Synthesis, characterization and applications of two dimensional nanosheets

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NANYANG
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**SYNTHESIS, CHARACTERIZATION AND
APPLICATIONS OF TWO DIMENSIONAL
NANOSHEETS**

ZENG ZHIYUAN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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2012

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ABSTRACT

Graphene has recently sparked great research interest in other type of two dimensional (2D) nanomaterials, such as metal dichalcogenides, which exhibit unique properties that correlate with their size and dimension. However, high-yield production of these single-layer materials from their layered precursors has not been realized with facile and reliable procedures. In the light of this, my aim is to find a new and effective way for high-yield preparation of 2D semiconducting nanosheets and explore their potential application.

First, I developed a controllable approach to fabrication of single-layer 2D inorganic nanomaterials, for example, MoS₂, WS₂, TaS₂, TiS₂, ZrS₂ and graphene, through an electrochemical lithiation process followed by ultrasonication and exfoliation. The Li insertion is precisely controlled in the battery testing platform, and the galvanostatic discharge can be stopped at an appropriate Li amount to prevent decomposition of the lithiated compounds. Particularly, the production of single-layer MoS₂ sheets is accomplished with a yield of as high as 92%. The physical and chemical properties of the prepared 2D nanosheets were investigated by XRD, TEM, SEM, AFM, XPS, EDX, Raman, UV and so on. Single-layer MoS₂ has a bandgap of 1.8 eV. The field-effect behavior indicates the p-type doping effect of the single-layer MoS₂ prepared by our method. As a proof-of-concept application, a single-layer MoS₂ based film transistor is fabricated, which is successfully used for sensing of NO with the detection limit of 190 ppt. Our method open a new way for the preparation of 2D nanomaterials with solution-based processability for device applications.

Second, through a systematic examination of nanomaterials obtained at different cut-off voltages, we have successfully optimized the electrochemical lithiation conditions and extended this controllable lithiation process into BN, metal selenides and metal tellurides such as NbSe₂, WSe₂, Sb₂Se₃ and Bi₂Te₃. More importantly, we have employed two approaches to improve the quality of the products, i.e., the use of a low discharge current to prevent the high-current induced structure degradation, and the deoxygenation of lithiated compound solutions to alleviate the surface oxidation of the nanosheets during sonication. As a proof-of-concept, the thermoelectric properties of the film sample of NbSe₂ nanosheets were tested, which exhibited both the enhanced Seebeck coefficient and electrical conductivity with the p-type semiconducting behavior as compared to the bulk material.

Third, two-dimensional materials have great potential in next-generation nanoelectronic devices. As for its application in field-effect transistors (FETs), the use of graphene is restricted because its band gap is zero and it shows semi-metallic property. To open up the band gap of graphene with increased driving current, we prepared large-area graphene nanomesh (GNM) by utilizing anodic aluminum oxide (AAO) as the etching mask, combined with O₂ plasma treatment. Through varying the pore size and cell wall thickness of AAO mask, GNM with different neck widths were prepared. Based on field-effect transistor behavior, GNMs exhibited the enhanced p-type semiconducting properties.

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CHAPTER 1 INTRODUCTION

1.1 Background

Inorganic layered compounds (ILC), such as graphene, MoS₂, TiS₂, WS₂, TaS₂, ZrS₂ and BN, have been intensively investigated in the area of catalytic materials [1], energy devices [2], electronic devices [3], and so on. Single-layer or few-layer nanomaterials of these layered compounds can be prepared utilizing the mechanical exfoliation method with adhesive tapes [4]. But, this technique is restricted to small-amount fabrication with low reproducibility. In this respect, the solution-phased exfoliation method and the growth of single-layer or multi-layer two dimensional materials are developed [2,5-7].

Direct sonication of the layered compounds in general solvents, for example, dimethylformamide (DMF), N-methylpyrrolidone (NMP), were used to synthesis large amount of graphene [8] and multilayer BN nanosheets [9] and a large number of layered materials containing WS₂, MoS₂, MoTe₂, MoSe₂, NbSe₂, TaSe₂, NiTe₂, Bi₂Te₃ and h-BN [10]. It was demonstrated that the ability to prepare large quantities of the exfoliated 2D flakes in common solvents allows for subsequent preparation of functional composite materials with promising properties. But, the direct sonication method, which mainly depends on the solvent to reduce the exfoliation energy, is difficult in scaling up the synthesis of single-layer nanosheets.

In addition, graphite, transition metal dichalcogenides and BN can be inserted making use of all kinds of intercalating agents, for example, alkali metals, organic molecules and metal halides [11]. Sonication of the lithiated materials will generate single-layer or multilayer 2D nanomaterials [2]. But, apart from graphene,

the mass production of high production, single-layer nanomaterials of these materials are not well exploited by using a facile and reliable method. Li intercalation procedure has been applied in the past, but it has only been used to prepare MoS₂ [12,13] and WS₂ [14,15] materials. To date, no one has reported the single-layer preparation of TaS₂, TiS₂ or ZrS₂ nanosheets by using Li intercalation method.

For the application of inorganic 2D nanosheets, the most popular member is graphene, which is a one-atom-thick planar sheet, is widely studied due to their comprehensive applications in electronics [16,17], synthesis of nanocomposites, chemical and biological sensors, solar cells, electric and optical devices. But it can not be used as field-effect transistors (FETs) owing to its semimetal properties with a zero bandgap [18,19]. Although several methods for production of a graphene nanomesh (GNM) have been reported previously, all these literatures depended on the process of reactive ion etching (RIE) utilizing toxic gases, e.g. CF₄ and CHF₃, to eliminate SiO₂ [20,21]. The problem is that CF₄ and CHF₃ will etch Si/SiO₂ wafer and produce cavities on the dielectric layer of SiO₂, which affect the modulation in the field effect transistors (FETs) [20]. Duan and coworkers [21] used HF to remove the oxide (SiO_x) mask, and Sinitskii and Tour [20] used HF to remove SiO₂ mask and Au mask. However, HF will at the same time corrode the Si/SiO₂ wafer below the single-layer of graphene. Recently, Liang et al [22] developed a method by using imprint template, which was prepared utilizing a self-assembled diblock copolymer mask to etch the pattern into a SiO₂ template blank. Such template preparation process is quite complicated and has the problem of the reproducibility issue. In the light of this, develop new method to open the band gap of graphene is demanded.

1.2 Literature Review

1.2.1 Introduction to two-dimensional (2D) nanomaterials

Two dimensional (2D) inorganic materials have been receiving great interest recently, because of their particular physical properties due to the quantum size effect which is related with their nanosized thickness [23-25]. For example, graphene, a two dimensional single-layer of carbon atoms in the hexagonal structure, has shown excellent electronic, thermal, mechanical and optical properties [4,26,27]. Inorganic 2D materials analogous to graphene, such as MoS₂, WS₂, TaS₂, TiS₂, ZrS₂, NbSe₂ and BN, are widely investigated and utilized in catalyst [1], energy [2], electronic devices [3], light-emitting diodes [28], magnetic flux [29] and so on.

Transition metals with oxidation state + 4 [Group IVB, VB and VIB metals] form dichalcogenides of the layered structure. Their crystal structure can be described as two layer of closely packed hexagonal sheets of chalcogenide atoms sandwiched with one layer of metal atoms (Figure 1-1) [30]. For the close packing case, the stacking principle of the chalcogenide atoms is 'an atom is placed over the centre of the triangle formed by the atoms of the adjacent layer'. While for the adjacent chalcogen sheets with no metal atoms in between are bond to each other by the van der Waals forces. In this arrangement, both octahedral and tetrahedral vacant sites in the ratio of 1 : 2 are exist in the interlayer space for the neighbouring triatomic X-T-X ··· X-T-X layers. Quantum-chemical calculations [31] reveals that a d² metal atom electron configuration (the Group VIB metals, Mo and W) prefer the trigonal prismatic coordination, while a d⁰ metal atom configuration (Group IVB metals, Ti and Zr) like the octahedral coordination. In the case of Group VB metals (Nb and Ta) with d¹ electron configuration, both coordination

surroundings are energetically close to each other. As a result, both trigonal prismatic and octahedral coordinations are present in real crystal structures. Besides the type of coordination polyhedron (octahedron or trigonal prism), the motives of the X-T-X layer stacking, the relative positions of the metal cations in the adjacent layers with respect to each other in the structures of metal dichalcogenides can also determine the syngony and the space group of the crystalline compound.

Figure 1-1. The main type of crystal structures of transition metal dichalcogenides: (A) 1T, (B) 2H [30].

The electronic structures of layered dichalcogenides TX_2 are decided by the nature of the metal T. The TX_2 valence band structure consists of two sub-bands, where the lower sub-band is formed by ns- and the upper sub- band by np-states of the chalcogen atom (Figure 1-2). The lower free energy state of the conduction band is composed of d-orbitals of the transition metal. A crystal field of the chalcogen causes the splitting of d-orbitals of the transition metal T, thus, the d_{z^2} -orbital shows the lowest in energy and forms a separate sub-band. As a result, for Group IVB metal chalcogenides (d^0 configuration), the d_{z^2} orbital is located in the conduction band, but for Group VB metal chalcogenides (d^1 configuration) this

orbital shows half-filled, and for Group VIB metal dichalcogenides (d^2 configuration), this orbital is fully occupied and locates in the valence band [32].

Figure 1-2. Band structures for dichalcogenides of Group IVB (A), VB (B, C) and VIB (D) transition metals with octahedral (A, B) and trigonal prismatic (C, D) coordination of the central atom [30].

1.2.2 Liquid exfoliation methods to prepare layered dispersions of inorganic layered compounds

The common characteristics of ILC is that they are layered structures, in each layer the atoms are connected with covalent bonding, between the layers is van der Waals force. Consequently, single-layer or multilayer nanosheets of these layered compounds were synthesized making use of the mechanical exfoliation method with adhesive tapes [4]. However, this method is restricted to small-amount preparation with low reproducibility, giving disadvantage in fabrication of single-layer nanosheet based electronic devices. Another effective way, this way relate to plasma etching and un-zipping of nanotubes, is engaged to prepare single-layer graphene [33] and BN [34] nanomaterials. But, this method can not be used for large-amount solution-phased process. In this respect, the solution-phased

preparation and the growth of single-layer or multilayer 2D layered compounds is well performed [2,5-7].

