exposure time increases, the on-current, resistance and mobility of the fabricated FET varies exponentially by up to 4 orders of magnitude. Importantly, the fabrication process for engineering electrical properties of MoS_2 can be applied to other TMDs to fabricate a wide range of tunable 2D nanodevices.

The above introductions have demonstrated that the oxygen incorporation is effective for manipulating the structure and physical/electronic properties of TMDs. Nevertheless, the aforementioned TMD nanosheets are produced through mechanically exfoliated 2D nanosheets or CVD growth, which have low production yield, making them difficult for practical applications that

require the large-scale 2D TMDs with solution processability. In contrast, the solution process can overcome the disadvantages of the mechanically exfoliated nanosheets, thereby achieving the oxygen-incorporated TMD hybrid materials with new functions and properties for potential applications. As an example, Xie and coworkers demonstrated the synthesis of ultrathin oxygen-incorporated MoS_2 nanosheets through hydrothermal treatment of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and thiourea.^[82] It was found that the oxygen incorporation greatly enhances the intrinsic conductivity of MoS_2 nanosheets by reducing the bandgap of MoS_2 from 1.75 eV to 1.30 eV. Importantly, the oxygen-incorporated MoS_2 nanosheets show excellent catalytic performance towards HER with a low overpotential and small Tafel slope value.

Figure 2. 4 Schematic illustration of the oxidization of TiS_2 nanodisk by using O_2 and H_2O .^[90]

In addition, the solution-processed TMD materials can be partially or fully oxidized through anion exchange reactions, generating metal sulfide-oxide hybrid or pure metal oxide. For instance, Cheon and coworkers demonstrated the structural transformation of TiS_2 nanodisks to TiO_2 nanodisks and TiO_2

nanodisks to toroids through “compositional metathesis” process and multistage “edge-selective structural transformation” process, respectively (the schematic illustration of the two processes is shown in Figure 2.4).^[90] Both of the two chemical reaction processes are greatly attributed to the unique structural and compositional anisotropy of TiS_2 , where the basal plane is covered with S atoms and edges are constituted of partially coordinated S and Ti atoms. Typically, the “compositional metathesis” reaction was operated by bubbling oxygen gas into a hot oleylamine mixture containing TiS_2 nanodisks. It was suggested that the high temperature generates the reactive $^1\text{O}_2$ species which act as an electrophilic Lewis acid to oxidize the electron rich sulfide ions (S^{2-}) on the basal surfaces and edges throughout the TiS_2 disks. Differently, the “edge-selective structural transformation” process was realized by reaction of H_2O with TiS_2 nanodisks, where TiO_2 gradually appeared on the TiS_2 nanodisk edges, and ultimately formed the pure TiO_2 toroidal nanocrystals. In comparison with the “compositional metathesis” process, the “edge-selective structural transformation” process is initiated by the nucleophilic chemisorption of H_2O toward the exposed titanium atoms on the edges. These chemical reactions provide new design concepts for the transformation of 2D layered nanostructures, and are anticipated to be applied to other layered nanomaterials.

Moreover, for well-exfoliated TMD nanomaterials, it has been known that the defects at the edges and structural dislocation area could generate highly active non-stoichiometric areas, facilitating oxidation of TMDs at relatively low temperatures. Bessonov and coworkers reported the fabrication of $\text{MoO}_x/\text{MoS}_2$ and WO_x/WS_2 heterostructures via deposition of few-layer MS_2 ($\text{M}=\text{Mo}, \text{W}$) flakes from solution followed by heat-assisted air oxidation, or by xenon flash light exposure.^[91] The as-prepared MS_2/MO_x ($\text{M}=\text{Mo}, \text{W}$) heterostructures were then utilized for fabrication of memristor devices (Figure 2.5a). Typically, the MoS_2 films were first collected through a modified Langmuir-Blodgett method,

Figure 2.5 (a) Photograph of a cross-point memristor array on polyethylene naphthalate (PEN) which uses MoO_x/MoS₂ films as active materials. The inset shows the schematic structure of the vertically stacked memristor with the configuration of Ag/MoO_x/MoS₂/Ag. (b) Cross-section scanning electron microscopy (SEM) image of the AgNW/MoO_x/MoS₂ switching device. The scale bar is 100 nm. (c) Molybdenum oxidation-state files obtained from XPS in the MoO_x/MoS₂ sample (heat treatment at 200 °C for 3 h). The filled pink area stands for the Mo⁶⁺ rich region. (d) The oxidation degree of surface Mo with respect to different treatment conditions.^[91]

followed by heating in air. During the heat treatment of the film, the oxygen diffusion is limited, allowing the formation of a thin MoO_x layer with a thickness less than 3 nm on surface (Figure 2.5b). It was suggested that the oxygen vacancy density on the surface is lower than that of bulk part, producing

a gradient distribution of oxygen deficiency (Figure 2.5c). Moreover, a high content of MoO_3 component was formed when the oxidation temperature was increased (Figure 2.5d). Using the MS_2/MO_x ($\text{M}=\text{Mo}, \text{W}$) heterostructures as active layer, which was sandwiched between two printed silver electrodes, memory devices were fabricated (Figure 2.5a), which exhibited bipolar switching effect with a large and tunable electrical resistance from 10^2 to $10^8 \Omega$ and low programming voltage of 0.1-0.2 V. Such bipolar resistive switching behavior is greatly attributed to the ultrathin oxide layer ($< 3 \text{ nm}$).

2.3.3 Size reduction of layered materials

In addition to tuning the crystal phase and composition, engineering the lateral size of layered materials by introducing another dimension confinement is of particular interest to endow them with new properties. Compared with bulk materials, the small size NDs show many fascinating properties due to the size and edge effects. For example, the ultra-small NDs exhibit good solubility in solution, high tunability in physiochemical properties, and good amenability to structure transformation and functionalization with other nanomaterials.^[92, 93] Particularly, the planar facets of layered NDs can be modified chemically same as 2D nanosheets, and the rich edge sites can function as chemically active sites for many applications, such as catalysis and bio-applications. In addition, when the size of layered materials is reduced to nanoscale, a large portion of low-coordination edge atoms and dangling bonds are produced, which offer interesting physicochemical/electronic properties and additional advantages for specific applications. Layered NDs are a unique type of 2D materials which have small lateral size and confined thickness. Compared with the ultrathin 2D nanosheets, the NDs show smaller aspect ratio of lateral size to thickness and have more edge sites.^[90, 94, 95] With preserving the layered structure feature and having a relatively small lateral size, the layered NDs can potentially combine the unique property of 2D materials with additional lateral size confinement

effect, creating novel physicochemical properties that are different from those of either ultra-thin nanosheets or common spherical QDs derived from 3D crystals.

Graphene quantum dots (GQDs) are one of the most attractive examples in layered NDs. In contrast to the semimetallic pristine graphene nanosheets, the GQDs have semiconductor properties with size-tunable bandgaps due to the quantum confinement effect.^[47, 96] For example, when the lateral size varies from 0.46 to 2.31 nm, the pristine GQDs emit light from UV (bandgap of 6.81 eV) to infrared (bandgap of 1.64 eV) region.^[97] Moreover, the PL properties of GQDs can be further modulated through diverse protocols, such as using heteroatom dopants, chemical groups, defects, geometry, and edge configurations. These intriguing properties endow GQDs with a wide range of applications in electronics, energy storage and conversion, bioimaging, optical sensing, photovoltaics, and bio-application. For example, Joo and coworkers fabricated the nonvolatile flash memory devices by using GQDs sandwiched between SiO₂ layer as tunnel and control layer.^[96] Three GQDs with different sizes, i.e., 6, 12, and 27 nm diameters, were used, and it was found that memory behaviors greatly depend on the size of dots.^[96] For example, the 12 nm NDs exhibited the highest program speed, while the 27 nm NDs showed the highest erase speed as well as the best endurance and data-retention performance. The memory behavior was attributed to the combined effect of quantum confinement effect and edge state of GQDs. The unique properties and promising applications of GQDs have stimulated a new direction of graphene research and raised great concerns on the potentials of other layered NDs.

Following the successful pace of GQDs, it is highly anticipated to prepare other layered quantum dots (or NDs). Currently, intensive studies have been conducted to explore efficient and controllable synthetic methods for preparing this class of emerging layered NDs. Broadly speaking, there are two categories

of methods for fabrication of the layered NDs, i.e., “top-down” method and “bottom-up” method. The “top-down” method relies on breaking bulk crystals or exfoliated nanosheets into small segments using external forces, and the “bottom-up” approach, such as CVD and wet chemical synthesis, employs chemical reaction to synthesize layered NDs from corresponding precursors.^{[98-}

^{104]} Note that most methods used for fabrication of GQDs, especially through “top-down” approach, such as ultrasonic shearing, hydrothermal/solvothermal cutting, electrochemical scissoring, and chemical exfoliation method, etc., can be successfully extended to synthesize other layered NDs. For instance, the single-layer MoS₂ and WS₂ QDs have been prepared by a similar method previously used for synthesis of GQDs using hydrothermal cutting protocol.^[105]

As another example, the alkaline metal ion intercalation has also been used to produce TMD QDs, which takes the advantage of the suitable interlayer distance. Seo and coworkers reported the preparation of MoS₂ QDs by combining sonication and Li-intercalation and exfoliation process.^[106] Firstly, the size of bulk MoS₂ was reduced by sonication of MoS₂ crystals in N-methylpyrrolidone (NMP), and then Li intercalation was conducted followed by sonication in water, which generated the single-layer MoS₂ with the size of 10-20 nm. The as-prepared MoS₂ QDs show blue luminescent emission at 415 nm. Note that except the size reduction process at the first step, the preparation procedure in this work is the same as that of atomic 2D nanosheets, i.e., intercalation and exfoliation process. Using a different intercalation way, Allwood and coworkers fabricated WS₂ QDs from WS₂ flakes through a multiple potassium intercalation and exfoliation process, i.e., (1) formation of the potassium intercalated WS₂ (K-WS₂), (2) de-intercalation via exposure of the K-WS₂ to air, and (3) exfoliation via reaction of K-WS₂ with ethanol-H₂O under sonication (Figure 2.6a).^[107] The obtained WS₂ QDs had a thickness of 0.95 nm (Figure 2.6b), corresponding to monolayer WS₂, and lateral size of around 8-15 nm (Figure 2.6c). Note that the intercalation of alkali metals can only be operated under water-/air-free conditions. Differently, the

electrochemical etching of bulk MoS_2 in ionic liquid has been demonstrated to be operated under ambient condition for mass-production of MoS_2 QDs.^[108]

Figure 2. 6 (a) Schematics illustrating the preparation of monolayered WS_2 QDs. (b) Atomic force microscopy (AFM) topography image and (c) Transmission electron microscopy (TEM) image of WS_2 QDs.^[107]

In addition to the aforementioned method, the bottom-up methods, relying on the chemical reaction from elemental precursors or assembly of small building blocks, show great advantages in controlling the morphology and structure of nanomaterials. Recently, Huang and coworkers reported the production of water-soluble MoS_2 QDs by using a facial one-pot hydrothermal treatment protocol.^[109] The resultant MoS_2 QDs had a single-layer structure and uniform size with a diameter of 1.5-2.5 nm and thickness of 0.9 nm. Due to the surface capping ligands, the MoS_2 QDs could be well dispersed in aqueous suspension with high stability. More intriguingly, the as-formed single-layer MoS_2 QDs exhibited unusual upconversion photoluminescence. The unique fluorescent

properties of the monolayer MoS₂ QDs were suggested to be promising for the selective detection of tetracycline hydrochloride under ultraviolet (UV) and near-infrared (NIR) light irradiation.^[110] Besides the hydrothermal method, Cheon and coworkers prepared high-quality single-layer WSe₂ QDs in solution and studied the optical spectra and anisotropic polarization properties of a single nanodisk. However, all the above methods need complicated process. Especially the QDs fabricated by wet-chemical method are usually protected with organic ligands.