Direct sonication of the layered compounds in commonly used solvents, for example, DMF, NMP have been widely utilized to dispersion graphene (Figure 1-3) [8] and multilayer BN sheets [9]. Recently, this technique was applied to synthesis single layer and multilayer nanomaterials from a number of layered inorganic materials such as MoS₂, WS₂, MoSe₂, NbSe₂, TaSe₂, NiTe₂, MoTe₂, h-BN and Bi₂Te₃ (Figure 1-4A-B) [10]. Nevertheless, the direct sonication technique, which mainly depends on the solvent to reduce the energy for exfoliation, is difficult in large amount preparation of single-layer nanosheets. After that, Smith et al shows that a number of layered crystals can be exfoliated in H₂O with sodium cholate as a stabilizing agent by surfactant coating (Figure 1-4C-D) [35]. Recently, Zhou et al demonstrated a mix solvent strategy to prepare highly stable ILC, by tune the volume ratio of water/ethanol, high quality dispersion can be obtained (Figure 1-4E-F) [36]. BN nanosheets can be obtained from direct sonication of h-BN crystals in different solutions, such as N,N-dimethylformamide (DMF) solution [9], the mixed solution of ethanol/water [36], the mixed solution of 1,2-dichloroethane and poly(phenylenevinylene) polymer [37] or the solution of Lewis bases such as octadecylamine (OD) [38], which takes the advantage of the strong affinity of BN layers with these organic molecules.

Figure 1-3. (A) SEM image of pristine, sieved graphite (the scale bar represent 500 nm). (B) The TEM images of single layer graphene prepared from NMP (C) The TEM images of a graphene sheet with edge folded and few-layer graphene, prepared from the solvent of NMP (the scale bars represent 500 nm). (D) Statistics of the number of sheets as a function of the number of single-layers per sheet for the dispersions using NMP as solvent [8].

Figure 1-4. Two dimensional nanosheets produced by liquid exfoliation (A-B) in a number of common solvent, such as NMP, IPA and so on [10]. (C-D) In water with sodium cholate as a stabilizing agent by surface coating [35]. (E-F) In mixed solvent by tune the volume ratio of water/ethanol [36].

1.2.3 Intercalation methods to prepare single or few layer dispersions of inorganic layered compounds

Transition metal dichalcogenides can be intercalated making use of numerous kinds of intercalating agents, but still face challenges. The exfoliation of transition metal dichalcogenide (TX_2) intercalation compound into highly dispersed X-T-X single layer dispersion system, was first reported for TaS_2 . With tantalum disulfide as a cathode, the H_xTaS_2 phase was formed by electrolysis in a sulfuric acid solution [39]. Opalescent dark-brown solutions of TaS_2 and NbS_2 were formed by hydration of the compound with a large excess of water [40]. With N-methylformamide as solvent, a dark-blue colloid solution was also observed upon solvation of the intercalation compound Na_xTiS_2 [41]. The solutions remained stable in an inert atmosphere for a long time with single-layer dispersion negative charged, which was confirmed by their movement to the positive electrode in the electrophoresis [41].

Another effective method to get exfoliated dispersion is ultrasound promoted hydration of TX_2 -lithium intercalation compounds. Frindt et al [12] pioneered the preparation of single-layer dispersions with n-butyl lithium dissolved in hexane as the intercalation agent to intercalate lithium atoms in the layered compounds, and then exfoliate them in DI water with sonication. The electrons from the lithium (guest) are transferred to the lowest-lying unoccupied energy levels of the MoS_2 (host), which are principally transition metal d bands (Figure 1-5) [42]. Similar protocol was later used to prepare dispersions from lithium intercalated compounds of WS_2 [14,15], TiS_2 [43], TaS_2 [44], NbSe_2 [45] and MoSe_2 [46].

Figure 1-5. Schematic representation of intercalation of lithium into MoS₂ [42].

Various methods were used to characterize MoS₂ single layers dispersion [47-49]. X-ray diffraction shows the absence of the reflections corresponding to translational periodicity along the *c* axis and the broadening and asymmetry of *hk*0 lines. These two features were found to be characteristic of the single layer dispersion. Based on analysis of X-ray diffraction pattern, it is concluded MoS₂ and WS₂ single layer dispersions have octahedral coordination, which are different from the trigonal prismatic coordination as stated in the initial TX₂ [50]. Figure 1-6A-D shows the TEM micrograph of Li intercalated MoS₂ in *n*-butyl-lithium [51]. The thickness of the sheet is 1.3 ± 0.3 nm (Figure 1-6E) [13].

Figure 1-6. Intercalated sample stayed for exactly 27 days in 1.6M *n*-butyllithium. (A) Selected area electron diffraction pattern. (B) The sample is fully cracked. (C) The new single crystalline phase is coexisted with the polycrystalline 2H-MoS₂. (D) Diffraction pattern after heating at 220 °C in situ. The disappearance of the

diffraction spots of superlattice is not reversible. The splitting of the diffraction spots still existed after cooling. The diffraction spots of superlattice also vanish when the specimen is exposed to the environment for long time [51]. (E) Large-area AFM image with MoS₂ single-layer platelets deposited on a mica substrate [13].

Furthermore, additional $hk0$ lines attribute to a super-structure in the TX₂ layers have been found in the diffraction patterns of these dispersions [46-48]. The energy band structure of the (MoS₂)^{x-} layers in single-layer dispersions is rearranged, as indicated by optical absorption spectra, where no absorption maximum corresponding to a transition between valence and conduction band at 700 nm is present, which is typical in the initial matrix [48].

Negative charge present on the layers of disulfide TS₂ dispersed in aprotic media. Experimental data shows that the exfoliated dispersions are ionic systems which contain macroanions (TX₂)^{x-}, retaining partial negative charge, solvated lithium cations and hydroxide anions (Figure 1-7) [52].

Figure 1-7. Coordination of the intercalated alkali metal cation with water molecules arranged in one-layer (A) or bilayer (B) packing in compounds Li_x(H₂O)_yTX₂ [52].

The interaction between water and the initial ionic compound, for example, $\text{Li}^+(\text{MoS}_2)^-$, in which valence electrons are present on the molybdenum disulfide layers, should include two processes, i.e., hydration of lithium cations leading to exfoliation of the matrix layers,

and redox interactions between the negatively charged $(\text{MoS}_2)^{x-}$ layers and water molecules will cause the precipitation of MoS_2 .

As the number of electrons on the layers decreases, the redox interaction (2) will decrease, which results in retention of a partial negative charge on these layers for a long time. Thus, the aggregative stability of aqueous dispersion $[\text{Li}^+ + (\text{MoS}_2)^{x-} + (1-x)\text{OH}^-]_{\text{aq}}$ is prolonged. Another evidence for this conclusion is that crystalline MoS_2 precipitation accelerates on removing the layer negative charge under the action of acid or air for the single-layer dispersion [53]. In acid condition, the precipitating process goes rapidly, which results in immediate precipitation of neutral molybdenum disulfide at low pH values. While in the condition of air, the process occurs much more slowly, it includes initial precipitation of the layered compound $\text{Li}_{0.1}^+(\text{H}_2\text{O})_y(\text{MoS}_2)^{0.1-}$.

The composition of this dispersion shows directly the number of electrons remaining on the layers of the matrix at the moment of sedimentation. Therefore, the minimum negative charge needed to retain the stability of this dispersed system

in water is close to 1 e per 10 molybdenum atoms. The results of chemical analyses, which indicate a negative charge in the range 0.10-0.25 per Mo/W atom, are consistent with the results of the analysis of fresh Li^+ encapsulated samples [54]. We can assume that $(\text{MoS}_2)^{x-}$ single-layer in the freshly prepared dispersions are capable for reducing cations, whose redox potentials (E^0) exceed the reduction potential of H^+ , it can covalently bind the M^{2+} cations ($\text{M} = \text{Pb}, \text{Cd}, \text{Hg}, \text{Pd}$) [55].

Although, there has been no report on the formation of BN nanosheets using intercalation method, it has been shown the formation of possible BN based intercalation compounds. Examples include the $(\text{BN})_3\text{SO}_3\text{F}$ compound [56], the BN-metal halides compound [57], and the Li-BN compound [58]. Therefore, it is feasible to make use of the intercalated compounds of BN to prepare single or few-layer BN nanosheets. Exfoliated NbSe_2 can be prepared by direct sonication of the layered materials in organic solvents [10], in sodium cholate/water solution [35] or intercalant-assisted thermal cleavage method [59]. A partial listing of the known layered intercalation compounds is shown in Table 1-1 [11].

Table 1-1. Layered compounds found to intercalate [11].

Host	Guests
Graphite	Alkali metals, transition metal halides and sulfides, ICl , Cl_2 , Br_2 , HNO_3 , CrO_3 , AlCl_3Cl_2 , many others
Graphite oxide	Water, acetone, ethers, acetic acid, nitric acid, alcohols
Boron nitride	Seems to behave much like graphite
Transition metal dichalcogenides	Amides, amines, amine oxides, phosphines and their oxides, metals, salts

1.2.4 Fabrication of two-dimensional (2D) nanosheets devices and their applications

Two-dimensional materials possess great potential in next-generation electronics, the reason is, compared to one-dimensional nanomaterials, they are much easy to prepare complex structures for devices. Single-layer MoS₂ have a bandgap of 1.8 eV, the first literature shows the mobilities is 0.5-3 cm² V⁻¹ s⁻¹ range (Figure 1-8A) [60] are too low for real devices application. In the light of this, Ayari et al prepared MoS₂ nanopatches by mechanical peeling, with high field-effect mobility in tens of cm²/Vs and an on/off ratio high than 10⁵ [3] (Figure 1-8B).

Figure 1-8. (A) MoS₂ transistors was prepared by micromechanical cleavage, the activation gap is large than 0.6 eV [60]. (B) MoS₂ nanopatches obtained by mechanical peeling, with high field-effect mobility and an on/off ratio higher than 10⁵ [3].

Recently, Radisavijevic et al [61] use a hafnium oxide as the dielectric layer to show a room-temperature single-layer MoS₂ mobility of at least 200 cm² V⁻¹ s⁻¹, which is comparable with graphene nanoribbons, the on/off ratio of current is 1×10⁸ (Figure 1-9). The reason is, single-layer MoS₂ is direct bandgap semiconductor [60,62], it can be used for interband tunnel field effect transistors (FETs), the power consumption is lower than classical transistors. Moreover,

single-layer MoS_2 is a thin transparent semiconductors, can be used in optoelectronics and energy harvesting.

Figure 1-9. (A-C) Preparation process of single-layer MoS_2 transistor. (D-E) The gate control of single-layer MoS_2 transistor [61].

For the layered metal chalcogenides, after exfoliation and subsequent restacking, the thermal conductivity decreases. The stacking of two-dimensional nanosheets in random way prevent thermal conduction pathways along the vertical direction, which cause the reduction of thermal conductivity. Thermopower measurements on restacked MoS_2 and WS_2 , indicate that they are p-type conductors (Figure 1-10A-B) [54]. Kim et al also investigated the p-type conducting behavior of WS_2 and WSe_2 after exfoliation and restacking, the electrical conductivity decreased because of the variation in carrier concentration. The compound MoSe_2 shows metallic conducting properties with a small Seebeck coefficient, which comes from the metastable structure of the 1T- MoSe_2 phase, as shown in Figure 1-10C-D [63].

Figure 1-10. (A) Thermopower measurements of restacked MoS_2 (triangles) and WS_2 (circles). (B) Schematic band diagram illustrating the distortion of an ideal octahedral system to form zigzag chains [54]. (C) Seebeck coefficient for (a) WS_2 , (b) WSe_2 , (c) MoSe_2 . Open symbols represent the pristine, and solid symbols indicate the exfoliated, then restacked materials. (D) Electrical conductivity for (a) WS_2 , (b) WSe_2 , (c) MoSe_2 . Open symbols represent the pristine, and solid symbols indicate exfoliated, then restacked materials [63].

Besides the application of 2D transition metal dichalcogenides, graphene, a one-atom-thick planar sheet, has tremendous application in electronics [16,17,64,65]. But, graphene can not be used in field-effect transistors (FETs) due to its semi-metallic property with a zero band gap [18,19]. Processing graphene sheets in the shape of nanoribbons has led to the band gap opening with the ON/OFF ratio of current increased a lot to fit the demand for transistor operation [66-70]. For example, GNRs was prepared by unzipping multiwalled carbon nanotubes by plasma etching of nanotubes partly embedded in a polymer film

(Figure 1-11A). However, individual nanoribbons for FET devices showed the low conductance [69]. To enhance the conductance for real applications, the preparation of high density nanoribbons is necessary, which is accomplished by the e-beam lithography (EBL) [71,72]. But the problem is that nanoribbon exhibit low driving currents and conductances. On the other hand, practical devices need ordered nanoribbons with high density, this is still a great challenge. To over the problems emerged, Bai et al [21] prepared GNM for the first time with neck width down to 5 nm, the preparation method is block copolymer lithography. Utilizing such prepared nanomesh as a conductive channel, they have showed the transistor with driving current almost 100 times larger than the individual graphene nanoribbon, but the on-off ratio is similar (Figure 1-11B).

Figure 1-11. (A) Making graphene nanoribbons (GNRs) from CNTs [69]. (B) Schematic of fabrication of a GNM using block copolymer lithography [21].

However, this technique use complicated processing procedures, such as electron beam evaporation, UV irradiation, CHF₃-based reactive ion etch and O₂ plasma treatment. After that, Liang et al [22] fabricated GNM by combining nanoimprint lithography, block-copolymer self assembly for high-resolution nanoimprint template patterning (Figure 1-12A), the ribbon width of the prepared GNM is down to less than 10 nm, the prepared GNM based FETs exhibit quite

different electronic characteristics in comparison with unpatterned graphene FETs. But the preparation process of hexagonal imprint template is difficult using different kinds of polymers such as poly(styrene-block-methyl methacrylate) (P(S-b-MMA)), P(S-r-MMA) random copolymer, also they do two step anneal processes, eg. 165 °C for 48 h, 185 °C for 24 h, use these treated polymers for etching template to get SiO₂ pillar structure [73,74]. The fabrication process is tedious due to these multi-processing steps. Later, Sinitskii prepared porous metal film by using nanosphere lithography and then utilized this film as an etch mask to prepare GNM (Figure 1-12B) [20]. But, these literatures depended on the reactive ion etching by utilizing gases with toxic property, e.g. CF₄ and CHF₃, to remove SiO₂ layer. Because CF₄ and CHF₃ can also corrode Si/SiO₂ wafer and produce cavities [20] on the SiO₂ dielectric layer, it is likely to effect the gate modulation and may lead to leakage of current in the FETs. Furthermore, these methods use HF to remove SiO₂ mask [20,21], could also corrode the substrate of Si/SiO₂ below the deposited graphene. Recently, Akhavan fabricated GNM by using photodegradation method assisted with UV, this method utilize ZnO nanorods as the photo-corrosive catalyst, the ZnO tips of the nanorods were contacted with the sheet like graphene oxide (GO) to realize the degradation of GO [75]. In this literature, the size of pore in GNM is ~200 nm, however, the hole density is low, the adjacent hole's distance is large, as a result, the band gap of GNM is not opened up for FET application.

Figure 1-12. (A) Schematic diagram of GNM prepared using nanoimprint lithography combined with block copolymer self-assembly [22]. (B) Fabrication of periodic graphene nanostructures via patterning graphene through the self-assembled single-layers of monodisperse colloidal microspheres [20].

CHAPTER 2 AIMS AND MOTIVATION

2.1 Objectives and Scope

Due to the importance of two dimensional (2D) nanomaterials and the limitations of current preparation methods, this project aims to develop a general method to prepare large amount single-layer 2D nanosheets. Fabricate 2D nanomaterials devices for electronic applications.

In order to achieve the objectives mentioned above, the following works are carried out in this project: First, the layered bulk compounds, for example, MoS_2 , WS_2 , TaS_2 , TiS_2 , ZrS_2 and graphite, are coated on copper foil as cathode. The anode is lithium foil. The intercalation of lithium ions is conducted at a constant discharge current in a battery testing system. The lithiated material is sonicated in DI water or pure ethanol, then exfoliated 2D nanomaterial dispersions are obtained.

Second, prepare few-layer BN, NbSe_2 , WSe_2 , Sb_2Se_3 and Bi_2Te_3 nanosheets from their layered bulk precursors by using the electrochemical lithiation process. The lithiation conditions, have been systematically studied and optimized, so that the high-quality BN and NbSe_2 nanosheets can be obtained, evidenced by SEM, TEM and AFM.

Third, develop an effective approach to fabrication ordered, large-area GNM, which utilizing AAO membrane as an etch mask to do O_2 plasma etching. GNM with narrow neck width and regular pore size is fabricated, which exhibits enhanced semiconducting properties.

2.2 Hypothesis

Based on works proposed above, the following hypotheses have been made.

The previous lithiation process, which uses n-butyl lithium dissolved in hexane as intercalate, needs to be carried out at high temperature (for example, 100 °C), for long time (for example, 3 days) and lacks the controllability on the amount of Li intercalation. Insufficient lithium insertion will result in low yield of single-layer production; whereas the over lithium insertion can lead to the decomposition and formation of metal nanoparticles accompanied with Li_2S . Hence, an electrochemical lithium intercalation technique can be realized at 25°C with less than 6 hours. By utilizing the layered compounds as cathode in a simulated cell, the lithium insertion can be exactly controlled in the galvanostatic discharge.

In order to get high quality 2D nanosheets, the control experiments can be conducted to systematically examine the morphology and quality of nanomaterials obtained at different cut-off voltages. The electrochemical lithiation condition can be optimized for preparation of few-layer BN, NbSe_2 , WSe_2 , Sb_2Se_3 and Bi_2Te_3 nanosheets. Two approaches are employed to improve the quality of the products, i.e., the use of a low discharge current, which can prevent the high-current-induced structure degradation, and the deoxygenation of lithiated compound solutions, this approach will alleviate the surface oxidation of the nanosheets during sonication.

Previous methods for production of a GNM depended on the reactive ion etching (RIE) by utilizing toxic gases, e.g. CF_4 and CHF_3 , to remove SiO_2 . The draw back of this method is that CF_4 and CHF_3 will also corrode the Si/ SiO_2 wafer and produce cavities on SiO_2 dielectric layer, which influence the back gate modulation and may lead to leakage of current in the field effect transistors (FETs).

This method only use plasma etching process with O_2 as reactive gas to produce GNM, which would not affect the dielectric layer of SiO_2 for the Si/ SiO_2 substrate, also the preparation process is simpler than previous methods.