Figure 2. 7 Colloidal WSe₂ QDs with controlled lateral size and their optical spectra. (a) TEM images of WSe₂ QDs with average diameters ranging from 2.5 to 9.7 nm. (b) Histograms of diameters for WSe₂ SQDs with diameter of 2.5, 4.1, 5.8, and 9.7 nm, respectively. (c) UV-vis absorption (dot) and photoluminescence spectra (solid) of the colloidal solutions of WSe₂ SQDs with diameter of 2.5, 4.1, 5.8, and 9.7 nm.^[111]

Note that the semiconductive layered NDs, such as TMDs and BP, can potentially combine the unique property of the 2D materials with additional lateral size confinement, generating new physiochemical properties that are different from more common spherical semiconductor QDs derived from 3D crystals.^[111] Theoretical works have demonstrated that the monolayer MoS₂ QDs are metallic due to the unsaturated coordination of edge Mo atoms. Experimentally, Lin and coworkers demonstrated that when the width of MoS₂

decreased to subnanometer, i.e., MoS₂ nanoribbon with 0.35 nm width, the semiconducting MoS₂ was transformed to metal^[112, 113] Note that, in most cases, the experimentally synthesized TMD QDs usually have relatively large lateral size and are found to be dominantly 2H phase with semiconductive properties due to the edge configurations. In comparison with the 2D nanosheets, the QDs show strong quantum confinement effects and the bandgaps of TMD QDs open up. For example, the MoS₂ QDs with lateral size of 2.1 nm prepared by hydrothermal method have a larger direct bandgap of 3.96 eV as compared with that of single-layer nanosheets (1.89 eV).^[109] Similarly, the WS₂ QDs with size of 8-15 nm prepared by Allwood et al. have a larger direct transition energy (3.16 eV) as compared to the 2D WS₂ sheets with direct band gap of ~2.1 eV, and show multiple photoluminescence in the short wavelength (blue-green) spectral region with a quantum yield of around 4%, which is greatly higher than that of single-layer WS₂ nanosheets.^[107] Furthermore, the WS₂ QDs showed enhanced giant spin-valley coupling (at around 570 meV) as compared to that of monolayered WS₂ nanosheets (~400 meV), indicating the promising potential for semiconductor-based spintronics. In addition to the size effect, the properties can also be significantly influenced by dopants, functional groups, and defects etc., thus giving rise to intriguing optical properties. For example, the MoS₂ QDs synthesized from a hydrothermal treatment using N-acetyl-L-cysteine (NAC) as the capping agent showed a large spin-valley coupling of 700 meV and their absorption and emission wavelengths show obvious blue shifts as compared to monolayer MoS₂ sheets. Interestingly, the NAC-capped MoS₂ QDs show unusual upconversion photoluminescence, which is likely caused by the energy transfer from the NIR absorption by the NAC capping reagent to the MoS₂ QDs. Cheon and coworkers explore the lateral confinement effects on the optical properties originating from 2D excitons in single-layer TMDs by studying the individual high-quality single-layer QDs (SQDs) of WSe₂ (Figure 2.7).^[111] It was found that the WSe₂ SQDs show large increase in the Stokes shift and spectral width due to the lateral confinement effect on the

optical transition energy and the enhanced vibronic coupling. Moreover, the single-particle polarization spectroscopy shows that the absorption and emission of colloidal WSe₂ QDs exhibit in-plane, 2D isotropic transition dipole and linear PL polarization anisotropy, which is same as those of the 2D exciton in the single-layer WSe₂ sheets. Moreover, different from WSe₂ nanosheets, no circular polarization anisotropy was observed in WSe₂ QDs, indicating that the valley polarization is lost in the laterally confined single-layer TMDs.

The aim of engineering the crystal phase, composition, and morphology of layered materials is to modulate their physical, electronic, and chemical properties, thus achieving optimized performance for specific applications. Recent studies have proved that the atoms with ‘missing’ coordination at the edges of MoS₂ nanosheets have metallic electronic states and are electrocatalytic active for HER.^[20] In order to make full use of the catalytic centers and optimize the HER activity, decreasing the dimension of TMDs or fabricating ultra-small nanoparticles to introduce more active edge sites is an effective and promising approach to improve the performance of TMD materials toward HER. Therefore, the MoS₂ NDs show great advantages towards the electrocatalysis as compared to the 2D counterpart. For example, Du and coworkers demonstrated that the MoS₂ dots with abundant active edge sites gave rise to the excellent catalytic HER performance, which showed a low overpotential, high cathodic current density, small Tafel slope and excellent stability, exhibiting advantages toward the HER catalysis over bulk MoS₂ and MoS₂ nanosheets. Similarly, other types of 2D TMDs, such as MoSe₂, WS₂, and WSe₂, show similar edge site activities towards the electrocatalytic HER. Besides the application in electrocatalysis, the layered NDs are also attractive for photocatalysis due to their tunable bandgap, excellent photochemical robustness, as well as the tunable optical and catalytic properties. Moreover, it has been known that the MoS₂ nanosheets are effective for fabrication of batteries because the suitable interlayer distance of MoS₂ allows intercalation of

exotic ions (e.g., Li^+ , Na^+ , and K^+). Moreover, it has been known that Mo has different valence states (from +2 to +6), which can be transformed upon intercalation, therefore, MoS_2 is also promising for supercapacitor with pseudo-capacitance behavior. By comparison, the MoS_2 QDs with small lateral size allow even easier ion transport, thus enhancing the intercalation rate. In addition, the planar facets of NDs can be modified chemically same as 2D nanosheets, and the rich edge sites can function as chemically active sites or composited with other nanomaterials for bio-applications and electronics.

2.4 Questions to be Answered Based on Literature

As discussed in the aforementioned literature review, great progress has been made in the synthesis and structure engineering (phase engineering, lateral size reduction, and heterostructure formation through oxidization) of layered materials, and a wide range of potential applications have been explored. Nevertheless, there are still questions remaining to be further investigated.

First, it has been proved that the hybridization of different components shows promising potential for electronic and energy applications. Especially for layered TMD materials, the hybridization with oxide materials is promising for producing new properties for potential applications. One may wonder whether the hybrid materials can be produced in large scale by in-situ oxidation of TMD materials, and what kind of oxidation process is the most effective and suitable one for hybridization of TMDs and metal oxide without organic ligand coating/contamination. Moreover, does the hybridization process introduce novel functions for potential electronic device fabrication? Are there any improvements or advantages of the devices based on the fabricated hybrid nanomaterial as compared with those using single materials or using traditional materials?

Second, the size of graphene has been reduced to nanoscale which has shown unique properties and applications. One may wonder whether the size of TMD materials can be reduced by the currently reported method to prepare small size NDs. What specific method is effective and suitable one to reduce the size of TMDs? Moreover, one may wonder which kind of applications the NDs can be applied to.

Third, as another kind of layered materials, BP has started to attract research interest for potential applications. One may wonder whether the structure of BP can be engineered to produce new kind of BP nanostructures. Whether the lateral size of bulk BP crystals can be reduced for preparation of small size BP quantum dots (BPQDs), and whether the size reduction can induce property changes, such as Raman shift, and light absorption changes. Moreover, except the proved applications of BP nanosheets, do they show additional new functions in other applications? Are there any improvements or advantages of the BPQD-based devices compared with those based on graphene and TMDs?

2.5 Ph.D. in Context of Literature

In my thesis, I focus on the synthesis of novel layered materials by composition and structure (physical and chemical) engineering of bulk crystals or exfoliated nanosheets, and exploration of the potential of as-prepared nanomaterials or nanostructures for some applications like LEDs and memory devices. The contribution of my thesis in this part is listed as follows:

First, we developed an in-suit oxidation process by spray coating the exfoliated MoS₂ nanosheets onto a heated substrate, and fabricated the MoS₂-MoO₃ hybrid materials in large scale. The fabrication process is easy to introduce oxygen into MoS₂ for synthesis of hybrid nanomaterials containing MoS₂ and MoO_x. During the oxidation process, no organic ligands or chemicals are

introduced, reducing the contamination of final products, which is important for electronics. Moreover, this facial process can be potentially extended to the preparation of other metal sulfide-metal oxide hybrid materials. The hybridization of MoS₂ with MoO₃ gives rise to *p*-type conductivity of the hybrid materials (denote as *p*-MoS₂-MoO₃). Therefore, a LED based on heterojunction composed of *p*-type MoS₂-MoO₃ (*p*-MoS₂-MoO₃) film and *n*-type 4H-SiC (denoted as *n*-SiC) substrate was fabricated. The LED exhibited multi-wavelength emission, and the origins of emission peaks were theoretically explored. We believe that the in-situ oxidization process for fabrication of layered hybrid nanomaterials might open up an avenue to engineer the 2D materials for diverse applications in optical/electronics, information storage, and clean energy applications.

Second, we proved that the lateral size of layered TMD materials can be reduced by combining the mechanical grinding and sonication process in solution. A series of TMD nanodot materials, including MoS₂, MoSe₂, WS₂, WSe₂, ReS₂, TaS₂, and NbSe₂ were prepared. Moreover, we also demonstrated a method to extract these NDs from the NMP solution by post-treatment with hexane and then chloroform. As a proof of concept, the synthesized MoSe₂, WS₂, or NbSe₂ NDs are mixed with PVP and then used as active layer for fabrication of memory devices. The obtained three memory devices with different active layers exhibited nonvolatile WORM memory effect and MoSe₂ QD-based device showed the highest ON/OFF ratio (4.0×10^5) with the longest time stability. The obtained ON/OFF current ratio is significantly higher than that of PVP-MoS₂ nanosheet-based memory device. We believe that these TMD NDs may have promising applications in electronics, solar cells, catalysis, sensing, and bio-imaging.

Third, we prepared BPQDs for the first time by grinding and sonication of bulk BP crystals. BP is a conceptually new layered material, and the BPQD structure

is totally new in the materials research area, which exhibits new properties and broadens the BP applications. Moreover, the as-fabricated BPQDs mixed with PVP were used for fabrication of flexible memory devices, showing nonvolatile rewritable memory effect with a high ON/OFF current ratio of more than 6.0×10^4 and good stability. The BPQD based electronic memory device in this work may open up the possibility for exploring new applications of BP nanomaterials in electronics, solar cells, sensing, etc.

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Chapter 3

Experimental Methodology

In this chapter, the rationale for selection of methods and materials is discussed first. Then the used chemicals and the experimental procedures are presented. Subsequently, the descriptions of the characterization techniques and equipment are described. Finally, the details of the device fabrication and performance measurements based on these novel layered materials are summarized.

3.1 Rationale for Material and Method Selection

In the first part of the thesis, the layered transition metal dichalcogenides (TMDs), i.e., ultrathin MoS₂ nanosheets, were selected as the materials, and the oxidization of MoS₂ nanosheets was utilized to tune the composition and structure of the MoS₂ nanosheets. From the materials point of view, the MoS₂ nanosheets, especially those processed in solution, are particularly attractive because of the inherently tunable bandgap, structural diversity, and large-scale processibility. Currently, the ultrathin MoS₂ nanosheets have been well synthesized and characterized for diverse applications. However, practical applications usually require the materials have a broad range of optimized functions and properties, which are difficult to realize in one single material without any modifications. One promising strategy to generate new functions of MoS₂ is engineering its structure, which can also be applied to other layered materials. From the method point of view, it has been known from Chapter 2 that the oxygen can be easily incorporated into MoS₂ nanosheets, generating new structures and functions to enhance the performance for some applications. The in-situ oxidation of MoS₂ nanosheets in air is one of the facial and straightforward processes to introduce oxygen into MoS₂ nanosheets and prepare the MoS₂-MoO₃ hybrid materials. The complete oxidation of MoS₂ can be expressed as:

Particularly, the process does not introduce any organic surfactant, which is important for fabrication of electronics. From the application point of view, the new hybrid materials prepared by oxidation of MoS₂ nanosheets show great potential in various applications. It has been proved that two-dimensional (2D) hybrid nanostructures are very attractive for optical-electronics, especially promising in making the *p-n* heterojunction for efficient light-emitting diodes (LEDs). Therefore, LEDs were fabricated by manufacturing heterojunction using the MoS₂-MoO₃ hybrid materials as active materials.

In the second part of the thesis, layered TMDs were selected as the starting materials to produce quantum dots (QDs) (or nanodots (NDs)), and “top-down” process, i.e., mechanical grinding and sonication protocol, was used to decrease their thickness and lateral size. From materials point of view, TMD materials are a particularly attractive candidate due to their diversified components, and a broad range of properties and applications. Especially the research on TMD NDs is still on early stage and further exploration is highly needed. From the method point of view, ultrasonication is one of the most facial and straightforward processes to reduce the size and thickness of layered materials down to nanoscale. During sonication, the strong hydrodynamic shear forces and cavitation, which are produced by the formation and collapse of small vacuum bubbles induced by the periodic pressure fluctuations, act on bulk materials and cut materials into small segments. Moreover, the mechanical grinding process, which detaches the layers from bulk crystals, can combine with sonication process to enhance the production yield. The combination of grinding and sonication process has been proved to be effective for preparation of graphene quantum dots with small lateral size. With similar layered structure, it is believed that this method should be also effective for engineering the size of TMDs and able to produce small size NDs. From the application point of view, the versatile TMDs, which can be metals (e.g., NbS₂ and VSe₂), semimetals (e.g., WTe₂ and TiSe₂), and semiconductors (e.g., MoS₂ and WS₂), provide a rich platform for investigation of their potential applications. Previously, it has been proved that the ultrathin TMD nanosheets can be functionalized for fabrication of memory devices. Therefore, the TMD NDs also have the potential for constructing memory devices. Importantly, it is meaningful to compare the performance of TMD nanosheet- and nanodot-based devices.

In the third part of the thesis, black phosphorus (BP) was selected as the target material and the similar “top-down” method, i.e., mechanical grinding and sonication process, was also employed for the preparation of BP quantum dots (BPQDs) with small lateral size and thickness. From the material point of view, BP is a conceptually new layered material, which has shown promising properties for nano-(opto)electronics due to its unique crystal structures. Specifically, it has been predicted that BP has a layer-dependent bandgap which can be turned from 0.3 eV to 2 eV as the thickness decreases from bulk to monolayer. The appealing sizeable bandgap of BP shows great promise in filling the space between zero-gap graphene and large-gap TMDs. Besides the layered flakes, ultra-small QDs are another form of nanomaterials which have shown broad applications in a variety of areas. But the size reduction of BP into small sized NDs in liquid phase has not been achieved yet. From the method point of view, we used the mechanical grinding and sonication method since it has been proved to be effective for reducing the size and thickness of 2D materials. Therefore, it is reasonable to extend this method to prepare BPQDs. From the application point of view, memory devices were fabricated making use of the semiconductive properties of BP.

3.2 Materials and Synthesis Process

3.2.1 Materials

N-methyl-2-pyrrolidone (NMP, 99.5%, anhydrous), polyvinylpyrrolidone (PVP, MW = 130,000), dichloromethane ($\geq 99.8\%$, anhydrous), hexane, chloroform, Poly(vinylidene fluoride) (PVDF), and tungsten (IV) disulfide (WS_2) were purchased from Sigma-Aldrich. Ethanol was purchased from Merck. Tetrahydrofuran (THF, analytic reagent grade) was purchased from Fisher Scientific. Poly(ethylene terephthalate) (PET, 0.3 mm thickness) was purchased from 3M Company (St. Paul, MN, USA). 4H-SiC substrate was purchased from

Cree Inc. (USA). Syringe filters (PTFE, 0.2 μm pore size) were purchased from Agilent Technologies. Molybdenum (IV) sulfide (MoS_2) was purchased from Rose Mill. Tantalum (IV) sulfide (TaS_2), rhenium (IV) sulfide (ReS_2), molybdenum (IV) diselenide (MoSe_2), tungsten (IV) diselenide (WSe_2) and niobium diselenide (NbSe_2) were purchased Alfa Aesar. The deionized water was purified using Milli-Q System (Millipore, Billerica, MA, USA). All the materials were used as received without any further purification.