CHAPTER 3 EXPERIMENTAL DETAILS

3.1 Chemicals and Materials

Molybdenum disulfide (MoS_2) (10-30um, Rose Mill, West Hartford, USA), titanium (IV) sulfide (TiS_2 , Sigma, Steinheim, Germany), tungsten (IV) disulfide (WS_2 , Sigma, Steinheim, Germany), zirconium (IV) sulfide (ZrS_2 , Strem, Massachusetts, USA), tantalum (IV) sulfide (TaS_2 , Alfa Aesar, Massachusetts, USA), natural graphite (Bay carbon Inc, Michigan, USA), Boron nitride (BN, Sigma, Steinheim, Germany), niobium selenide (NbSe_2 , Alfa Aesar, Massachusetts, USA), Tungsten (IV) selenide (WSe_2 , Alfa Aesar, Massachusetts, USA), Antimony triselenide (Sb_2Se_3 , Sigma, Steinheim, Germany) bismuth telluride (Bi_2Te_3 , Sigma, Steinheim, Germany), *N*-methylpyrrolidone (Sigma, Steinheim, Germany), poly (vinylidene fluoride) (PVDF, Sigma, Steinheim, Germany), 98% H_2SO_4 , 30% H_2O_2 , 70% HClO_4 , oxalic acid, 95% H_3PO_4 , mercuric chloride (HgCl_2), chromic (III) oxides, Anisole, poly(methyl methacrylate) (PMMA), aluminum foil (0.25 mm thick, 99.999% metals basis), potassium permanganate (KMnO_4) were purchased from Sigma-Aldrich (Milwaukee, WI) and used as received. Lithium foil (ACME Research Support Pte Ltd, Bukit Batok Street, Singapore), lithium ion battery electrolyte (Charslton Technologies Pte Ltd., International Business Park, Singapore), copper foil (ACME Research Support Pte Ltd, Bukit Batok Street, Singapore), Polypropylene (pp) film (Celgard 2300, North Carolina, USA), Silicon oxide wafers were bought from Bonda Technology, Singapore. Ethanol (>99.9%, Merck, Darmstadt, Germany), acetone (Tech Grade, Aik Moh Paints & Chemicals Pte Ltd, Singapore) were used as received. The deionized (DI) water was purified using Milli-Q System (Millipore, Billerica, MA).

3.2 Synthesis, characterization and application of single-layer transition metal disulfides and graphene nanosheets

3.2.1 Preparation of transition metal disulfides and graphite test cells for intercalation

The Li insertion in layered compounds was conducted in simulated cells, the anode is Li foil, 1 M LiPF₆ in the mixture of ethyl carbonate (EC) and dimethyl carbonate (DMC) (volume ratio 1 : 1) is used as electrolyte. The layered compound (for example, MoS₂, TiS₂, WS₂, ZrS₂, TaS₂ and graphite) was prepared as cathode with PVDF and acetylene black as binder and conductive agent, respectively. All of which were dissolved in NMP. For the mixed slurry, the weight ratio of the layered compound, PVDF and acetylene black was 8:1:1. The obtained slurry was coated on a Cu foil and dried at 100 °C for 12 hours. The installation of the battery for various layered compounds was carried out in an Ar filled glove box.

3.2.2 Electrochemical intercalation in transition metal disulfides and graphite

The electrochemical insertion of the layered compounds in the home made simulated cell was realized in a Neware battery machine at 25°C. The lithium insertion was accomplished utilizing the constant current discharge at 0.05 mA. After finishing the lithiation process, the lithiated samples were cleaned with acetone, followed by sonication in DI water. During this period, a large amount of gas was emerged and an opaque dispersion was obtained. The dispersion was rinsed several times using DI water, the obtained solid product was used for further characterizations.

3.2.3 Application of single-layer MoS₂ as field effect transistor (FETs)

0.1 mg/mL MoS₂ nanosheets dispersion was drop-cast onto the Si/SiO₂ (300 nm) wafer with O₂ plasma pretreated, after that, the substrate with sample sheets on it was annealing at 450 °C in Ar for 2 h. A Ti (10 nm)/Au (50 nm) pad were thermal evaporated on substrate using e-beam lithography (EBL), they were connected to two ends of a single-layer MoS₂ nanosheet. The current-voltage (*I-V*) curve for the single-layer device was recorded at vacuum level of $\sim 10^{-5}$ Torr, the doping influence caused by air can be avoid in this condition.

3.2.4 Application of MoS₂ nanosheets thin film transistors (TFTs) as NO sensor

The MoS₂ dispersion with water as solvent was centrifuged and then dispersed again in the solvent methanol with sonication. The methanol dispersion of MoS₂ nanosheet was spin-coated on a cleaned Si/SiO₂ wafer with speed of 4000 rpm. The film thickness of MoS₂ nanosheets was exactly dominated by the amount of MoS₂ dispersion. Then, the obtained MoS₂ nanosheets film was dried in vacuum condition at 25°C for 2 h and it was utilized for preparation of TFT. Au electrodes with thickness of 50 nm were thermal evaporated as drain electrode and source electrode. The length of the MoS₂ channel was 5 mm with the width 400 μ m. The gas detection was accomplished using NO gas with continuous flow (with certain density in N₂ gas) to the surface of MoS₂, at the same time, the current from drain to source was monitored. The desorption of NO was accomplished by changing NO gas to pure N₂ gas. The density of NO gas was exactly adjusted by the ratio of NO gas (5 ppm) and N₂ gas flowed. All tests were carried out at 25°C in air condition.

3.3 Synthesis, characterization and application of few-layer BN, metal selenides and metal tellurides nanosheets

3.3.1 Preparation of BN, metal selenides and metal tellurides test cells for intercalation

The Li insertion of the layered material was carried out in a simulated cell with the Li foil as anode and 1 M LiPF₆ dissolved in the mixture of ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume ratio) as electrolyte. The layered bulk material (i.e. BN, NbSe₂, WSe₂, Sb₂Se₃ and Bi₂Te₃) was prepared as cathode by mixing with PVDF and acetylene black, all of which were dispersed in N-methylpyrrolidone (NMP) solvent. The weight ratio of the layered compound, PVDF and acetylene black in the mixed slurry was 8:1:1. The prepared slurry was then deposited on Cu foil and then dried at 100 °C in vacuum condition overnight. The simulated cells for various kinds of layered compounds were assembled in an Ar-filled glove box.

3.3.2 Electrochemical intercalation in BN, metal selenides and metal tellurides

The electrochemical intercalation (galvanostatic discharge) of the layered compounds in the simulated cells was conducted in a Neware battery machine with a constant current of 0.025 mA. Finishing the lithiation, the lithiated sample was cleaned with acetone, finally, it was sonicated in N₂-saturated Milli-Q water in a closed vial. During the experiment, a large quantity of gas was emerged and a dispersion of the layered compounds was formed. The dispersion was rinsed several times with DI water, the solid product was obtained.

3.3.3 Preparation of NbSe₂ thin films for thermoelectric devices

After a glass slide was cleaned with ethanol, NbSe₂ nanosheets dispersed in ethanol was sprayed onto the glass substrate which was pre-heated at 80 °C. The thickness of NbSe₂ nanosheet film was 0.5 - 0.6 μm, measured by the Alpha-Step IQ surface profiler. The resistivity and Seebeck coefficient were measured from 50 to 225 °C using a commercially available ZEM 3 Seebeck meter under the helium environment. The reference sample of bulk NbSe₂ was prepared by the following experiments. First, the commercial NbSe₂ powders (Sigma Aldrich) was pressed under 10 MPa pressure to form a 15 mm-diameter pellet. Then the pellet was cut to several small rectangular bars with dimensions of 14 × 2 × 2 mm³, which were used as reference samples.

3.4 Fabrication of graphene nanomesh (GNM) devices

3.4.1 Preparation of anodic aluminum oxide (AAO) membrane

AAO membrane was prepared via the electrochemical method [76,77]. First, with HClO₄ (60 wt%) mixed with pure ethanol (> 99.9 wt%) (volume ratio is 1:4) as electrolyte, an Al foil was electro-polished at the voltage of 20 V, the reaction temperature is 0 °C. After that, with Al foil, Pt mesh as the working, counter electrode, respectively [76,77], the first anodizing process lasted about three hours with the voltage is 40 V and the temperature is 0 °C. After first anodization, the Al foil was put into water dissolved with chromic acid (1.8 wt %) and phosphoric acid (6 wt%) overnight. The reaction temperature is 75 °C and the alumina generated in first anodization was removed. The second anodization was carried out for about 20 min, while the other parameters are the same as the first anodization step. Then, the anodized surface layer (or AAO) was detached by immersing the Al foil in

saturated HgCl_2 solution for 3 hours. Finally, in order to obtain the enlarged and uniform pore size, the AAO template was put into 5 wt% phosphoric acid for 40 min. In this typical condition, the size of pore is 80 nm and the thickness of AAO cell wall is 20 nm for the fabricated AAO membrane.

3.4.2 Preparation and deposition of graphene oxide (GO) on Si/SiO₂ substrates

Graphene oxide (GO) was synthesized by a modified Hummers method with the microwave-expanded graphite as the source [78-81]. The prepared GO was re-dispersed again in a solvent mixed with methanol and water (v:v = 5:1). Freshly washed Si/SiO₂ substrate was used to deposit GO sheets by utilizing the LB method [82,83]. In brief, 8 -12 mL GO solution was dripped onto water surface. The dripping rate is 100 $\mu\text{L}/\text{min}$ in the machine of LB trough. On the surface of water, the GO film was compressed with pressure is 15 mN m^{-1} . After dipped into the solution vertically, the washed Si/SiO₂ wafer was pulled up, the speed is 1 mm/min, finally, the single-layer GO film on the surface of Si/SiO₂ wafer was formed [84]. In order to reduce the GO film into rGO film, the GO film deposited Si/SiO₂ was heated in the condition of hydrazine vapor at 60 °C for about 12 hours [85].

3.4.3 Fabrication of graphene nanomesh (GNM)

PMMA were dissolved in anisole to get clear solution. The spin coating of PMMA on the surface of Si/SiO₂ substrate was carried out at 4,000 rpm and it lasted 90 s. The concentrations of PMMA in anisole were 1 wt %, 0.5 wt % and 0.25 wt %, while the thicknesses of the prepared PMMA films were 45 nm, 15 nm and 8 nm, respectively. Based on experimental result, the best PMMA thickness is 8 nm. First, 8 nm-thick poly(methyl methacrylate) (PMMA) film was deposited on

the rGO film, As an etch mask, thin film AAO template was put on top of PMMA film. After that, another cleaned Si/SiO₂ substrate was placed on up side of AAO template. As a result, two Si/SiO₂ substrates sandwiched with rGO/PMMA/AAO multilayers was formed. And then, this multilayers was heated in the condition of vacuum with annealing temperature is 180 °C and time is 2 h, the purpose of this process is to make the AAO template adhere closely on the surface of rGO/PMMA. On removing the cover Si/SiO₂ wafer, the plasma etching using O₂ was implemented to produce nanoholes on the thin layer of PMMA and generate nanosized holes on the sheet like rGO. The plasma etching time using O₂ is changed in the range of 30 ~ 120 s. In the end, the remaining PMMA layer and AAO template were removed using acetone and 3M NaOH, respectively. The best plasma etching time is 40 s, at which condition the quality of the prepared GNM is the best.

3.4.4 Fabrication of graphene nanomesh (GNM)-based field-effect transistors (FETs)

FFT devices based on GNM were prepared on SiO₂ (300nm)/Si substrate. The Ti (10 nm)/Au (50 nm) pads were coated on SiO₂(300nm)/Si with the thermal evaporation, the exact location is defined by e-beam lithography. The current-voltage (*I-V*) plots for the prepared devices were tested at environment condition.

3.5 Characterizations

3.5.1 Transmission Electron Microscopy (TEM)

TEM was conducted at 200 keV with either a JEOL JEM-2010 or JEM 2100F instrument. TEM samples were prepared by placing a drop of the sample solution on a holey carbon film supported by copper grids and dried naturally. High

resolution TEM (HRTEM) images were simulated with the multislice method implemented in JEMS.

3.5.2 Field Emission Scanning Electron Microscopy (FE-SEM)

FE-SEM was performed with a JEOL JSM-6700 field-emission scanning electron microanalyzer. All samples were deposited on Si/SiO_x substrates, dried naturally, and imaged with the accelerating voltage of 5 keV.

3.5.3 Atomic Force Microscopy (AFM)

AFM images were characterized by a Dimension 3100 AFM (Veeco, CA, USA), NSCRIPTOR system with a Si tip (resonance frequency: 320 kHz; spring constant: 42 N/m) in the tapping mode. Images were acquired under ambient conditions with a scanning rate of 1 Hz and scanning line of 512.

3.5.4 X-Ray Diffraction (XRD)

Powder X-ray diffraction (Shimadzu, Japan) was used to identify the crystalline phases present in the samples. Most samples were prepared by dropping a concentrated sample solution on a glass slide prior to mounting in a sample holder. The XRD patterns were collected using CuK α radiation by step-scanning over the range of 30 ° to 80 ° in 0.05° intervals, at a dwell time of 1s.

3.5.5 X-Ray Photoelectron Spectroscopy (XPS)

XPS data were collected by Axis Ultra XPS system with AlK α source (1486.6 eV). The samples solutions were deposited on Si/SiO_x substrates and dried naturally. The analysis area was 300 × 700 μm^2 . High resolution spectra for N1s and Au4f were collected in their respective energy ranges. The C1s peak (284.5eV) was used as the reference for calibration.

3.5.6 Raman Spectroscopy

Raman spectra were collected on a WITec CRM200 confocal Raman microscopy system with an air cooling charge coupled device (CCD) as the detector (WITec Instruments Corp, Germany). The excitation line was 488 nm and the Raman band of a silicon wafer at 520 cm^{-1} was used for calibration.

3.5.7 Ultraviolet-Visible Spectroscopy (UV-vis)

UV-vis transmittance spectra were obtained on a UV-1800 spectrophotometer (Shimadzu, Asia Pacific Pte Ltd). The spectra of MoS_2 , WS_2 , TaS_2 , TiS_2 were collected by recording the UV-vis spectra.

3.5.8 Photoluminescence (PL) Measurement

PL measurement of MoS_2 nanosheet was conducted by a UV Nd:YAG laser with an excitation wavelength of 488 nm (LOT-Oriel GmbH & Co. KG, Darmstadt, Germany).

CHAPTER 4 RESULTS AND DISCUSSIONS

4.1 Single-layer transition metal disulfides and graphene nanosheets preparation, characterization and application

4.1.1 Introduction

Transition metal disulfides (for example, MoS_2 , TiS_2 , WS_2 , ZrS_2 and TaS_2) have been intensively investigated and developed in catalyst [1], energy [2], electronic device [3], and so on. Graphite, transition metal dichalcogenides can be inserted utilizing numerous kinds of intercalation agents, for example, alkali metals, organic molecules and transition metal halides. Ultrasonic vibration of the intercalated materials can generate single-layer and few-layer 2D nanomaterials [5]. But, except for graphene, the large amount preparation of high-quality, single-layer nanosheets of these materials is not well developed by using a simple method. For examples, the preparation of MoS_2 and WS_2 single-layer materials can be accomplished utilizing n-butyl lithium as the insertion agent to intercalate Li atoms into these compounds, the lithiated samples were exfoliated in water with sonication [5,12,86,87]. Nevertheless, except for the long intercalation time [5] and high intercalation temperature, there is another major disadvantage, that is we can not exactly control the degree of lithium inserted. Insufficient lithium intercalation will result in low yield of single-layer production; but the over lithium insertion can induce the decomposition and formation of Li_2S and metal nanoparticles [88]. In recent years, utilizing a sulfidation-induced shape conversion, 2D WS_2 nanomaterials were fabricated from one dimensional

nanorods of $W_{18}O_{49}$. However, the size of obtained WS_2 nanosheets was just ~ 100 nm, the size limitation was restricted by the rod dimension [2].

Here, we exploit a general method to prepare large amount single-layer 2D nanosheets, making use of a controllable lithium intercalation procedure. By utilizing the layered compounds, for example, MoS_2 , TiS_2 , WS_2 , ZrS_2 , TaS_2 and graphite, as the cathode in a simulated cell, the insertion of lithium in these compounds is exactly controlled. After sonication in water or ethanol, large amount single-layer nanosheets of these compounds can be prepared, which provides solution-based processability for device fabrications.

4.1.2 Synthesis of single-layer transition metal disulfides and graphene nanosheets

The lithium intercalation process was accomplished in a battery testing platform as shown in Fig. 4-1. As cathode, the layered compounds, *i.e.* MoS_2 , TiS_2 , WS_2 , ZrS_2 , TaS_2 or graphite, were assembled in a simulated cell (Step 1 in Fig. 4-1). To provide lithium ions, the anode was lithium foil. The lithiation process was realized using galvanostatic discharge at 0.05/0.025 mA. Finishing the lithiation (Step 2 in Fig. 4-1), the lithiated material was sonicated in DI water (pure ethanol) to get the 2D dispersions (Step 3 in Fig. 4-1).

Figure 4-1. Schematic illustration of the electrochemical lithiation process to produce 2D nanosheets from layered bulk compound.

Figure 4-2 shows the detailed electrochemical lithiation procedures to produce the 2D nanomaterials. First, the layered bulk compound is mixed with poly (vinylidene fluoride) (PVDF) and acetylene black, all of which were dispersed in N-methylpyrrolidone (NMP). The weight ratio of the layered compound, PVDF and acetylene black in the mixed slurry is 8:1:1. The prepared slurry is coated on a Cu foil and dried at vacuum at 100 °C for 12 h (Figure 4-2A). Then, the bulk material-coated Cu foil as cathode, lithium foil as anode and polypropylene (PP) film as separator are assembled into a lithium ion battery in an Ar-filled glove box, with 1M $LiPF_6$ in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (v:v = 1:1) as electrolyte (Figure 4-2B). The obtained battery cell is connected to a Neware battery machine at the condition of room temperature. The electrochemical Li-insertion is accomplished via the discharge process at constant current density of 0.05/0.025 mA (Figure 4-2C). By optimizing the cut-off voltage (or the discharge capacity), we can

control the amount of the intercalated Li ions between the layers of the bulk material, so that the Li-insertion process can stop at an appropriate Li amount to prevent the decomposition of the Li-intercalated compound. After the lithiation process, the battery cell is dismantled (Figure 4-2D), and the Li-intercalated material coated on the Cu foil is taken out, rinsed with acetone to clean sample, and naturally dried. Finally, the lithiated material on Cu foil is immersed in the Milli-Q water in a closed vial (Figure 4-2E), subsequently sonicated for 10 min. During the sonication, a large amount of gas can be obtained and a brown exfoliated dispersion formed (Figure 4-2F). During the whole experimental process, the lithium plays critical roles. First, Li^+ ions are inserted into the interlayer space of the layered bulk material, which expand the distance and weaken the van der Waals interaction between the neighboring layers of the compounds. Second, the inserted Li^+ ions are subsequently reduced to Li^0 by receiving electrons in the process of discharge. The metallic Li can react with DI water to generate LiOH and produce H_2 gas [12,89]. The generated H_2 gas pushes the layers of the compounds further apart. Under vigorous agitation by sonication, the well dispersed 2D nanosheets are thus obtained. The molecular weights and discharge capacities of different layered compounds are shown in Table 1. According to Table 1, I transformed the discharge capacity into lithium content for the galvanostatic discharge curve (x-axis), i.e., discharge voltage versus the content of lithium x, as in Li_xMN .

Figure 4-2. Schematic illustration for the detailed electrochemical lithiation procedures to produce 2D nanomaterials from layered bulk compound. (A) Coat layered materials on Cu foil using PVDF as a binder. (B) Assemble lithium ion batteries in glove box: Cu foil with samples materials as cathode, Lithium foil as anode, polypropylene (pp) film as separator, 1M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) as electrolyte (C) Connect to battery testing system, do galvanostatic discharge process until certain cut off voltage. (D) Disclose battery jar, take out spring, lithium foil, polypropylene (pp) film, and rinse lithiated layered bulk material with acetone and then dry it. (E) Immerse lithiated material on Cu foil in H_2O . (F) Immediately ultrasonic vibration of the lithiated sample for 10 min and take out Cu foil, and we get the homogeneous 2D layered dispersion.

Table 4-1. The molecular weights of different layered compounds, and the corresponding discharge capacities as lithium ion batteries with one lithium ion intercalated, i.e., LiMN.