3.2.2 Preparation of MoS_2 - MoO_3 hybrid nanomaterials

Figure 3. 1 Schematic illustration of spray coating process.

The MoS_2 nanosheets were prepared by using electrochemical lithium-intercalation/exfoliation method described in our previous report.^[1] Briefly, the commercial MoS_2 powders mixed with acetylene black and PVDF binder were used as cathode, the Li foils were used as anode to assemble battery cells. The electrochemical intercalation was then operated using galvanostatic discharge and the MoS_2 nanosheets were collected by sonication and centrifugation of the lithium-intercalated MoS_2 . In this work, the lithium-intercalated MoS_2 nanosheets were first broken into small pieces by sonication in water bath for 3 h (during this process, the water bath temperature rose up to $\sim 45^\circ\text{C}$). After that,

the sonicated MoS₂ nanosheets were washed twice using Milli-Q water, and finally re-dispersed in water. Then, the sonicated MoS₂ nanosheets were spray coated on solid substrate (SiC, Si, glass or quartz). During the coating process, a 90 °C hot plate was used to heat the substrate in order to accelerate solvent evaporation as well as increase the oxidation content. The spray coating process is schematically shown in Figure 3.1. Subsequently, the as-formed MoS_{2-x}O_x underwent thermal treatment in 5%H₂ diluted argon gas at 450-500 °C for 1h to crystallize MoS₂-MoO₃ hybrid nanomaterials.

3.2.3 Preparation of transition metal dichalcogenide nanodots

The raw TMD materials were dispersed in NMP in a mortar with initial concentration of 50 mg/ml. After grinding in mortar for 30 min, the suspension was transferred to a glass bottle containing 3 mL NMP solution. Then the suspension was sonicated in an ice-bath for 3 h at the power of 200 W. Subsequently, the suspension was re-ground for another 30 min, and then diluted with NMP to 15 ml. After sonication of the suspension for another 3 h at the power of 200 W in ice-bath, the resultant dispersion was centrifuged at 8,000 rpm for 20 min. The supernatant was then gently taken out and filtered using a PTFE filter (pore size is 0.2 μm). Eventually, the filtered materials were collected in a clean glass vial. Note that the sonication of TaS₂, MoSe₂, WSe₂ and NbSe₂ should be operated in an inert gas atmosphere to avoid their oxidation.

3.2.4 Synthesis of black phosphorus quantum dots

Bulk BP was synthesized from red phosphorus at pressure of 4 GPa and temperature of 800 °C for 10 min, which was described in the previous report.^[2] The obtained bulk BP was kept in a glove box filled with Ar gas (<0.1 ppm H₂O and <0.1 ppm O₂) prior to use. In a typical experiment for synthesis of

BPQDs, 5 mg of BP powder was added into 1 mL of NMP in a mortar and then ground for 20 min. The mixture was transferred to a glass vial containing 3 mL of NMP. After it was sealed carefully, the vial was taken out from glove box and sonicated in ice-bath for 3 h at the power of 200 W. The resultant dispersion was centrifuged for 20 min at 6,000 rpm, and the supernatant containing BPQDs was decanted gently. Except the sonication and centrifugation processes, the other experiments were conducted in glove box.

3.3 Characterizations

After structural engineering of these layered materials, proper techniques are required to characterize their structure features, such as the composition, morphology, crystal phase, optical and electronic properties. With the advancement of manufacturing technology, various characterization techniques have been well developed, providing valuable information about material structures and properties. Note that each technique has its own function, needs specific characterization requirement, and shows different advantages and shortcomings. Therefore, in this section, the different characterization techniques in the thesis used to characterize the layered materials will be briefly described.

3.3.1 Scanning electron microscopy

The exfoliated MoS₂ nanosheets were spin-coated on well-cleaned Si substrate for scanning electron microscopy (SEM) characterization, and the bulk BP powder was first ground to microsize and then cast on the conductive adhesive for SEM characterization. The SEM images were obtained using a field emission scanning electron microscope (FESEM, JEOL JSM-7600F) at the accelerating voltage of 5 keV with a working distance of 8 cm and probe current of 7 μ A. The energy dispersive X-ray spectroscopy (EDS) spectra from

SEM were collected at the accelerating voltage of 15 keV, a working distance of 15 cm and a probe current of 7 μA . The transmission mode SEM images were collected by using a transmission electron detector (TED) at the accelerating voltage of 5 keV with a working distance of 8 cm and probe current of 7 μA .

SEM is one of the most widely used electron microscopies for observing the morphology, topographical features, and crystal orientation of materials.^[3] When electron beam scans the samples, the electrons interact with atoms in the sample, and generate signals that contain information about the sample surface topography and composition. Then the signals are collected using detectors, and images are presented by reconstructing the signals. In this thesis, the SEM images are used to characterize the morphology and size of the exfoliated MoS_2 nanosheets and bulk BP layered crystals. The size can be directly observed through SEM images. Specifically, due to the unique anisotropic layered structure, these materials prefer to form plate-like crystals with well-defined orientation and crystal faces. The plate-like surface can be reflected on SEM images. Moreover, most of the layered crystals have a relatively large distance and gap perpendicular to surface plane direction, which can be determined by closer inspection of the cross-section of the crystal through SEM. Moreover, the SEM can also be operated in transmission mode by using TED. In addition, the EDS spectra and corresponding elemental mapping from SEM equipment can be used as an analytical technique to confirm the elemental compositions and roughly determine the relative ratio (mass ratio and molar ratio) for each element. Specifically, the elemental mapping can be used to image the distribution of each element in nanosheets.

3.3.2 Transmission electron microscopy

Samples for transmission electron microscopy (TEM) characterization were prepared by dropping the scratched MoS_2 - MoO_3 alcoholic solution on lacy carbon coated 300 mesh copper grids or TMD and BP ND suspensions onto an ultrathin carbon-coated lacy carbon support film (300 mesh, copper). TEM and selected area electron diffraction (SAED) images were collected by a JEOL JEM 2100F instrument at an accelerating voltage of 200 kV. EDS and element mapping were performed on a JEOL 2100F instrument coupled with an EDS detector.

TEM is a microscopy technique for obtaining high-resolution images of nanomaterials.^[3, 4] 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 nanosheets or NDs can be directly and precisely measured through low magnification TEM images.

The high-resolution TEM images (HRTEM) and SAED patterns are widely used to investigate the crystal structure, structure dislocations, crystal orientation and exposed crystal facets of nanosheets and NDs. 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 HRTEM can also be used to determine the crystallinity of materials, for example, nanocrystals normally give clear crystal lattice fringes, while amorphous materials do not show any crystal lattices in HRTEM 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 NDs 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 NDs, 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.

3.3.3 Atomic force microscopy

The TMD and BP nanodot solutions were dropped on Si/SiO₂ wafer, and the MoS₂ nanosheets in water were spin-coated onto Si/SiO₂ substrate for atomic force microscopy (AFM) characterization. AFM (Dimension ICON with NanoScope V controller, Bruker, USA) was operated in tapping mode in air.

Before dropping or spin-coating samples, the substrate Si/SiO₂ wafer should be clean enough. The cleaning process of Si/SiO₂ substrate is as following: the Si/SiO₂ wafer was first cut into small segments of about 1×1 cm. Then they were sequentially sonicated in acetone, water, and isopropanol for 30 min. After that, the Si/SiO₂ wafer was treated with a mixture of sulphuric acid and hydrogen peroxide with volume ratio of 1:1 at 120 °C for 2 h to remove residual organic contaminations. Finally, the cleaned substrates were rinsed with DI water for five times and then dried under N₂ flow. After cleaning the Si/SiO₂ wafer, the samples were spin-coated or dropped on the surface before characterization.

AFM is a surface topographical imaging technique with high resolution up to atomic scale, where a small probe with a sharp tip is scanned across a sample in a controlled manner.^[5] Based on the nature of tip motion, there are three scan modes of AFM, i.e., contact mode, tapping mode, and non-contact mode. As compared with the electron microscopies (e.g., SEM, TEM) which provide a 2D image of samples, AFM can provide a three-dimensional (3D) surface profile. Moreover, samples for AFM measurement do not need any special treatment (such as metal coating) that may damage sample. Currently, AFM has been widely used in materials science as a powerful surface analytical technique to provide high-resolution topographic image of materials, especially frequently utilized to measure the thickness of 2D nanomaterials.

In this thesis, the AFM height images were used to characterize the thickness of exfoliated MoS₂ nanosheets and TMD and BP NDs. By analyzing the height profiles, the layer number of the nanosheets or prepared NDs can be confirmed. Note that the thickness values measured by AFM are easily interfered by surrounding substrates, confined water layer molecular and adsorbed contaminants on the surface. Therefore, there exist discrepancies between theoretical and measured values.

3.3.4 X-ray diffraction

X-ray diffraction (XRD) is a non-destructive analytical technique used to analyze the crystallographic information of materials.^[3, 6] In the thesis, the XRD characterization was used to identify the crystal structure of the bulk BP crystals and the as-prepared MoS₂-MoO₃ hybrid nanomaterials.

The bulk BP crystals were first ground to microsize and then tested on an XRD sample holders. The MoS₂-MoO₃ formed on quartz substrate was pasted on an XRD sample holder for characterization. The XRD patterns were recorded

using a Bruker D8 diffractometer (German) with a Cu K α ($\lambda=1.54178$ Å) X-ray source by step-scanning over the range of 10 ° to 80 ° at an interval of 0.05°, and a dwell time of 1s.

3.3.5 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 NDs was drop-casted on a clean Si substrate and then naturally dried in air, which then can be used for XPS measurement. For the NDs in NMP solution, the NDs were first transferred into ethanol, and then drop-casted on a clean Si substrate for XPS characterization.

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.^[6, 7] 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 de-convention 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. For instance, due to the different configuration, the binding energy of 2H and 1T phase MoS₂ can be distinguished by using XPS characterization. It has been reported that the phase changes of MoS₂ can be determined through XPS because the binding energy of metallic 1T phase MoS₂ shifts to low energy side by ~0.9 eV as compared with 2H phase MoS₂. In this thesis, the XPS was mainly used to determine the oxygen content in MoS₂-MoO₃ nanohybrid, and the chemical composition and oxidation state of elements in products of BP and TMD dots. Moreover, the phase transformation from 1T to 2H of MoS₂ upon heating was also characterized. Therefore, it provides a facile and reliable way to identify the structure and electronic feature before and after structural manipulation.

3.3.6 Raman spectroscopy

Raman spectra were measured by using a 532 nm micro-Raman spectrometer (Renishaw INVIA Reflex) with the 1800 lines/mm grating at room temperature. All the Raman spectra were calibrated by the Raman band of a silicon wafer at 520 cm⁻¹ as the standard peak. The sample preparation for Raman spectroscopy is the same for the preparation of samples for XPS test described in Section 3.3.5.

Raman spectroscopy is a fast and non-destructive spectroscopic technique that provides structural and electronic information based on the vibration, rotation and other low-frequency modes in materials.^[8] In this thesis, the Raman spectroscopy was used to investigate the composition and crystal phase information of NDs. Generally, both the bulk crystals and prepared nanosheets and NDs were explored by Raman spectroscopy.

3.3.7 UV-vis absorption spectroscopy

A UV-2700 (Shimadzu) with QS-grade quartz cuvettes (111-QS, Hellma Analytics) was used to characterize the UV-vis absorption spectra of products at room temperature.

The UV-vis spectroscopy (ultraviolet-visible spectroscopy), referred as the absorption spectroscopy (or transmission spectroscopy, reflectance spectroscopy) in the ultraviolet-visible (UV-vis) spectral region, is an effective and traditional technique to characterize the optical properties of materials.^[9] Typically, when a material is exposed to a beam of light, the material may absorb a fraction of the light energy if the light energy matches the energy difference between the possible electronic transition of the material, and electrons would be promoted from low energy state to high energy state. The degree of absorption at different wavelengths is recorded by a spectrometer, forming the spectrum with absorbance versus wavelength. Therefore, there are two parameters in the spectrum, i.e., the absorption wavelength and the absorption intensity. Due to the simplicity, the UV-vis absorption spectroscopy has been widely used for a wide range of area, such as the quantitative determination of analytes in analytical chemistry and investigation of the energy levels of materials.

In this thesis, the UV-vis spectroscopy is used to characterize the absorption spectra of nanodot materials and their bulk counterpart in the UV-vis optical range. As known, the characteristic absorption peaks of a material are closely related to its electronic structure, i.e., bandgap. Due to the quantum confinement and size effect, the absorption peak of NDs will show shift compared with their bulk counterpart. Therefore, the UV-vis absorption spectroscopy was used here to identify the light absorption feature of the prepared NDs, and compare the differences before and after the size reduction process.

3.3.8 Hall effect

The doping characteristics of $\text{MoS}_2\text{-MoO}_3$ were characterized using Hall Effect Measurement System (HL5500, Bio-Rad Microscience Limited, UK) at room temperature. The thickness of $\text{MoS}_2\text{-MoO}_3$ film used for Hall effect measurements was $\sim 1.1 \mu\text{m}$. The film thicknesses were measured using Alpha-Step IQ surface profiler.