Layered compound	Molecular weight (g mol ⁻¹)	Capacity(1 Li) = LiMN (mAh g ⁻¹)
MoS ₂	160	167.2
WS ₂	248	107.9
TiS ₂	112	238.9
TaS ₂	245	109.2
ZrS ₂	155	172.5
Graphite	12	2229.6
BN	25	1070.2
NbSe ₂	251	106.6

As shown in Figure 4-3A, the lithiation process is controlled by a discharge profile (the discharge voltage *vs.* the content of lithium *x*, as stated in Li_{*x*}MoS₂). The discharge voltage declines quickly in the voltage range of 1.8 ~ 1.2 V, which corresponding to the lithium content of 0 < *x* < 0.2, and at the lithium content *x* = ~0.2, a discharge plateau appears until the lithium content *x* = ~1.6, which indicate there is a phase transformation for the compound. As reported from previous literatures, the lithium intercalation of MoS₂ can result in two-phase transformation: from the coordination of trigonal prismatic (2H) to the coordination of octahedral (1T). At the lithium content *x* = 1.6, the transition from 2H to 1T is finished. In the process of phase transition, lithium atoms like to occupy in the tetrahedral and octahedral interstices for layered MoS₂, which enlarges the distance among the layers connected

with the van der Waals interaction. But, the over Li intercalation caused the decomposition for MoS₂ layers and generate Li₂S and Mo nanoparticles [90]. Actually, Mo particles were appeared on the sheets like structure of MoS₂, if the reaction was carried on till $x = 3$. Therefore, this exact control of discharge curve let us to cease the intercalation at an appropriate Li content, which can prevent the decomposition of lithiated compounds. The galvanostatic discharge curves for WS₂ is shown in Figure 4-3B, the cell voltage decreases smoothly from 2.0 to 0.96 V in the lithium content $0 < x < 0.5$; while at $x = \sim 0.5$ a discharge plateau appears which continues until $x = \sim 2.5$. The x value reaches 2.7 when the cell voltage has dropped to 0.9 V. Discharge curve for TiS₂ are shown in Figure 4-3C, the discharge voltage decreases smoothly from 2.5 to 1.8 V at lithium content $0 < x < 0.9$, at lithium content $x = \sim 0.9$ a discharge plateau appears which continues until $x = \sim 1.3$, From $x = \sim 1.3$ till $x = \sim 1.6$, the discharge voltage declines quickly in the range of 1.6 ~ 0.9 V, where we stopped the lithiation process. For TaS₂, The galvanostatic discharge curves is shown in Figure 4-3D, the discharge voltage declines smoothly from 1.9 to 1.6 V in the lithium content of $0 < x < 0.46$, and decrease rapidly to 1.2 V from $x = 0.46$ to $x = 0.62$, then a short plateau occurs and then decrease again until 0.9 V, the x value reaches 1.2. The lithium atoms resides in the interstices of the WS₂, TaS₂, TiS₂ layers and expand the gaps of the interlayers bound by the van der Waals interactions. Further increase in the Li content will lead to the decomposition and formation of WS₂, TiS₂ and TaS₂ nanoparticles.

Figure 4-3. Galvanostatic discharge curve for (A) MoS₂, (B) WS₂, (C) TiS₂, (D) TaS₂.

4.1.3 Characterization of single-layer MoS₂, TiS₂, WS₂, TaS₂ nanosheets

Figure 4-4A illustrates the TEM image of a single-layer MoS₂ nanosheet. The selected area electron diffraction (SAED) pattern (Figure 4-4B), also high resolution TEM (HRTEM) image of the MoS₂ nanosheet (Figure 4-4C) exhibit a hexagonal lattice structure, the lattice space is 2.7 Å, which is attributed to the (100) planes [14]. The folded edge of such an MoS₂ nanosheet gives its thickness of about 6.3 Å (Figure 4-4D), which matches with the theoretical value for the S-Mo-S building layers, *i.e.* 6.2 Å [49], indicating the single-layer MoS₂ sheets were successfully fabricated. The prepared WS₂ nanomaterials were also evaluated and the images are exhibited in Figure 4-4E-H. The WS₂ single-layer also exhibits the hexagonal lattice structure (Figure 4-4F), the lattice space is 2.7 Å, as measured in the HRTEM image (Figure 4-4G), which is consistent with that of the WS₂ (100) planes [5,91]. The folded edge of a

single-layer WS_2 nanosheet gives its thickness of $\sim 6.3 \text{ \AA}$ (Figure 4-4H), consistent with the thickness of S-W-S layer in bulk WS_2 [2,91].

Figure 4-4. (A) TEM image for a single-layer MoS_2 nanomaterial. Top right inset: Photograph of MoS_2 dispersion. (B) SAED pattern of single-layer MoS_2 nanomaterial. (C) HRTEM image for single-layer MoS_2 nanomaterial. (D) TEM image for the folded edge of single-layer MoS_2 nanosheet. (E) TEM image for a single-layer WS_2 nanomaterial. Top right inset: Photograph for WS_2 dispersion. (F) The SAED pattern of single-layer WS_2 nanomaterial. (G) HRTEM image for the single-layer WS_2 nanomaterial. (H) TEM image for the folded edge of single-layer WS_2 nanosheet.

TEM images of the prepared TiS_2 , TaS_2 single-layer nanomaterials are exhibited in Figure 4-5A-C and Figure 4-5D-F, respectively. The structure of TiS_2 , TaS_2

belongs to space group of $P\bar{3}1c$, this structure is different from the space group of $P6_3/mmc$, as shown in MoS_2 and WS_2 . This difference is proven by the SAED for TiS_2 nanosheet (Figure 4-5B) and TaS_2 nanosheet (Figure 4-5E), that is, the inner six spots for (100) planes are much weak than the out six spots for (110) planes, which is in contrast to the SAED of single-layer MoS_2 (Figure 4-4B) and WS_2 (Figure 4-4F). HRTEM shows the lattice spacing of TiS_2 is 1.7 Å for (110) planes (Figure 4-4C), and the lattice spacing of TaS_2 is 2.9 Å for (100) planes (Figure 4-5F), which are in accordance with their theoretical data [92,93].

Figure 4-5. (A) TEM image of a representative single-layer TiS_2 nanomaterial. Top left inset: Photo of TiS_2 dispersion. (B) The SAED for single-layer TiS_2 nanomaterial. (C) HRTEM image for single-layer TiS_2 nanomaterial. (D) TEM image of a representative single-layer TaS_2 nanomaterial. Top left inset: Photo of TaS_2 dispersion.

(E) The SAED for single-layer TaS₂ nanomaterial. (F) HRTEM image for single-layer TaS₂ nanomaterial.

The AFM result of a typical MoS₂, TiS₂, WS₂, TaS₂ sheets reveals a thickness of ~1.0, ~1.0, ~0.7, ~1.0 nm, respectively. (Figure 4-6A-D), confirming the obtained MoS₂, TiS₂, WS₂, TaS₂ nanosheets are single layers, respectively.

Figure 4-6. (A) AFM result of a typical (A) MoS₂ nanosheet, (B) WS₂ nanosheet, (C) TiS₂ nanosheet, (D) TaS₂ nanosheet, gives an average thickness of ~1.0 nm, ~1.0 nm, ~0.7 nm, ~1.0 nm respectively.

After purification by centrifuge, we can get high yield single-layer MoS₂ nanosheets. As shown in Figure 4-7, by measuring 100 MoS₂ nanosheets using AFM, we can conclude that 92% of them are single layers. The average of the measured thickness of MoS₂ nanosheets is 0.99 ± 0.17 nm. The same procedure, we purify the TaS₂ nanosheets, can see from Figure 4-8, after measuring 100 TaS₂ nanosheets, it is

found that 93% of them are single layers. The average of the measured thickness of TaS₂ nanosheets is 0.88 ± 0.08 nm. For TiS₂, as shown in Figure 4-9, it is hard to say the purified TiS₂ nanosheets are single layers or not, by measuring 100 TiS₂ nanosheets, the average of the measured thickness of TiS₂ nanosheets is 1.63 ± 0.23 nm.

Figure 4-7. (A-E) AFM images of large-area MoS₂ nanosheets deposited on Si/SiO₂ substrates. (F) By measuring one hundred MoS₂ nanosheets, it is found that 92% of them are single-layers. The average of the measured thickness of MoS₂ nanosheets is 0.99 ± 0.17 nm.

Figure 4-8. (A-E) AFM images of large-area TaS₂ nanosheets deposited on Si/SiO₂ substrates. (F) By measuring 100 TaS₂ nanosheets, it is found that 93% of them are single layers. The average of the measured thickness of TaS₂ nanosheets is 0.88 ± 0.08 nm.

Figure 4-9. (A-E) AFM images of large-area TiS_2 nanosheets deposited on Si/SiO_2 substrates. (F) By measuring 100 TiS_2 nanosheets, the average of the measured thickness of TiS_2 nanosheets is 1.63 ± 0.23 nm.

The composition of exfoliated MoS_2 nanosheets was confirmed by the energy dispersive X-ray spectroscopy (EDS) analysis, the atomic ratio of S was 2.12%, with Mo 1.07%, which further confirm the stoichiometric composition of MoS_2 (Figure 4-10A-C). The composition of exfoliated WS_2 nanosheets was shown in Figure 4-10D-F, with the atomic ratio of S 6.03% and W 3.67%, indicates the prepared nanomaterial are composed of substoichiometric WS_2 . Figure 4-11A-C shows the composition of exfoliated TiS_2 nanosheets, with the atomic ratio of S 9.04% and Ti 4.47%, indicates that the prepared nanosheets are comprised of superstoichiometric TiS_2 . For TaS_2 , as shown in Figure 4-11D-F, the atomic ratio of are S 5.45%, Ta 2.85%, indicating that the prepared nanosheets are composed of substoichiometric TaS_2 . Why it is substoichiometric for WS_2 and TaS_2 , and superstoichiometric for TiS_2 ? The possible reasons are, as lithium ions intercalate into MS_2 (where $\text{M} = \text{Mo}, \text{W}, \text{Ta}, \text{Ti}$), the structure changes from α phase (2H structure) to β phase (1T structure), when the intercalated lithium ion in MS_2 exceeds certain value, the intercalation compound becomes unstable and decomposes to a mixture of free metal M ($\text{M} = \text{Mo}, \text{W}, \text{Ta}, \text{Ti}$) and insulator Li_2S . This mixture was originally considered to be a third intercalated phase: γ phase [90]. Once the galvanostatic discharge is conducted to the voltage lower than the discharge plateau, the γ phase starts to form in little amount. As a result, the produced 2D nanosheets may contain mixtures of M and Li_2S particles, or some compounds of M and S [90]. Since MoS_2 is most stable after certain amount of lithium

intercalation, the structure change is only from α to β , then the prepared MoS_2 nanosheets show fairly matched stoichiometric ratio. However, for WS_2 , TaS_2 and TiS_2 , besides the phase change of α to β on certain amount of lithium intercalation, they also accompanied with the phase change of α to γ in small amount [90]. In the case of WS_2 and TaS_2 , little amount of free metals W and Ta rather than sulfur compounds may accompany with the exfoliated WS_2 and TaS_2 nanosheets, respectively, which results in substoichiometric of WS_2 and TaS_2 . While for TiS_2 , little amount of Li_2S rather than Ti exists with the exfoliated TiS_2 nanosheets, then EDS shows the superstoichiometric TiS_2 . Another possible reason, since energy dispersive X-ray spectroscopy (EDS) analysis is a semi-quantitative technique. Many elements will have overlapping peaks. The accuracy of the spectrum can also be affected by the nature of the sample. X-rays can be generated by any atom in the sample that is sufficiently excited by the incoming beam. These X-rays are emitted in any direction, and so they may not all escape the sample. The likelihood of an X-ray escaping the specimen, and thus being available to detect and measure, depends on the energy of the X-ray and the amount and density of material it has to pass through. This can results in reduced accuracy in inhomogeneous and rough samples.