The Hall effect is an important and effective measurement tool for the characterization of the physical properties of materials, particularly semiconductors.^[10, 11] It provides a relatively simple way to accurately determine the physical characteristics of materials, such as electrical resistivity, carrier density, and the carrier mobility in semiconductors. Because the Hall Effect is simple and cheap and has fast turnaround time, it has been widely used as an indispensable technique for material characterization.

3.4 Applications

3.4.1 Fabrication of $\text{MoS}_2\text{-MoO}_3$ based light-emitting diodes

Figure 3. 2 Schematic structure diagram of the LED device based on the heterojunction composed of $p\text{-MoS}_2\text{-MoO}_3$ and $n\text{-SiC}$. The device has configuration of $\text{Au/Ti/n-SiC/p-MoS}_2\text{-MoO}_3\text{/ITO/glass}$.

The LEDs were prepared by spraying MoS₂ suspension onto a small piece of *n*-type 4H-SiC substrate (denoted as *n*-SiC). In order to obtain good wetting of MoS₂ suspension during the film coating, the SiC substrate was rinsed with acetone and DI water and subsequently treated with O₂ plasma. Then, the MoS₂ suspension was sprayed onto the well-cleaned *n*-SiC substrate to in-situ oxidize MoS₂ into MoS_{2-x}O_x. The thickness of sprayed MoS_{2-x}O_x film was ~3 μm. After annealing in 5%H₂ diluted Argon at 450-500 °C for 1 h, the oxide component structure of MoS_{2-x}O_x film was constructed and crystallized to form MoS₂-MoO₃ film on *n*-SiC substrate. It should be noted that the MoS₂ crystal can be severely degraded in pure Argon gas when annealing temperature is above 500 °C.^[12] The obtained *n*-SiC/*p*-MoS₂-MoO₃ heterojunction was then utilized as the active layer for fabrication of LEDs. The Ti(10 nm)/Au(120 nm) film was then coated on the opposite side of *n*-SiC using e-beam evaporation and used as the rear electrode. The front transparent electrode was made of commercial ITO coated glass. Finally, the LED device with configuration of Au/Ti/*n*-SiC/*p*-MoS₂-MoO₃/ITO/glass was fabricated. The schematic and real device structure of the fabricated LED are shown in Figure 3.2 and Figure 3.3, respectively. Yokogawa GS610 source and measurement unit were utilized to measure the current-voltage (I-V) curve, and a PDS-1 photomultiplier tube detector connected to a monochromator was used to record the electroluminescence (EL) spectra.

Figure 3.3 The fabricated LED device based on the fabricated MoS₂-MoO₃ hybrid nanomaterials with the configuration of Au/Ti/*n*-SiC/*p*-MoS₂-MoO₃/ITO/glass.

3.4.2 Fabrication of transition metal dichalcogenide nanodot-based memory devices

Memory devices were fabricated on the glass electrode covered with indium tin oxide (ITO). The active layer was made of the PVP-TMD ND nanocomposite. First, 30 mg PVP was dispersed in 1 mL NMP suspension containing 0.15 mg NDs, followed by sonication in ice bath for 1h. The mixture, referred to as PVP-TMD ND nanocomposite, was then spin-coated onto an ITO electrode at 1,000 rpm for 30 s and then 3,000 rpm for 20 s. The obtained sample was annealed in vacuum oven at 60 °C for 12 h. Then, the top Au electrode with a thickness of 120 nm and an area of 0.25 mm × 0.25 mm was coated with PVP-TMD ND film by thermal evaporation under vacuum of $\sim 10^{-6}$ mbar. The schematic structure of the MoSe₂ ND-based memory device is shown in Figure 3.4, where the PVP-TMD ND nanocomposite is used as the active layer, and the Au and ITO coated glass is used as electrodes.

Figure 3. 4 The Schematic illustration of the structure of MoSe₂ ND-based memory devices with the configuration of Au/PVP-MoSe₂ NDs/ITO/Glass.

3.4.3 Fabrication of black phosphorus quantum dot-based memory devices

After 1 mL of BPQD suspension in NMP was centrifuged at 12,000 rpm for 20 min, the supernatant was removed and the precipitate was re-dispersed in 1 mL of THF, which was then dispersed in 1 mL PVP solution in THF (10 mg mL^{-1}) to form the mixture of BPQDs and PVP, referred to as PVP-BPQDs. After 10 min sonication, the mixture was spin-coated onto a PET substrate, which was patterned with 100 nm Au line electrodes (width=0.5 mm, length=25 mm), at 1,000 rpm for 10 s and then 3,000 rpm for 30 s. After drying in vacuum oven at 60°C for 6 h, Ag line electrodes (thickness=100 nm, width=0.5 mm, length=25 mm), perpendicular to the Au bottom line electrodes, were deposited by thermal evaporation under vacuum of 10^{-6} torr with shadow mask. As a result, 8×8 device arrays with PVP-BPQDs as the active layer were prepared. The device structure is referred to as PET/Au/BPQD-PVP/Ag. The schematic structural illustration of the fabricated BPQD-based flexible memory device is shown in Figure 3.5. In the device, the PVP-BPQDs composite is used as active layer, the PET is used as flexible substrate, and the Ag and Au are used as the electrodes.

Figure 3.5 The Schematic illustration of the structure of BPQDs based memory devices with the configuration of Ag/PVP-BPQDs/Au/PET.

3.5 Theoretical Calculation

First-principles calculations were carried out by using Vienna ab initio simulation package (VASP).^[13] The Perdew-Burke-Ernzerhof functional (PAW-PBE)^[14] and spin-polarized calculations with a cutoff energy of 400 eV were conducted. The atomic models with a $3 \times 3 \times 3$ supercell together with a

$2 \times 2 \times 2$ mesh in k -space were used. All the structures were fully relaxed until the forces on each atom became smaller than 0.01 eV/Å. The hybrid functionals (HSE06)^[15] were performed to calculate the defective states in the bandgap and reproduce electronic features of the highly delocalized defective states in MoO₃. The calculated bandgap of MoO₃ is 3.10 eV which is in good agreement with the previously reported value (3.2 eV).^[16]

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Chapter 4

MoS₂-MoO₃ Hybrid Nanomaterials for Light-Emitting Diodes

This chapter describes the oxidization of MoS₂ nanosheets and preparation of MoS₂-MoO₃ hybrid nanomaterials for fabrication of light emitting diodes (LEDs). The oxidation of MoS₂ nanosheets is realized by using heat-assisted spray-coating procedure during the film preparation by following an annealing-driven-crystallization process. The obtained MoS₂-MoO₃ shows p-type conductive behavior. As a proof of concept, LEDs based on heterojunction composed of p-type MoS₂-MoO₃ (p-MoS₂-MoO₃) film and n-type 4H-SiC (n-SiC) substrate is fabricated, which exhibited multi-wavelength emission. The electroluminescent mechanism is theoretically investigated.

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4.1 Introduction

Recently, the ultrathin layered MoS₂ nanosheets have been widely studied due to the unique physical, optical, and electrical properties.^[1-3] Currently, many methods have been developed to synthesize ultrathin MoS₂ nanosheets, including mechanical exfoliation,^[4, 5] liquid exfoliation,^[6] lithium-intercalation and exfoliation^[7,8] and chemical vapor deposition (CVD) method.^[9,10] Moreover, the characteristics of MoS₂ nanosheets have been intensively investigated through experiments. For instance, the electrocatalytic activity of MoS₂ towards the hydrogen evolution was reported to be close to that of the Pt-based metals and even better than most common metals.^[11, 12] In addition, the single-layer MoS₂-based top-gated field effect transistors (FETs) showed ultra-high current ON/OFF ratio ($\sim 10^8$) and channel mobility ($200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),^[13] which make the single-layer MoS₂ a competitive candidate for replacing Si in CMOS-like logic devices.^[4-6,8,13-15] Furthermore, the enhancement of photoluminescence (PL) intensity along with decreasing the thickness was observed in both mechanically^[16,17] and chemically^[8] exfoliated MoS₂ nanosheets. What's more, the phototransistors based on single-layer MoS₂ showed high photoresponsivity^[18,19] and the diodes showed excellent electroluminescence (EL) performance.^[20, 21]

Moving forward, the 2D hybrid nanostructures derived from ultrathin nanosheets are also a class of materials with growing interest. For example, the vertically arranged heterostructures, i.e., graphene/WS₂/graphene^[22] and graphene/BN/graphene^[23] prepared by dry transfer technique, exhibited field-effect vertical tunneling characteristic. The FETs based on *n*-MoS₂/graphene and *n*-MoS₂/graphene/*p*-Bi₂Sr₂Co₂O₈/graphene vertical heterostructures, prepared by CVD method combined with mechanical exfoliation, showed the functions of complementary inverters and logic transistors.^[24] The MoS₂/graphene layered hybrid prepared through solvothermal method was utilized as anode material for lithium-ion batteries (LIBs).^[25,26] The

nanojunction of MoS₂/CN, prepared by wet-impregnation followed by high-temperature sulfidation, exhibited excellent performance for photocatalytic H₂ evolution.^[27] Moreover, the EL and photocurrent properties of the WSe₂/MoS₂ VdW heterostructure were investigated.

In this chapter, we demonstrate a facile oxidation process to oxidize MoS₂ nanosheets and prepare MoS₂-MoO₃ hybrid nanomaterials. The in-situ partial oxidation of MoS₂ nanosheets was achieved using heat-assisted spray-coating protocol during the formation of film. After spray-coating, the partially oxidized MoS_{2-x}O_x film on arbitrary solid substrates, such as SiC, Si, glass or quartz, undergoes annealing treatment and hence crystallizes to MoS₂-MoO₃ hybrid nanomaterials composed of (100)-dominated MoS₂ and (021)-dominated α -MoO₃. The obtained MoS₂-MoO₃ exhibits *p*-type conductive behavior. A heterojunction composed of *p*-type MoS₂-MoO₃ (*p*-MoS₂-MoO₃) film and *n*-type 4H-SiC (*n*-SiC) substrate was made for fabrication of LEDs, which exhibits multi-wavelength emission. Two peaks in its EL spectrum are ascribed to the internal radiative recombination of electrons (from conduction band (CB)) and holes (from valence band (VB)) of MoS₂ and MoO₃, respectively. The other two peaks are correlated to the defect energy levels in MoO₃ supported by the theoretical calculation.

4.2 Results and Discussion

4.2.1 Synthesis and characterization of MoS₂ nanosheets

The MoS₂ nanosheets were prepared using electrochemical Li intercalation/exfoliation method reported by our group.⁷ The exfoliated MoS₂ nanosheets were dispersed into water. The field emission scanning electron microscopy (FESEM) images in Figure 4.1a reveal that all samples are composed of flakes with lateral size from 200 nm to 2 μ m. Transmission

electron microscope (TEM) was performed to study the morphological and structural feature of the sonicated MoS₂ nanosheets. The high-resolution TEM (HRTEM) image of the prepared MoS₂ nanosheets in Figure 4.1b shows clear lattice fringe of 0.27 nm, corresponding to the (100) of MoS₂. The atomic force microscopy (AFM) image indicates that most of the MoS₂ nanosheets have a thickness of about 1.8 nm (Figure 4.1c). Moreover, due to the strong interaction, the obtained MoS₂ nanosheets prefer to stack together, as shown in Figure 4.1d.

Figure 4.1 (a) FESEM images of the sonicated MoS₂ nanosheets. A magnified SEM image is inserted in (a). (b) HRTEM image of the sonicated MoS₂ nanosheets. (c,d) AFM images and the thickness measurement of (c) thin and (d) thick/stacked MoS₂ nanosheets deposited on Si/SiO₂ substrates.

4.2.2 Oxidation process and characterization of MoS₂-MoO₃ hybrid nanomaterials

Figure 4. 2 Schematic illustrations for preparation of MoS₂-MoO₃ hybrid nanomaterials and fabrication of LED device: (a) Sonication of MoS₂ nanosheets in water. (b) In-situ partial oxidation of MoS₂ to MoS_{2-x}O_x during Step (1): heat-assisted spray-coating of MoS_{2-x}O_x on *n*-SiC in air. (c) *n*-SiC/MoS₂-MoO₃ film formed after Step (2): annealing of *n*-SiC/MoS_{2-x}O_x film. (d) Schematic diagram of the LED device based on Step (3): fabrication of heterojunction composed of *p*-MoS₂-MoO₃ and *n*-SiC.