Figure 4-10. EDS of (A-C) exfoliated MoS₂ nanosheets. (D-F) Exfoliated WS₂ nanosheets deposited on Si/SiO₂ substrate.

Figure 4-11. EDS of (A-C) exfoliated TiS₂ nanosheets. (D-F) Exfoliated TaS₂ nanosheets deposited on Si/SiO₂ substrate.

XPS results obtained for Mo3d and S2p core levels are illustrated in Figure 4-12A and Figure 4-12B. Three kinds of molybdenum environment have been characterized: an usual sulfide environment corresponding to Mo⁴⁺ ions (229.7 - 232.9 eV) attribute to the MoS₂; an oxide environment assigned to Mo⁶⁺ ions (233.0 - 236.2 eV)

analogous to cations in MoO_3 ; a mixed environment (229.0 - 232.1 eV) are the Mo3d oxidation state of $\text{Li}_\alpha\text{MoS}_2$ (α means residual amount of Li ions on MoS_2 nanosheet). Three kinds of sulfur atoms have been identified through S2p core peaks inspection (S^{2-} as in MoS_2 : 162.7 - 163.9 eV; S_2^{2-} as in MoS_3 : 163.8 - 165.0 eV; S2p oxidation state as in $\text{Li}_\alpha\text{MoS}_2$: 162.0 - 163.2 eV). The Spectra of W4f and S2p core peaks evolution have been reported in Figure 4-12C and Figure 4-12D. A doublet (33.5 - 35.7 eV) is attributed to W^{4+} ions in WS_2 , a doublet (36.6 - 38.7 eV) is assigned to W^{6+} ions as in WO_3 . For the evolution of S2p core peak, the doublet (163.0 - 164.2 eV) corresponding to S^{2-} as in WS_2 .

Figure 4-12. XPS spectra of MoS_2 nanosheets (A) $\text{Mo}3d_{5/2-3/2}$ and (B) $\text{S}2p_{3/2-1/2}$, WS_2 nanosheets (C) $\text{W}4f_{7/2-5/2}$ and (B) $\text{S}2p_{3/2-1/2}$.

Figure 4-13A and Figure 4-13B show the spectra of Ti2p and S2p core peaks evolution. The Ti2p peak was fitted into four components that corresponding to four

different environments (Figure 4-13A): a doublet (456.2 - 462.2 eV) is attributed to Ti2p oxidation state as in $\text{Li}_\delta\text{TiS}_2$ (δ means residual amount of Li ions on TiS_2 nanosheet); a doublet (457.7 - 463.7 eV) corresponding to Ti^{4+} as in TiS_2 ; a doublet (458.9 - 464.9 eV) is assigned to Ti2p oxidation state as in mixed environment; an oxide environment (459.3 - 465.3 eV) was observed and assigned to Ti^{4+} as in TiO_2 . For the spectra of S2p (Figure 4-13B), a specific doublet (161.2 - 162.3 eV) attributed to S2p oxidation state as in $\text{Li}_\delta\text{TiS}_2$; a doublet (161.8 - 162.9 eV) was assigned to S^{2-} as in TiS_2 ; a doublet (162.6 - 163.7 eV) was observed and assigned to $\text{S}^{\frac{4}{x}}$ as in TiS_x ($1 < x < 2$); The high binding energy doublet (163.4 - 164.5 eV) corresponding to S_2^{2-} as in TiS_3 . The spectra of Ta4f and S2p core peaks are shown in Figure 4-13C and Figure 4-13D. A doublet (24.1 - 26.0 eV) is attributed to Ta4f oxidation state as in $\text{Li}_\varepsilon\text{TaS}_2$ (ε means residual amount of Li ions on TaS_2 nanosheet); a doublet (24.7 - 26.6 eV) corresponding to Ta^{4+} ions as in TaS_2 ; an oxide environment (26.6 - 28.5 eV) assigned to Ta^{5+} ions as in Ta_2O_5 . The evolution of S2p core level are shown in Fig. 4-13D, a doublet (162.1 - 163.3 eV) is attributed to S2p oxidation state as in $\text{Li}_\varepsilon\text{TaS}_2$; a doublet (163.1 - 164.3 eV) is assigned to S^{2-} ions as in TaS_2 ; The doublet (164.1 - 165.3 eV) corresponding to S_2^{2-} ions as in TaS_3 .

Figure 4-13. XPS spectra of TiS_2 nanosheets (A) $\text{Ti}2p_{3/2-1/2}$ and (B) $\text{S}2p_{3/2-1/2}$, TaS_2 nanosheets (C) $\text{Ta}4f_{7/2-5/2}$ and (B) $\text{S}2p_{3/2-1/2}$.

The lattice vibration of the prepared MoS_2 nanomaterial was characterized by Raman (Figure 4-14A). A representative single-layer MoS_2 nanosheet shows bands at the position of $382.1, 407.5 \text{ cm}^{-1}$. These two peaks are corresponding to the E_{2g}, A_{1g} modes [94]. The full widths at half maximum (FWHM) for these two bands are $18.4, 16.0 \text{ cm}^{-1}$, respectively. The Raman peaks for bulk MoS_2 sample are at $380.7, 406.2 \text{ cm}^{-1}$ with the FWHM are 6.6 and 7.3 cm^{-1} , respectively. It is shown that the single-layer MoS_2 nanosheet shows much broader bands compared to its bulk form, which is attributed to the confinement of phonon in structures with ultra-thin thickness [5]. Raman spectra of WS_2 obtained exhibit softening of the bands because of the A_{1g} mode (see Figure 4-14B). In comparison with the narrow bands at $352 (E_{2g})$ and $417 \text{ cm}^{-1} (A_{1g})$ of bulk WS_2 with FWHM values around 10 and 9.2 cm^{-1} , respectively, the

spectra of WS₂ prepared by Li insertion shows bands at 351 and 415 cm⁻¹ with FWHM of 24.6 and 22.3 cm⁻¹, respectively.

Figure 4-14. Raman spectra of (A) single-layer MoS₂ (bottom) and bulk MoS₂ (top). (B) Single-layer WS₂ (bottom) and bulk WS₂ (top).

Figure 4-15A shows absorption spectra of single-layer MoS₂ in suspension in water, no obvious absorption peak is observed, but the absorption increases gradually as the wavelength decreases down to 400 nm. Figure 4-15B is the absorption spectra of the exfoliated WS₂, four peaks are observed, which are located at 437, 518, 614, 634 nm, respectively. For TiS₂, three peaks: 561, 930, 1043 nm are presented as shown in Figure 4-15C. The same, there are three peaks located at 689, 936, 1095 nm, which are attributed to exfoliated TaS₂ nanosheets (see Figure 4-15D).

Figure 4-15. Absorbance spectrum for exfoliated dispersions of (A) MoS₂, (B) WS₂, (C) TiS₂ and (D) TaS₂.

4.1.4 Characterization of single-layer ZrS₂, graphene nanosheets

The monolayer graphene and ZrS₂ nanomaterials are successfully fabricated using our method. The galvanostatic discharge curves for ZrS₂ and graphite (open circuit voltage vs. x ; x as in Li _{x} ZrS₂, Li _{x} C) are shown in Figure 4-16. For ZrS₂, the discharge voltage decreases smoothly from 2 to 1.7 V (Figure 4-16A) in the lithium content of $0 < x < 0.33$; at lithium content $x = 0.33$ a discharge plateau appears and it will continue until $x = 1.1$, then another plateau at 1.2 V for the lithium content of $1.68 < x < 2.0$ and it will decrease rapidly down to 0.9 V while x reaches 3. Discharge curve with a similar profile was observed for graphite samples (Figure 4-16B), the discharge voltage declines quickly from 1 to 0.42 V in the lithium content $0 < x < 0.014$; at

lithium content $x = \sim 0.014$ a discharge plateau appears and it continues until $x = \sim 0.054$, then another plateau at 0.18 V for the lithium content of $0.08 < x < 0.12$ and it will decrease rapidly down to 0.1 V while x extend to 0.16. Figure 4-17A shows TEM image of single layer ZrS_2 with no diffraction pattern, while for graphene as shown in Figure 4-17B, the clear hexagonal diffraction spots is attribute to the prepared graphene nanosheets. In addition, AFM images (Fig. 4-18A and Fig. 4-18B) of the single-layer ZrS_2 and graphene nanosheets with thickness of 0.9 and 1.0 nm further confirm our prepared single layer nanosheets.

Figure 4-16. Galvanostatic discharge curve for (A) ZrS_2 and (B) Graphite.

Figure 4-17. (A) TEM images of the obtained (A) ZrS_2 nanosheets. (B) Graphene nanosheets.