To prepare MoS₂-MoO₃ hybrids, MoS₂ sheets (Figure 4.2a) were first in-situ partially oxidized into MoS_{2-x}O_x assisted by heating in air during the spray-coating process (Figure 4.2, Step 1). The as-obtained MoS_{2-x}O_x film on *n*-SiC substrate was referred to as *n*-SiC/MoS_{2-x}O_x film (Figure 4.2b). Subsequently, the MoS_{2-x}O_x film was annealed at high temperature to increase the crystallization (Figure 4.2, Step 2), forming SiC/MoS₂-MoO₃ film (Figure 4.2c). The fabrication process was also confirmed through X-ray photoelectron spectroscopy (XPS) characterization. The XPS spectrum of original Li-exfoliated MoS₂ is shown in Figure 4.3a, where peaks of 1T and 2H MoS₂ are obviously observed. It was found that sonication of Li-exfoliated MoS₂ contributed negligible effect to MoS₂ oxidation, which can be seen from the XPS spectra for the Li-exfoliated and sonicated MoS₂ in Figure 4.3b. After spray-coating at high temperature in air, the oxygen content starts to increase,

where there is co-existence of Mo⁴⁺ and Mo⁶⁺ in MoS_{2-x}O_x (Figure 4.3c). The two peaks at ~232.6 eV (Mo⁴⁺ 3d_{3/2}) and 229.1 eV (Mo⁴⁺ 3d_{5/2}) in both Figure 4.3c and 4.3d are ascribed to the semiconducting 2H-phase MoS₂, and the peaks at ~235.6 eV (Mo⁶⁺ 3d_{3/2}) and 232.2 eV (Mo⁶⁺ 3d_{5/2}) are from MoO₃. Note that two peaks in Figure 4.3c centered at ~231.6 eV (Mo⁴⁺ 3d_{3/2}) and 228.3 eV (Mo⁴⁺ 3d_{5/2}) are assigned to the 1T phase MoS₂. The decrease of binding energy has been observed when the 2H phase converted to 1T phase MoS₂, which was also introduced in Chapter 3.^[8, 28] It has been known that the 1T phase MoS₂ can be transformed to the 2H phase MoS₂ upon thermal annealing above 300 °C.^[8, 29] As shown in Figure 4.3d, after thermal annealing, only 2H phase MoS₂ was observed in MoS₂-MoO₃. The weight ratio of MoO₃ to MoS₂ is calculated to be 2:3 according to the XPS results in Figure 4.3d. The co-existence of MoS₂ and MoO₃ was also confirmed through the elemental mapping of both MoS_{2-x}O_x (Figure 4.4a) and MoS₂-MoO₃ (Figure 4.4b).

Figure 4.3 XPS spectra of (a) Li-exfoliated and (b) sonicated MoS₂, (c) MoS_{2-x}O_x after spray-coating, i.e., before annealing, and (d) MoS₂-MoO₃ obtained after annealing of MoS_{2-x}O_x.

Figure 4.4 Transmission mode SEM images using transmission electron detector (TED) and their elemental mapping results of (a) MoS_{2-x}O_x (few-layer thickness) and (b) MoS₂-MoO₃ (a thick flake) samples. Note that the sample of MoS₂-MoO₃ was obtained by annealing of MoS_{2-x}O_x and the fragment in (b) was scratched from the annealed film.

The final products, i.e., MoS₂-MoO₃ hybrid nanomaterials, were further characterized by TEM (Figure 4.5). The TEM image of one MoS₂-MoO₃ fragment, which was directly scratched from the annealed MoS₂-MoO₃ film followed by the sonication, is shown in Figure 4.5a. The selected area electron diffraction (SAED) pattern in Figure 4.5b includes the signals from both MoS₂ and MoO₃. The diffraction pattern can be assigned to the (100) indexed diffraction spots from MoS₂ and the (021) indexed diffraction spots from MoO₃. Moreover, as shown in Figure 4.5c, the lattice distance of 0.33 nm is consistent with the lattice fringe of orthorhombic α -MoO₃ (021) planes.^[30, 31] Meanwhile, the typical lattice fringe of MoS₂ with distance of 0.27 nm is also observed, which indicates the co-existence of MoO₃ and MoS₂ in the fragment (Figure 4.5c).

Figure 4.5 (a) TEM image of a typical MoS₂-MoO₃ fragment. (b, c) SAED pattern and HRTEM image taken from the sample in (a).

Figure 4.6 XRD spectra of quartz, quartz/MoS_{2-x}O_x film, and quartz/MoS₂-MoO₃ film. Note that the quartz/MoS₂-MoO₃ sample was obtained by annealing of quartz/MoS_{2-x}O_x in 5%H₂ diluted Ar gas at 450-500 °C for 1 h. The peak at 27.3° from MoO₃ component verified the partial oxidation of MoS₂.

Furthermore, as shown in Figure 4.6, the XRD pattern of the MoS₂-MoO₃ film also suggested that the thermal annealing treatment enables the oxide component of MoS_{2-x}-O_x to construct and crystalize. The crystalline MoS₂-MoO₃ hybrid nanomaterial was formed on the basis of the aforementioned TEM results (Figure 4.5) and XRD patterns with the strong MoO₃ (021) peak dominated at around 27.3 ° (Figure 4.6).

4.2.3 The application of MoS₂-MoO₃ hybrid materials for light-emitting diodes

Hall measurement confirmed the MoS₂-MoO₃ film is *p*-type conductive and the measured doping concentration is around 10¹⁶-10¹⁸ cm⁻³. Then the theoretical modeling was conducted to ascertain the origin of this *p*-type doping. Due to the *p*-type hole conductivity of MoS₂-MoO₃, we then construct the heterojunction by using the *p*-MoS₂-MoO₃ and *n*-type SiC (*n*-SiC) as the active layers to fabricate LED device (Figure 4.2, Step 3. The device structure is schematically shown in Figure 4.2d). The cross-section SEM image in Figure 4.7 indicates that the thickness of the as-prepared MoS₂-MoO₃ film is around 3 μm.

Figure 4. 7 The cross-section SEM image of MoS₂-MoO₃ on quartz substrate.

Figure 4.8a presents the current-voltage (I - V) curve of the fabricated LEDs, which exhibited a turn-on voltage of ~ 4.5 V. Moreover, a current of ~ 15 mA was obtained when the applied forward bias reached 10 V. A color photograph of the LED at forward bias of 18 V was inset in Figure 4.8a, which shows intense light emission of the LED. The I - V characteristic and light emission of n -SiC/ p -MoS₂-MoO₃ heterojunction based LED device indicate that p -type conductivity of the MoS₂-MoO₃ hybrid nanomaterials can realize efficient hole injection in the device. Figure 4.8b displays the EL spectra of the fabricated LEDs operated at different voltages (i.e., 3, 9, 12, 15, 18 V). The broad EL spectra taken at 18 V were deconvoluted into four sub-peaks centered at 411, 459, 553 and 647 nm (inset in Figure 4.8b).

Figure 4.8 (a) I - V curve of the fabricated LED with configuration of Au/Ti/ n -SiC/ p -MoS₂-MoO₃/ITO/glass. Inset is a photograph of the LED biased at forward voltage of 18 V. (b) The EL spectra of the LEDs operated at different forward voltages. The inset exhibits the fitted sub-peaks for the EL spectrum at forward voltage of 18 V.

First-principle density functional theoretical calculations were performed to explain p -type conduction and the peaks in the EL spectra of MoS₂-MoO₃ layer by examining the band structure and the alignment of energy bands. Note that the effect of sulfur vacancy which is the most possible defect in MoS₂ is

ignored because it is well-known to induce *n*-type conductivity together with formation of deep-gap states.^[32] Also the case of oxygen replacing sulfur in MoS₂ is ruled out as no additional states are created in the band gap associated with this type of defect (Figure 4.9).

Figure 4. 9 Density of states (DOS) of single oxygen substitution of sulfur atom in MoS₂ monolayer. No defective state is observed in the gap.

A thorough study is performed on the defects in MoO₃ which are believed to play important roles in the electronic properties as they are easily introduced during the oxidation of MoS₂. In MoO₃, the most possible defects are the oxygen vacancies (V_O) which are found to induce a deep level of 1 eV below the CB (denoted as D1 in Figure 4.10e).^[33] Another possible defect is S substitution of O atom (denoted as S_O) in the MoO₃, originating from the incomplete oxidation of MoS₂ during thermal treatment. As there are three different types of oxygen atoms in α -MoO₃ with single, twofold, and threefold coordination which are denoted as O1, O2 and O3, respectively, there are three types of the sulfur substitutions of O1, O2, and O3 which are referred as S_{O1}, S_{O2}, and S_{O3}, respectively (Figure 4.10a). Compared with the V_O defect, the S_O defects induce level of around 0.5 eV above the top of VB and labeled as the D2 (Figure 4.10e). The partial DOS analysis shows that the D2 state is a hybridized state of $p_x, p_y(S)-d_{xz}(Mo)$, $p_y, p_z(S)-d_{xz}(Mo)$, and $p_x(S)-d_{xy}(Mo)$ with the ratio of *p*:*d* orbital occupation of 1:0.29, 1:0.4, and 1:0.40, respectively. It is believed that

they are the origin of the *p*-type conduction and account for the peaks in EL spectra. As shown in Figure 4.10b-d, the isosurface plots of the real space distribution of these states show that the *p* states mainly distribute at substituting S atoms.

In Figure 4.10e, the band alignments of the defective MoO₃ with the *n*-type 4H-SiC (*n*-SiC) are plotted. A close-up view (Figure 4.10e) of the bands of MoS₂ and MoO₃ is presented. With this alignment, the holes produced at the top of VB of MoO₃ can partially transfer to the D2, following with radiative recombination of activated electrons of the CB of MoO₃, thus allowing EL emissions based on the selection rule ($\Delta l = \pm 1$, like *s-p*, *p-d* transitions). The emission peak, i.e., centered at ~411 nm (3.02 eV), is attributed to a direct recombination of the electrons and holes from CB and VB of MoO₃, respectively. The fourth emission peak at 647 nm (1.92 eV) is related with the recombination of holes and electrons in the MoS₂ layer. It should be noted that the Fermi level of the MoS₂ can shift greatly below the VB due to the weak screening effect.^[34, 35] Thus the holes from ITO can populate at the top VB at the K point of the Brillouin zone of MoS₂, accounting for the A exciton with a nearly thickness-insensitive peak positions (~1.86-1.89 eV).^[8, 16] The recombination of excited carriers at D1 and D2 levels in MoO₃ layer, with quenching of the electrons at CB and the holes at the D2 level and transition from the D1 level related with V_O to the VB of MoO₃, leads to another two peaks located at 553 nm (2.24 eV) and 459 nm (2.7 eV). There is also clear peak broadening due to lattice distortion and defects. The experimental emission peaks and the theoretical assignment are compiled in Table 4.1.

Previous studies have demonstrated the critical functions of the proper contacts to tune the Schottky barrier height.^[36, 37] The oxide barrier such as MgO^[38] and TiO₂^[39] can significantly alleviate the conduction mismatch and

decrease/eliminate the contact resistance. Modulation of the Schottky barrier height and width by contact engineering is promising for tuning the polarity

Figure 4.10 (a) DOS of MoO₃ containing S_{O1}, S_{O2}, and S_{O3} defects, the spin up and spin down states are shown with blue and red lines, respectively. The defective states in the bandgap are indicated by black arrows. (b-d) Plots of partial charge density induced by the localized states of S_{O1}, S_{O2}, and S_{O3}, respectively. (e) Energy-level diagram of the coupled systems consisting of 4H-SiC, MoS₂, and MoO₃. The EL transition scheme is indicated with arrows. Transition 1 is associated with the electron-hole recombination from CB to VB of MoO₃, whereas transition 4 is ascribed to the transition of holes (at the top of the valence band at K point of the Brillouin zone) and the electrons (at CB) of MoS₂ with thickness changing from monolayer to few layers. In (e), the monolayer MoS₂ was employed to show the bandgap, where the dash lines in the bandgap indicate that the minor decrease of the gap happens when increasing the layer number of MoS₂. Transition 2 and 3 correspond to the emission from the CB of MoO₃ to S_{Ox} (x=1, 2, 3) related D2 level and D1 level of V_O to VB of MoO₃, respectively. The work function of ITO and Au/Ti are 4.7 and 4.75 eV, respectively, referring to the references ^[40] and ^[41], respectively; and the electron affinity for MoS₂ (4.2 eV), 4H-SiC (3.1 eV) and MoO₃ (2.3 eV) is from references ^[42], ^[43] and ^[44], respectively.

and mobility of conducting carriers. The Schottky barrier between the metal contacts and the MoS₂-MoO₃ hybrid film are similarly affected by work function, defective states and interfacial states. Therefore, manipulation of the Schottky barriers will be very promising for fabrication of devices based on MoS₂-MoO₃ hybrid nanomaterials and needs further exploration.

Table 4. 1 Experimental and theoretical study of the electroluminescence transitions for *n*-SiC/*p*-MoS₂-MoO₃ based LEDs

Peak No.	Transition	EL peaks (experiment)	EL peaks (theory)
1	CB (MoO ₃) → VB (MoO ₃)	411 nm (3.02 eV)	400 nm (3.1 eV)
2	CB (MoO ₃) → D2	459 nm (2.7 eV)	459 nm (2.7 eV)
3	D1 → VB (MoO ₃)	553 nm (2.24 eV)	590 nm (2.1 eV)
4	CB (MoS ₂) → VB (MoS ₂)	647 nm (1.92 eV)	653 nm (1.9 eV)

In conclusion, a facile process was developed for preparation of MoS₂-MoO₃ hybrid nanomaterials through partial oxidation of MoS₂ nanosheets in air and crystallization at high temperature. The as-prepared MoS₂-MoO₃ hybrid exhibited *p*-type conductivity. By combining with *n*-SiC, the *n*-SiC/*p*-MoS₂-MoO₃ heterojunction was used for LEDs. The mechanisms of EL peaks from the LED device were investigated from both theoretical calculation and experimental observation. It was found that the radiative electron-hole recombination from band edges and the energy level of defective states played the key roles. Due to the easy fabrication process and excellent performance for LEDs, we believe that our method might open up an avenue to develop new advanced layered hybrid nanomaterials in electronics, optoelectronics, information storage, and clean energy applications.

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Chapter 5

Transition Metal Dichalcogenide Nanodots

In this chapter, the preparation of transition metal dichalcogenide (TMD) nanodots (NDs), e.g., MoS₂, MoSe₂, WS₂, WSe₂, ReS₂, TaS₂, and NbSe₂ NDs, from their bulk crystal counterpart by combination of grinding and sonication techniques, and the potential application for memory devices are presented. The as-prepared NDs are characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), UV-vis and Raman spectroscopy. All the TMD NDs have small lateral size less than 10 nm and high dispersity in N-methyl-2-pyrrolidone (NMP) solution. Moreover, a facial process is also demonstrated to isolate these NDs from the NMP, i.e., post-treating these NDs with hexane and then chloroform. As a proof of concept, the TMD NDs (e.g., MoSe₂, WS₂ or NbSe₂) were mixed with polyvinylpyrrolidone (PVP) for fabrication of memory devices, which exhibit nonvolatile write-once-read-many behavior. We believe that these TMD NDs should have a broad range of applications in optoelectronics, catalysis, solar cells, and bio-applications.

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5.1 Introduction

Engineering the size and dimension of layered materials is one of the most fascinating ways to endow them with novel properties and broaden their applications. As a typical example, graphene quantum dots (GQDs), one kind of nanodots (NDs), with lateral size less than 10 nm, exhibit extraordinary semiconducting properties and unique electrical/optical behaviors, which are greatly different from the gapless graphene nanosheets^[1-3]. Therefore, it is believed that the preparation of other quantum dots (QDs) of layered materials is fundamentally important and urgent since they are also expected to exhibit unusual properties and have promising applications.

Similar to graphene, single- or few-layer nanosheets of transition metal dichalcogenides (TMDs), as a unique class of inorganic nanomaterials, showed various applications in electronics, catalysis, biomedicine, sensing and energy storage.^[4-8] Different from the conventional chalcogenide semiconductors, e.g., CdS, PbS, and ZnS, TMDs with two-dimensional (2D) layered structures exhibit the thickness-dependent physical properties.^[6] Recent work mainly focuses on the preparation of high-quality single- and few-layer TMD nanosheets, which exhibited dramatic change in electronic and optical properties.^[6, 7, 9, 10] Compared to the intrinsic 2D layers, the small-sized TMD semiconductors with diameter less than 10 nm, i.e., TMD QDs, show stronger quantum confinement and edge effects, offering unique and extra electrical/optical properties beyond the single-/few-layer TMD nanosheets.^[11-13] To date, most effort has been devoted to the exfoliation of 2D nanosheets.^[4, 8, 9] Although sometimes the small-sized TMD nanostructures can be found during the preparation of 2D nanosheets, they are by-products and the production yield is very low.^[14, 15]

As known, monodispersed QDs synthesized in organic solvents using chemical methods,^[16] i.e., bottom-up methods, suffer from the insulating ligands coated

on QDs, which are seriously detrimental to the electrical transport, especially in the applications of electronics^[17, 18] and catalysis.^[18, 19] Alternatively, top-down approaches, such as laser ablation^[20] and e-beam lithography^[21], can be used to reduce the crystal size. Unfortunately, such methods are not feasible for the high-yield preparation of QDs in solution phase and also restricted by the extremely expensive facility. Up to now, high-yield production of TMD QDs is still under investigation and their applications remain to be explored.

Herein, we report a general method by combination of grinding and sonication process to prepare a number of layered TMD NDs, e.g., MoS₂, MoSe₂, WS₂, WSe₂, ReS₂, TaS₂, and NbSe₂ NDs, in high yield from the corresponding bulk TMD crystals at room temperature. All the prepared TMD NDs are less than 10 nm with narrow size distribution and exhibit high dispersity. As a proof-of-concept application, the synthesized TMD NDs mixed with polyvinylpyrrolidone (PVP) are used as active layers for fabrication of flexible memory devices with non-volatile memory effect.

5.2 Results and Discussion

5.2.1 Preparation and characterization of transition metal dichalcogenide nanodots

Figure 5. 1 Preparation of TMD NDs from layered bulk TMDs.

Layered TMDs with the form of MX_2 (M=transition metal and X=chalcogenide) are depicted by a planar covalently chemical bound X-M-X sandwich structure. The basic structural characteristics of layered TMDs are displayed in Figure 5.1. Each single layer consists of two layers of hexagonally close-packed chalcogenide atoms stacked to one layer of close-packed transition metal atoms. Every two consecutive atomic layers stack together by the weak VdW interaction. In order to obtain small size TMD NDs, the in-plane X-M-X bonds should be broken. As known, grinding^[22] and sonication^{[9],[23]} are two typical processes to weaken the VdW interaction of TMDs, resulting in few-layer TMD nanosheets.^[24] Moreover, the shear/compress force of grinding and the high-energy sonication are able to break up the covalently chemical bonds and disintegrate bulk crystals.^[22, 25, 26] Herein, MoSe_2 is used as a typical example to prove our method. The preparation process is shown in Figure 5.1. Briefly, MoSe_2 crystals were first ground with N-methyl-2-pyrrolidone (NMP) followed by sonication. The aforementioned process, grinding and then sonication, was repeated twice in order to improve the yield of MoSe_2 QDs and further decrease their size. It was found that the color of the MoSe_2 suspension changed from black to dark brown (Figure 5.2), which can be ascribed to the size difference before and after treatment.

Figure 5. 2 Photograph of the suspensions of (a) raw MoSe_2 and (b) MoSe_2 treated with grinding and sonication.

Figure 5.3 (a) TEM image of MoSe₂ QDs. Inset in (a): Statistical analysis of the size of 150 MoSe₂ QDs measured from TEM images. (b) Magnified TEM image of MoSe₂ QDs. Inset in (b): Photo of MoSe₂ suspension in NMP. (c, d) HRTEM images of MoSe₂ QDs. (e) AFM image of MoSe₂ QDs. (f) Height profiles along the red line in (e). (g) Statistical analysis of the height of 100 MoSe₂ QDs measured from AFM images. (h) UV-vis absorption spectrum of MoSe₂ QDs in NMP.

After purification of the MoSe₂ suspension in Figure 5.2, the MoSe₂ QDs were obtained. The transmission electron microscopy (TEM) images showed that the size of MoSe₂ QDs is 2.7 ± 0.8 nm without aggregation (Figure 5.3a, b). High-resolution TEM (HRTEM) images of MoSe₂ QDs gave a clear lattice fringe of 0.21 nm derived from the (104) planes of MoSe₂ crystal (Figure 5.3c, d), indicating the high crystallinity of as-produced MoSe₂ QDs. Energy-dispersive X-ray spectroscopy (EDX) gave the signal of Mo, Se, and O (Figure 5.4).

Different from the black color of original MoSe_2 suspension (Figure 5.2), the color of MoSe_2 QDs in NMP is brown (insert in Figure 5.3b).

Figure 5.4 EDX spectrum of MoSe_2 QDs in TEM mode.

Figure 5.5 XPS spectra of (a) Mo 3d and (b) Se 3d of MoSe_2 QDs.

The chemical composition of MoSe_2 QDs was further confirmed by X-ray photoelectron spectroscopy (XPS). As shown in Figure 5.5, MoSe_2 QDs exhibited nearly the same binding energies of well-defined spin-coupled Mo

Figure 5.6 (a-f) TEM, HRTEM images and the size statistical analyses of MoS_2 , WS_2 , ReS_2 , TaS_2 , WSe_2 , and NbSe_2 NDs. The corresponding photos of TMD NDs in NMP are inserted.

and Se doublets as those of MoSe_2 crystal. The peaks around 228.8 and 232.0 eV correspond to the Mo $3d_{5/2}$ and Mo $3d_{3/2}$, respectively (Figure 5.5a), while the peaks at 54.4 and 55.2 eV can be attributed to Se $3d_{5/2}$ and Se $3d_{3/2}$ orbitals (Figure 5.5b), which are agreed well with the binding energies of Mo^{4+} and Se^{2-} in 2H phase of MoSe_2 .^[27, 28] No obvious signal from the oxidation state of Mo^{6+} was observed, indicating that there is no obvious oxidation of MoSe_2 QDs. Atomic force microscopy (AFM) characterization confirmed that the height of

MoSe₂ QDs is 1.8 ± 0.6 nm (Figure 5.3e-g), i.e., $\sim 2 \pm 1$ layers, as the thickness of single-layer MoSe₂ is ~ 0.7 nm.^[29] The optical property of MoSe₂ QDs was measured by UV-vis absorption spectroscopy (Figure 5.3h). The characteristic excitonic peaks at 795 nm (A) and 696 nm (B) are clearly observed, which arise from the direct transition from the valence band (VB) to the conduction band (CB) at the K point of the Brillouin zone,^[30] indicating that the MoSe₂ QDs preserved the 2H polytype structure.^[31, 32]

Figure 5.7 UV-vis spectra of (a) MoS₂, (b) WS₂, (c) ReS₂, (d) TaS₂, (e) WSe₂ and (f) NbSe₂ NDs in NMP.

Besides MoSe₂ QDs, our method has been successfully used to prepare a number of other TMD NDs, such as MoS₂, WS₂, ReS₂, TaS₂, WSe₂, and NbSe₂. The corresponding TEM and HRTEM images confirmed their high crystallinity and the diameters of NDs are less than 10 nm (Figure 5.6). Due to different light extinction coefficient, the prepared NDs showed different color (inserted

photographs in Figure 3) and the corresponding UV-vis absorption spectra are shown in Figure 5.7.

Figure 5. 8 The isolation process by addition of hexane and then chloroform, followed by centrifugation. (a) The supernate collected after centrifuging MoS₂ and MoSe₂ QD suspension in NMP at 14,000 rpm for 20 min. (b) MoS₂ and MoSe₂ dispersed in NMP after addition of hexane (NMP:hexane=1:1, v:v). (c) The dispersions in (b) after addition of chloroform (NMP:chloroform=1:1, v:v). (d) Samples after centrifugation of (c) at 5,000 rpm for 10 min.

Recently, Coleman et al. proved that NMP is the most effective solvent for exfoliation of TMDs because its surface energy well matches that of TMD

materials, leading to the maximum dispersion of TMDs with high stability.^[9] However, the high dispersity and small size of NDs make it difficult to extract them from NMP, even using the high-speed centrifugation and/or solvent evaporation method. In this work, we report a simple method to realize the separation of NDs from NMP. After addition of hexane (poor solvent) and then chloroform (less polar solvent), the TMD ND dispersion can be easily precipitated through centrifugation (Figure 5.8). The obtained products containing TMD NDs could be easily re-dispersed in other polar solvents, such as water and ethanol.

5.2.2 Transition metal dichalcogenide nanodot-based memory devices

Previous studies have demonstrated that the polymer-inorganic hybrid-based memory devices show unique conductance-switching effect and thus are regarded as the most promising alternative or supplementary devices for conventional inorganic semiconductor-based memory devices.^[33-35] As a proof-of-concept application, the electronic property and switching effect of PVP-MoSe₂ QD nanocomposite-based memory device with the configuration of glass/indium tin oxide (ITO)/PVP-MoSe₂ QDs/Au (inset in Figure 5.9) was fabricated and investigated by current–voltage (I – V) characteristics (see Methods for the detailed fabrication process of the device). As shown in Figure 5.9a, starting from the low conductivity state (OFF state) in the device (Stage 1), the current increased abruptly from 1.8×10^{-5} to 4.0×10^{-2} A as the applied positive voltage increased to +3.8 V, indicating that the electrical property transformed from low current state (OFF state) to high current state (ON state) (Stage 2). The transition from the OFF state to ON state is equivalent to the “writing” process in a digital memory. In the subsequent positive sweep (Stages 3 and 4), the device remained in its high conductivity state with ON/OFF ratio of over 4.0×10^5 at +0.5 V, which is significantly higher than that of PVP-MoS₂ nanosheet-based memory device.^[36] This feature promises a low misreading

rate during the device operation. After a reverse sweep to -4.0 V (Stage 5), the device remained at the high conductivity state (Stage 6), indicating the inerasable data storage characteristic. Moreover, the high conductivity state still remained in the following sweeps (Figure 5.9b), suggesting the nonvolatile write-once-read-many (WORM) memory behavior of the fabricated PVP-MoSe₂ QD nanocomposite-based memory device.

Figure 5.9 (a) The $I-V$ characteristics of MoSe₂ QD-based flexible memory device. Inset in (a): The configuration of the fabricated memory device. (b) The $I-V$ characteristics of glass/ITO/PVP-MoSe₂ QDs/Au memory device in the 2nd sweep. (c) The $I-V$ characteristics of Au/ITO/Au. (d) The retention-ability test of MoSe₂ QD-based memory device in the ON and OFF states at reading voltage of $+0.5$ V.

For comparison, the $I-V$ characteristics of device with configuration of Au/ITO/Au without any active layer between ITO and Au exhibited higher

Figure 5.10 The I – V characteristics of glass/ITO/PVP-WS₂ QDs/Au memory device.

Figure 5.11 The I – V characteristics of glass/ITO/PVP-NbSe₂ NDs/Au memory device.

electrical conductivity compared to the PVP-MoSe₂ QD nanocomposite-based memory device after the electrical switching (Figure 5.9c), indicating that a short circuit did not occur during the operation of the device. In order to explore the stability of our device, the retention time test was carried out in the ON and OFF states, respectively (Figure 5.9d). The ON and OFF states of the device did not undergo significant fluctuation even after more than 5.0×10^3 s of test at reading bias of +0.5 V under ambient conditions. The long retention time demonstrates the highly stable information storage capability of our device.

Moreover, under the same experiment conditions, both of PVP-WS₂ QD and PVP-NbSe₂ ND nanocomposite-based devices exhibited the WORM memory effect (Figure 5.10, 5.11). The switching voltage of PVP-WS₂ QD nanocomposite-based device is at +1.5 V and the ON/OFF current ratio is over 1.7×10^3 at +0.5 V. For the PVP-NbSe₂ ND nanocomposite-based device, the transition from the OFF state to ON state occurred at voltage of -1.3 V, and the ON/OFF current ratio is over 1.3×10^3 at -0.5 V. These two devices with low switching voltage reveal low writing voltage, suggesting promising application in the memory device with low power consumption.

5.3 Conclusion

In this chapter, we have systematically prepared the TMD NDs in high yield through a facile, universal top-down process. All the prepared NDs with diameters less than 10 nm showed narrow size distribution. As a proof-of-concept application, several types of NDs, i.e., MoSe₂, WS₂, and NbSe₂, mixed with PVP were used as active layers for fabrication of memory devices, which showed nonvolatile WORM memory effect with high ON/OFF current ratio. Among the tested devices, MoSe₂ QD-based memory showed the best performance with ON/OFF ratio of over 4.0×10^5 and long-time stability. It is

believed that the TMD NDs may have more promising applications in electronics, catalysis, solar cells, sensing, and bio-medicine.

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Chapter 6

Black Phosphorus Quantum Dots

As a newly emerging layered nanomaterial, the black phosphorus (BP) has shown great promise in electronic devices. Although BP nanosheets have been successfully prepared through mechanical exfoliation method, it is still challenging to produce other novel BP nanostructures in high yield. This chapter describes the preparation of small size black phosphorus quantum dots (BPQD) from bulk BP crystals through a solution-based top-down process, and investigation of its potential application in memory devices. The as-prepared BPQDs are characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), UV-vis absorption spectroscopy, and Raman spectroscopy. Moreover, flexible memory device is fabricated by using BPQDs mixed with polyvinylpyrrolidone (PVP) as the active layer. The memory device exhibits a nonvolatile rewritable memory effect with a high ON/OFF current ratio and good stability.

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6.1 Introduction

Two-dimensional (2D) layered materials, such as graphene and transition metal dichalcogenides (TMDs), have emerged as a class of promising nanomaterials in both fundamental studies and potential applications owing to their intriguing properties.^[1-6] Besides the 2D layered structure, ultra-small quantum dots (QDs), as another form of nanomaterials, exhibit unique electronic and optical properties due to the quantum confinement and edge effects.^[7, 8] For example, graphene and MoS₂ QDs have been successfully prepared and widely used in photovoltaic devices,^[9] opto-electronics^[10] and biological analysis.^[11, 12]

Inspired by the unique 2D feature of graphene and TMDs, considerable efforts have been devoted to the exploration of new members in the 2D family. As a typical example, the black phosphorus (BP), a conceptually new layered material, has triggered a recent resurgence of interest due to its unique structure as well as fascinating optical and electronic properties.^[13-16] Since bulk BP consists of puckered layers stacked together via the weak Van der Waals (VdW) interaction, the mechanical exfoliation method has been successfully used to prepare single- and few-layer BP nanosheets.^[13, 17] Importantly, BP has a layer-dependent bandgap, which can be tuned from 0.3 to 2 eV as its thickness decreased from bulk to monolayer.^[15, 18, 19] The appealing tunable bandgap of BP holds great promise in bridging the space between zero-gap graphene^[1] and large-gap TMDs (1-2 eV).^[3] Moreover, it has been theoretically predicted that the bandgaps of its monolayer (phosphorene) and nanoribbon are highly sensitive to the plane strain and edge structures.^[20-22] Based on its intriguing properties, BP nanosheets have been used in field-effect transistors (FETs),^[13, 16] and theoretically predicted for thin film solar cell^[21] and gas sensing^[23] applications. Despite the recent progress in mechanically exfoliated BP nanosheets, it is still challenging to prepare new BP nanostructures in high yield especially through solution-based approaches.

In this chapter, we prepared black phosphorus quantum dots (BPQDs) from the bulk BP crystal by using a facile solution-based method. The as-synthesized BPQDs with average size of 4.9 ± 1.6 nm and thickness of 1.9 ± 0.9 nm (i.e., $\sim 4 \pm 2$ layers) showed good stability in N-methylpyrrolidinone (NMP). As a proof-of-concept application, the mixture of BPQDs and polyvinylpyrrolidone (PVP), referred to as BPQD-PVP, was used as active layer for the fabrication of flexible memory device, which exhibited a nonvolatile rewritable memory effect with high ON/OFF current ratio of more than 6.0×10^4 and good stability.

6.2 Results and Discussion

6.2.1 Preparation and characterization of bulk black phosphorus crystals

Bulk BP crystal, the most stable allotrope of phosphorus (P), is composed of layered orthorhombic crystal structure with the space group *Cmca* (64), in which the VdW interaction is along the crystal *y* axis (Figure 6.1a). In each BP layer, which is composed of a puckered honeycomb structure, P atom bonds with three ones, among which three atoms located at the same plane while the fourth one is in the parallel adjacent one (Figure 6.1b, c).

Figure 6.1 (a) Schematic diagram of BP crystal. (b) Three adjacent puckered sheets with linked phosphorus atoms. (c) Top view of (a).

The micrometer-sized bulk BP crystals were synthesized from red phosphorus under high pressure and high temperature.^[24] Figure 6.2 shows the X-ray diffraction (XRD) pattern of bulk BP and the standard pattern for BP (JCPDS No. 73-1358). All diffraction peaks can be readily indexed to the orthorhombic BP with space group *Cmca* (64). Figure 6.3a shows the scanning electron microscopy (SEM) image of bulk BP. The size of bulk BP is in the range of several hundred nanometers to a few micrometers. Despite varying size and shape with no obvious lamellar feature, the crystalline BP flakes can be obtained after 10 min sonication of bulk BP in NMP (Figure. 6.3b, c, d). The lattice spacing of 0.26 nm is observed in the high-resolution transmission electron microscopy (HRTEM) image (Figure 6.3c), which is consistent with the (040) face of orthorhombic phase of BP. Figure 6.3d gives the selected area electron diffraction (SAED) pattern of a selected BP flake, which contains several diffraction spots and concentric diffraction rings, indicating that BP is polycrystalline. As well known, the liquid exfoliation method is commonly used to isolate 2D layered materials and prepare QDs.^[2, 25, 26] However, graphene and MoS₂ QDs prepared by this technique usually suffer from the wide size distribution and quite low yield. Bearing this in mind, we combined grinding and sonication processes to exfoliate bulk BP crystals and high-yield BPQDs were obtained.

Figure 6. 2 XRD pattern of bulk BP. The standard data for orthorhombic BP (JCPDS No. 73-1358) is used as reference.

Figure 6.3 Characterization of bulk BP and BP flakes. (a) SEM image of bulk BP. (b) TEM image of BP flakes prepared by sonication of bulk BP in NMP for 10 min. (c) HRTEM image of BP flake. (d) SAED pattern of BP flake.

6.2.2 Preparation and characterization of black phosphorus quantum dots

The morphology of as-prepared BPQDs was characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM). From TEM images in Figure 6.4a, b, the average size of BPQDs is 4.9 ± 1.6 nm (Figure 6.4e). HRTEM images of BPQDs give lattice fringes of 0.34 nm (Figure 6.4c) and 0.52 nm (Figure 6.4d), which can be ascribed to the (021) and (020) planes of BP crystal, respectively. AFM image shows the topographic morphology of

BPQDs (Figure 6.4f). The measured heights of 2.7 and 1.6 nm (Figure 6.4g, h) correspond to BPQDs with ~ 5 and 3 layers, respectively. Statistical AFM analysis gives their average thickness, which is 1.9 ± 0.9 nm (Figure 6.4i), i.e., corresponding to $\sim 4 \pm 2$ layers (see the morphology sketch of a BPQD in inset of Figure 6.4a).

Figure 6.4 (a) TEM image of BPQDs. (b) Enlarged TEM image of BPQDs. (c, d) HRTEM images of BPQDs with different lattice fringes. Scale bar=5 nm. (e) Statistical analysis of the sizes of 200 BPQDs measured from TEM images. (f) AFM image of BPQDs. (g, h) Height profiles along the white lines in (f). (i), Statistical analysis of the heights of 200 BPQDs measured by AFM. A morphology sketch of a BPQD is inserted in Figure 6.4a.

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition of BPQDs. As seen in Figure 6.5a, the XPS survey shows a predominant P2p peak at around 129.9 eV and O1s peak at 532.1 eV. It has been reported that BP is sensitive to water and oxygen and can degrade to P_xO_y

under visible light irradiation.^[26] Therefore, the O signal should arise from the oxidation of BP, due to the exposure of BP sample to the atmosphere before XPS measurement. The high-resolution P2p spectrum shows two peaks at around 130.3 eV and 129.5 eV (Figure 6.5b), which are assigned to $2P_{1/2}$ and $2P_{3/2}$ binding energy, respectively. A peak at high energy region (around 133.9 eV) is indicative of the oxidation of BPQDs (Figure 6.5b).

Figure 6.5 (a) XPS survey and (b) P2p spectrum of BPQDs.

UV-vis absorption spectroscopy was used to investigate the optical property of BPQDs (Figure 6.6a). In addition, Raman spectroscopy was used to characterize the BPQDs (Figure 6.6b). Three prominent peaks can be ascribed to one out-of-plane phonon modes (A_g^1) at 361.6 cm^{-1} , and two in-plane modes, i.e., B_{2g} and A_g^2 , at 438.7 and 466.1 cm^{-1} , respectively. Compared to the bulk BP, both of the B_{2g} and A_g^2 modes of BPQDs are red-shifted by around 8.9 cm^{-1} , while the A_g^1 mode is only red-shifted by 5.6 cm^{-1} (Figure 6.6b). The frequency difference between A_g^1 and B_{2g} modes changes from 73.8 cm^{-1} for bulk BP to 77.1 cm^{-1} for BPQDs. This red shift phenomenon is quite similar to the mode change of boron nitride,^[27] MoS_2 ^[28] and graphene QDs^[9] with thin thickness and small lateral dimensions. The obtained BPQDs can be dispersed in NMP, showing a faint claybank phase (left inset in Figure 6.6a), which can stabilize without any noticeable aggregation at room temperature for more than 1 month, confirmed by the Tyndall effect (right insert in Figure 6.6a).

Figure 6.6 (a) UV-vis absorption spectrum of BPQDs in NMP. Inset: Photos of the BPQD suspension (left) and Tyndall effect of BPQD suspension (right). (b) Raman spectra of BPQDs and bulk BP crystal.

6.2.3 Fabrication of memory devices using black phosphorus quantum dots

Previous studies have demonstrated that polymer/organic-inorganic hybrid nanomaterials showed unique conductance-switching effect, and thus can be used in data storage devices.^[29, 30] As a proof-of-concept application, after PVP was used as a polymer matrix to mix with BPQDs, referred to as BPQD-PVP, it was used as active layer for memory device with the structure of poly(ethylene-

Figure 6.7 (a) Photograph and schematic illustration of the fabricated flexible memory device. (b) The current-voltage (I - V) characteristics of BPQD-based flexible memory device. (c) The retention-ability test of BPQD-based memory device in the ON and OFF states at reading voltage of 0.2 V.

terephthalate) (PET)/Au/BPQD-PVP/Ag (Figure 6.7a). The electronic properties and switching effects were then investigated. As shown in Figure 6.7b, the BPQD-PVP based device exhibits electrically bistable behavior. Starting with the high-resistance state (HRS) (OFF state) in the device (Stage 1), when the applied negative voltage increased to -1.2 V, the current state increased abruptly from 2.0×10^{-7} to 3.8×10^{-3} A (Stage 2), indicating the electrical property transformed from HRS to low-resistance state (LRS, i.e., ON state). The low operating voltage (-1.2 V) is desirable for low-power memory devices. The transition from HRS to LRS is equivalent to a “writing” process in digital memory devices. This diode shows good stability in the LRS during the subsequent voltage sweep (Stage 3) and can be retained even the power is turned off (Stage 4). It also exhibits good stability in the LRS during the

subsequent positive sweep (Stage 5), indicating a nonvolatile effect of the memory. Impressively, the HRS can be recovered by applying a reverse voltage at 2.8 V (Stage 6), which is equivalent to the “erasing” process of a digital memory device. The device remained in its HRS during the subsequent positive sweep (Stage 7). During the cycle (Stages 1-7), LRS can be maintained even without voltage, but a suitable positive voltage can switch the LRS to HRS. This feature allows the application of BPQD-PVP nanocomposite as the electrically bistable material for flash memory devices.^[31] A high ON/OFF current ratio of more than 6.0×10^4 is obtained at the reading voltage of 0.2 V, which is significantly higher than that of C₆₀-PVP,^[32] MoS₂-PVP^[33] Au nanoparticle/ZnO nanorod-PVP based diodes.^[34] This feature promises a low misreading rate during the device operation. Since no switching phenomenon was observed in the pure PVP-based device,^[34] BPQDs exhibit an important role in the electrically bistable behavior. In order to explore the stability of our device, retention time test was carried out in the ON and OFF states, which did not undergo obvious fluctuation after 1.1×10^3 s test under ambient conditions at a reading voltage of 0.2 V (Figure 6.7c), indicating its good stability.

Figure 6.8 Experimental data and fitted lines of the I - V characteristics in the OFF state (a) and ON state (b).

To understand the carrier transport mechanism of the device, the experimental and fitted data of I - V curves are investigated (Figure 6.8a, b). In the OFF state,

the plot of $\ln(I)$ vs. $V^{1/2}$ from 0 to -0.5 V is fitted to a straight linear (inset in Figure 6.8d). Such a linear characteristic indicates that the conduction mechanism probably comes from the thermionic emission,^[33] arising from the low injection efficiency because of the large barrier between the electrodes and BPQD-PVP active layer.^[35] During this process, the charge injection from electrode to the active layer is dominant. After that, a linear relation was observed in the plot of $\ln(I)$ vs. $\ln(V)$ for the voltage sweep from -0.5 V to -1.2 V with a slope of 1.63, suggesting that space-charge-limited-current (SCLC) dominates the carrier transport process.^[33] During this process, charges were transferred from PVP to BPQDs, and then trapped by BPQDs, due to the lower energy level of BPQDs compared to PVP^[35] and a lower free carrier density than the trap density induced by BPQDs, following the SCLC model. With the further increase of bias to exceed the switching voltage, the injected carriers increase exponentially, resulting in the abrupt current transition. After this transition, almost all the traps are occupied by charges. Consequently, the device shows the ohmic behavior in the ON state (Figure 6.8e). Moreover, due to the insulating property of the PVP dielectric material used as matrix, the trapped charges in BPQDs are retained after the power off, which enables the high conductivity and nonvolatility of the memory device. When a reverse voltage is applied, the trapped charges will be detrapped. The internal electrical field induced by the trapped charges disappears. Therefore, the device returns to its initial HRS, and the erasing process of data storage is performed.

6.3 Conclusion

In this chapter, we synthesized BPQDs from its bulk crystal via a facile solution-based method. The as-prepared BPQDs have lateral size of 4.9 ± 1.6 nm and thickness of 1.9 ± 0.9 nm (ca. 4 ± 2 layers) with a bandgap of 2.37 eV. As a proof-of-concept application, the memory performance of BPQD-PVP was investigated, which showed a flash memory effect with a high ON/OFF current

ratio of more than 6.0×10^4 with good stability. It is believed that the new BPQDs might open up more applications in electronics, solar cells, sensing, and bio-imaging.

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Chapter 7

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. Based on the current research status, the work that can be focused on in the near future is also discussed.

7.1 General Discussion

In this thesis, I am focusing on the synthesis and structural engineering of novel layered materials, i.e., preparation of transition metal dichalcogenide-transition metal oxide heterostructure, and size reduction of transition metal dichalcogenide (TMD) materials and black phosphorus (BP). Moreover, I also investigated their applications in fabrication of electronic devices, such as light-emitting diodes (LEDs) and memory devices.

7.1.1 Discussion on the preparation of MoS₂-MoO₃ hybrid nanomaterials for light-emitting diodes

In this section, the oxidation of MoS₂ nanosheets and fabrication of MoS₂-MoO₃ hybrid nanomaterials for LEDs are demonstrated. First, the ultrathin MoS₂ nanosheets are exfoliated through electrochemically lithium intercalation/exfoliation process.^[1] The obtained MoS₂ nanosheets have lateral size from ~200 nm to 2 μm and few-layer thickness. We then develop an in-situ oxidation process to oxidize the MoS₂ nanosheets and synthesize MoS₂-MoO₃ hybrid materials. The oxidization process is realized by heat treatment of the MoS₂ film by spray-coating of the MoS₂ nanosheets on heated arbitrary solid substrates, such as SiC, Si, glass or quartz. After re-crystallization of the film at high temperature, the MoS₂-MoO₃ hybrid materials are obtained. Note that in addition to the re-crystallization of MoS₂-MoO₃ hybrid materials, the heat treatment at high temperature also induces the phase transformation of MoS₂ from metallic 1T phase to semiconductive 2H phase. The obtained MoS₂-MoO₃ hybrids exhibit *p*-type conductivity. Based on the *p*-type behavior of MoS₂-MoO₃, a LED is fabricated, which is composed of *p*-type MoS₂-MoO₃ (*p*-MoS₂-MoO₃) film and *n*-type 4H-SiC (*n*-SiC) substrate. The as-fabricated LED shows multi-wavelength emission. The electroluminescence (EL) behavior is then investigated. It is suggested that two peaks in its electron luminance

spectrum are assigned to the radiative electron-hole recombination, i.e., electrons from conduction band (CB) and holes from valence band (VB) of MoS₂, and electrons from CB and holes from VB of MoO₃. The other two peaks, supported by theoretical calculation, originate from the defective levels in MoO₃.

In this part, we have proved that the in-situ oxidation of MoS₂ in air by spray coating of MoS₂ nanosheets on a heated substrate is an effective approach to oxidize MoS₂ nanosheets and prepare the MoS_{2-x}O_x hybrid nanomaterials. Moreover, we prepare the MoS₂-MoO₃ hybrid nanomaterials by thermal annealing of the MoS_{2-x}O_x at high temperature. During this oxidation process, no organic surfactants or contaminations are introduced, which is particularly important for fabrication of electronics. In addition, we also demonstrate that the as-prepared MoS₂-MoO₃ hybrid nanomaterials show *p*-type conductive behavior and the measured doping concentration is around 10¹⁶-10¹⁸ cm⁻³. It indicates that the oxidation of MoS₂ nanosheets can bring new functions and properties. Furthermore, we demonstrate that the *p*-type MoS₂-MoO₃ hybrid materials can be used for fabrication of *p-n* heterojunction by combination with *n*-type materials, e.g., *n*-type 4H-SiC (*n*-SiC). The heterojunction is promising for a broad range of applications such as LEDs presented in the thesis by using the *p-n* heterojunction composed of the as-formed *p*-type MoS₂-MoO₃ film (*p*-MoS₂-MoO₃) and *n*-type 4H-SiC (*n*-SiC) with the configuration of Au/Ti/*n*-SiC/*p*-MoS₂-MoO₃/ITO/glass. Moreover, the electroluminescent mechanism of the LEDs has been investigated, which provides a valuable example for studying the electroluminescent properties of other materials and other optical/electronic devices.

7.1.2 Discussion on the preparation of the transition metal dichalcogenide nanodots for memory devices

In addition to the oxidization of the exfoliated MoS₂ nanosheets, preparation of small size TMD materials by decreasing their lateral size is also promising for tuning the properties for various applications. Therefore, we demonstrate the preparation of a number of layered TMD nanodots (NDs), including MoS₂, WS₂, ReS₂, TaS₂, MoSe₂, WSe₂ and NbSe₂ from their corresponding bulk TMD crystals by combination of grinding and sonication process. The fabrication process is a well-known “top-down” method to decrease the size of materials. All the prepared TMD NDs have small size less than 10 nm. Particularly, the solution-processed TMD NDs can be hybridized with organic polymer. As a proof-of-concept application, the fabricated TMD NDs (e.g., MoSe₂, WS₂, and NbSe₂) are mixed with polyvinylpyrrolidone (PVP), and then used as active layers for fabrication of flexible memory devices. As one of the represent example, the device based on MoSe₂ NDs show nonvolatile write-once-read-many (WORM) memory effect with ON/OFF ratio of over 4.0×10^5 and long-time stability. It is believed that these TMD NDs may have more promising applications in catalysis, solar cells, sensing, and biomedicine.

In this part, we prove that the thickness and lateral size of TMD materials can be reduced by using the mechanical grinding and sonication process. This process is facial to operate without using any organic capping ligand and surfactant. Furthermore, we also demonstrate that the small size TMD NDs are promising for fabrication of memory devices. As reported before, the MoS₂ nanosheets hybrid with PVP can be used as the active layer for fabrication of memory devices.^[2] In our work, we extend the concept to TMD NDs and demonstrate that the TMD NDs (e.g., MoSe₂, WS₂, and NbSe₂) mixed with PVP can also be used for fabrication of memory devices. Impressively, the MoSe₂ ND based memory device shows better performance with significantly higher ON/OFF ratio as compared with that of 2D MoS₂ nanosheet-based devices. Furthermore, the WS₂ and NbSe₂ ND based memory devices show low

writing voltage, suggesting promising in the memory device with low power consumption.

7.1.3 Discussion on the preparation of black phosphorus quantum dots for flexible memory devices

Third, based on the achievement of the second part, we extend the concept to fabricate black phosphorus quantum dots (BPQDs), which is a newly emerging layered material. We prepare BPQDs from the bulk BP crystal. The obtained BPQDs have lateral size of 4.9 ± 1.6 nm and thickness of 1.9 ± 0.9 nm (ca. 4 ± 2 layers). Furthermore, as a proof-of-concept application, we fabricate the memory devices by using BPQDs mixed with PVP as the active layer. The as fabricated memory devices exhibit a nonvolatile rewritable memory effect with a high ON/OFF current ratio of more than 6.0×10^4 and good stability.

In this part, we produce a new nanostructure of BP and prepare the small size BPQDs. Previously, most studies mainly focused on the investigation of 2D ultrathin BP nanosheets, while the study on other BP nanostructures is rare. Herein, the zero-dimensional (0D) BPQD nanostructure enriches the structure type of BP, which is promising for studying the BP nanostructure and potential applications. Moreover, we also find that the size reduction of BP can induce some unique properties such as the light absorption and Raman spectrum shift. Furthermore, we also demonstrate the potential application of the fabricated BPQDs. The BPQDs are mixed with PVP and used as the active layer for fabrication of flexible memory devices. Importantly, the performance of the BPQD based memory device show high ON/OFF current ratio with more than 6.0×10^4 at reading voltage of 0.2 V, which is significantly higher than that based on traditional materials like C_{60} -PVP,^[3] MoS_2 -PVP,^[2] Au nanoparticle/ZnO nanorod-PVP^[4], indicating the great potential of the BPQDs for fabrication of memory devices. Moreover, we also study the carrier

transport mechanism of the BPQD based devices. It is believed that the new BPQDs might open up the applications of BP in electronics, solar cells, sensing, and bio-imaging.

7.2 Reconnaissance

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

7.2.1 Preparation of new hybrid nanostructures using the in-situ oxidation process

Metal oxides are a class of materials widely used in energy storage and conversion.^[5, 6] The ability to incorporate metal oxides into 2D layered TMD materials is quite fascinating to combine different advantages of these materials, thus optimizing their performance for specific applications. Particularly, the unique layered heterostructures provide a smooth way to transport electrons through their basal plane, and in-situ oxidation process demonstrated in the thesis eliminates the influence of organic ligands, both of which are attractive for electronics as well as energy storage and conversion applications. For example, the work in chapter 4 of the thesis has demonstrated that the $\text{MoS}_2\text{-MoO}_3$ hybrid material shows great promising potential in light-emitting diodes (LEDs). Moreover, it has been reported that the core-shell $\text{MoO}_3\text{-MoS}_2$ nanowires show excellent performance for electrocatalytic hydrogen evolution reaction (HER).^[7] In addition to the $\text{MoO}_3\text{-MoS}_2$ hybrid materials, synthesis of other transition metal sulfide-transition metal oxide hybrid materials are also fascinating. For example, it has been demonstrated that the band-structure of TiO_2 , one of the most attractive materials for photocatalysis, can be modulated by alloying TiO_2

with TiS_2 .^[8,9] The as-formed $\text{TiO}_{2(1-x)}\text{S}_{2x}$ hybrid materials have smaller bandgap as compared with that of TiO_2 , which is promising for photocatalysis.^[8,9] In our work, only MoS_2 - MoO_3 hybrid nanomaterials were presented (introduced in chapter 4). Except that, other kinds of heterostructures, such as WS_2 - WO_3 , MoSe_2 - MoO_3 , TiS_2 - TiO_2 hybrid materials, are expected to be prepared using the similar method, i.e., in situ oxidization in air followed by anneal-driven crystallization. Moreover, it is anticipated that the hybridization process can induce some unique physical and electronic properties and the prepared hybrid materials show optimized or improved performance for specific applications.

7.2.2 Preparation of TMD nanodots with high concentration of 1T phase

As introduced in the Literature Review in Chapter 3, it has been known that the 2H phase MoS_2 nanosheets can be transformed to 1T phase upon lithium intercalation, and the metallic 1T phase MoS_2 nanosheets have shown great potential in electronics, electrocatalysis and electrochemical supercapacitors. Therefore, the preparation of pure 1T-phase MoS_2 by solution-based methods is valuable and promising to improve the performance for some applications. However, it is still a great challenge to prepare MoS_2 nanosheets with 100% of metallic 1T phase, which means 2H and 1T phases always coexist in the exfoliated metal chalcogenide nanosheets. In the thesis, the size of TMD materials has been decreased to nanoscale, and we suppose the small NDs will be more efficient for lithium intercalation and the phase transformation in these NDs will be easier as compared to large size TMD crystals. Therefore, it is possible to improve the fractions of metallic 1T phase MoS_2 , and even prepare pure 1T phase MoS_2 , by using the as-prepared 2H MoS_2 NDs as raw materials for intercalation and finely tuning the experimental conditions, such as reaction time and reaction temperature. In addition, a large portion of edges of MoS_2 NDs with high fraction of 1T phase are potentially promising for improving the performance in electrocatalysis and electrochemical supercapacitors.

7.2.3 Preparation of new structured layered nanodots

Currently, the family of layered materials is growing, and a number of new atomic nanosheets, such as phosphorene,^[10, 11] silicene,^[12] germanene,^[13] borophene,^[14] MXene^[15] and organic-inorganic hybrid perovskites,^[16] have been prepared for a wide range of applications. These layered materials provide us plenty of sources for engineering their structures and functionalities. However, most of the research works focus on the exfoliation of new 2D layered nanosheets, while the other structural types (e.g., nanodots, nanowire, nanotube, etc.) are rarely investigated. Therefore, synthesis of new nanostructured layered materials, especially the small size NDs, following the pace of 2D nanosheets hold great promise for continually enriching the family of layered. Our works presented in chapter 5 and chapter 6 can serve as valuable reference for the study.

Moreover, with the advancement of synthetic methods and characterization protocols, the investigation on an individual ND has been realized. For example, Cheon and coworkers prepared high-quality single-layer WSe₂ NDs in solution and studied the optical spectra and polarization anisotropy properties of an individual ND.^[17] This study provides a good example for precisely testing the optical property of a single ND, especially meaningful for systemically studying the size effect of small size NDs. Therefore, continually fabrication of novel layered NDs is valuable for exploration of the structure-property relationship of new layered NDs and promising for practical applications.

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