Figure 4-18. AFM result of a representative (A) ZrS₂ nanosheet. (B) Graphene nanosheet deposited on Si/SiO₂ substrates, shows the average thickness of ~0.9 nm, ~1.0 nm respectively.

4.1.5 Single-layer MoS₂ nanosheet and film for field effect transistor and gas sensor

To investigate the physical property of MoS₂, under excitation of 488 nm laser, the photoluminescence (PL) of single-layer MoS₂ nanomaterial (Figure 4-19) shows a peak located at 667 nm, the FWHM is 33 meV, also, there is a shoulder located at 618 nm. Based on the Planck relation, $E = h\nu$. Since the frequency ν , wavelength λ and speed of light c are related by $\lambda\nu = c$, the Planck relation can also be expressed as $E = \frac{hc}{\lambda}$. The Planck constant $h = 4.135667516 \times 10^{-15}$ eV s, the speed of light $c = 3 \times 10^8$ ms⁻¹. Then the band gap of MoS₂ is 1.86 eV calculated according to the Planck relation. This result is in accordance with single-layer MoS₂ cleaved by mechanical method [60,62]. The observed peak located at 667 nm originates from the electron-hole transition that result in the high relaxation rate for intra-band carriers, while the shoulder (618 nm) is attributed to the splitting of spin-orbital in the form of valence

band [62]. According to Eda et al [95], increases the thickness of MoS₂ nanosheet from single layer to multiple-layer will results in slight red shift in photoluminescence energy. The single layer MoS₂ exhibits the strongest photoluminescence, while the emission intensity decreases rapidly with increasing nanosheet thickness [95]. Annealing can effectively enhances the PL spectrum of single layer MoS₂. The characteristic MoS₂ excitonic features emerge and grow in intensity with increasing the annealing temperature up to 300°C [95].

Figure 4-19. Photoluminescence spectrum of a single-layer MoS₂ nanosheet deposited on Si/SiO₂ substrate. After the nanosheet was annealed at 450 °C in Ar gas for 2 h, it was excited with 488 nm laser in air at room temperature to give the PL spectrum.

Through casting a drop of MoS₂ nanosheets dispersion onto a Si/SiO₂ wafer, coating two Ti/Au pads on a single-layer MoS₂ using EBL, a single-layer MoS₂ based FET (Figure 4-20) was fabricated. The *I*-*V* plot recorded at high vacuum condition ($\sim 10^{-5}$ Torr) shows the *p*-type semiconducting properties (Figure 4-21), the result is different from the *n*-type conducting for the scotch-tape exfoliated or the exfoliated

MoS₂ with sonication [10]. The possible reason is, the electrons of the residual lithium were transferred to molybdenum sulfide, which generated a band with more than half-filled electrons for MoS₂, in this case, it results in the *p*-type conducting effect of the prepared single-layer MoS₂ nanomaterial.

Figure 4-20. (A-B) Optical microscope images of the single-layer MoS₂ based FET device, where the scale-bars in (A) and (B) represent 2 μm and 1 μm, respectively. (C) SEM image for the single-layer MoS₂, where Au bars were used as the marks for defining the final Au electrodes made by EBL (see optical images in A-B. Scale bar = 1 μm.

Figure 4-21. (A) Plot of drain-to-source current *vs.* drain voltage. (B) Curve for drain to source current (I_{ds}) *vs.* gate voltage (V_g) when drain voltage (V_{ds}) is 6 V. The inset: schematic illustration of single layer MoS₂ FET prepared on heavily doped silicon wafer with 300 nm SiO₂.

In order to display the advantage for our method for high production of single-layer nanosheets, we use the prepared MoS₂ nanomaterials to prepare thin film transistors (TFTs). The thin film MoS₂ prepared by spin-coating method was conductive in large area (Figure 4-22). After thermal evaporation of Au electrodes onto MoS₂ thin film, the detection of adsorbed NO using MoS₂ TFT was conducted. Figure 4-23 shows the response of current for MoS₂ film gas sensor with different concentrations of NO (0.4 ~ 5 ppm). The adsorption of NO molecules resulted in the increase of conductance under NO flow, while desorption of NO led to the reduction of current under the flow of N₂. Due to the *p*-type nature of the MoS₂ TFTs, the increased current when exposed to NO is originated from the doping effect of the *p*-type NO molecules, which can withdraw electrons from MoS₂ [96]. Figure 4-23B gives the curve of current *vs.* concentration of NO. Based on the experimental result, the detection limit was 190 ppt. The detection limit is lower than the detection limit for TFTs with graphene as the source material [96], which suggest that our MoS₂ based TFTs provides a promising sensing application for NO.

Figure 4-22. (A) AFM image and (B) SEM image of MoS₂ thin film used as the active channel for thin film transistor.

Figure 4-23. Response of gas sensor based on MoS₂ TFT. (A) Real-time current response to exposure to NO with increasing concentration. Dashed lines are used to separate the regions of NO adsorption and desorption under N₂ flow. Inset: Schematic illustration of MoS₂ TFT. (B) Plot of percentage change of current to the concentration of NO.

4.1.6 Short summary

This section presents a general method to controlled fabrication of high-production single-layer transition metal disulfides and graphene nanosheets, through an electrochemical lithium intercalation. By using the layered compound, for example, MoS₂, TiS₂, WS₂, ZrS₂, TaS₂ and graphite powder, as the cathode in a simulated battery, the insertion of lithium in the layered compound is exactly dominated in the galvanostatic discharge procedure. By sonicating these lithiated compounds in DI water (in some case ethanol), high-production single-layer nanomaterials are obtained. Particularly, after characterizing a large area of the prepared single-layer MoS₂, we found the yield of single-layer is as high as 92%. For the application, a single-layer MoS₂ FET device is fabricated, which exhibits *p*-type conducting property. The MoS₂ based TFT was also fabricated for sensing of NO. Therefore, our report provides a facile, novel, fast and controlled method for preparation of high-production, large-amount, single-layer 2D nanosheets, which could be used in heterogeneous catalysis, gas sensors and electric devices.

4.2 Few-layer BN, metal selenides and metal tellurides nanosheets preparation, characterization and application

4.2.1 Introduction

Two-dimensional (2D) nanomaterial is very attractive owing to their unique properties and potential applications in electronics, catalysis, etc. Besides graphene, inorganic 2D materials such as hexagonal boron nitride (h-BN) and transition-metal

chalcogenides (TMCs) have also exhibited the novel mechanical [9], optical [97] and thermoelectric properties [54]. For example, NbSe₂ and h-BN have been intensively investigated and applied in the light-emitting diodes [28], magnetic flux [29], dielectric layer [98] and so on. Since the interaction between the layers of the bulk material is van der Waals force, the mechanical cleavage method by using scotch tapes has been applied to fabricate single-layer and few-layer NbSe₂ nanosheets. However, this method is restricted to the large-amount production of nanosheets. Alternatively, the other exfoliation-based methods or the direct growth method have been developed.

BN nanosheets can be obtained from the direct sonication of the bulk h-BN crystals in different solvents [9,36-38]. In the aforementioned reports, the strong affinity of the organic molecules or solvents on the h-BN surface weakened the van der Waals interaction between the adjacent BN layers and thus facilitated the exfoliation and isolation of the individual nanosheets upon sonication. In order to prepare the NbSe₂ nanosheets, the direct sonication of bulk NbSe₂ crystals in organic solvents and sodium cholate/water solution [35] as well as the intercalant-assisted thermal cleavage method [59], have been reported. In the first section, we developed a general method to prepare the single-layer 2D nanomaterials, for example, MoS₂, TiS₂, WS₂, ZrS₂, TaS₂ and graphene, through a controllable process of lithium intercalation and subsequent sonication of the lithiated layered compounds in DI water (in some case is ethanol) [99]. However, there is a big challenge to simply apply this lithiation process to prepare other types of 2D materials, such as h-BN and metal selenides or tellurides (e.g. NbSe₂, WSe₂, Sb₂Se₃ and Bi₂Te₃). Unlike the previously reported

transition metal sulfide crystals, which showed the distinct discharge plateau during the electrochemical lithiation process, the h-BN and metal selenides or tellurides give the continuous descending discharge curves without the presence of an obvious plateau. This makes it difficult to determine the cut-off voltage (i.e. the voltage to stop the discharge) to obtain the optimized Li amount inserted to the bulk materials. Note that the insufficient Li-insertion can lead to the ineffective exfoliation, while the over Li-insertion will result in the chemical decomposition of the crystals [99].

In this section, through a systematic examination of nanomaterials obtained at different cut-off voltages, we have successfully optimized the electrochemical lithiation conditions for preparation of few-layer BN, NbSe₂, WSe₂, Sb₂Se₃ and Bi₂Te₃ nanosheets. More importantly, we have employed two approaches to improve the quality of the products, i.e., the use of a low discharge current to prevent the high-current-induced structure degradation, and the deoxygenation of lithiated compound solutions to alleviate the surface oxidation of the nanosheets during sonication. For the real application, the thermoelectric properties of the film of NbSe₂ nanosheets were tested, which exhibited both the enhanced Seebeck coefficient and electrical conductivity with the p-type semiconducting behavior as compared to the bulk material.

4.2.2 Synthesis of few-layer BN, metal selenides and metal tellurides nanosheets

Figure 4-24 shows the systematic optimization of the electrochemical lithiation conditions for the preparation of few-layer BN, NbSe₂, WSe₂, Sb₂Se₃ and Bi₂Te₃ nanosheets. we have employed three approaches to improve the quality of the products, i.e., determine the optimized cut-off voltage by carrying out a series of control

experiments at different discharge voltage, and systematically examine the obtained products, the use of a low discharge current to prevent the high-current-induced structure degradation, and the deoxygenation of lithiated compound solutions to alleviate the surface oxidation of the nanosheets during sonication.

Figure 4-24. Systematic optimization of the electrochemical lithiation conditions by (A) Lower down the cut-off voltage. (B) Decrease the discharge current and (C) Deoxygenation of the lithiated sample with N₂ gas.

4.2.3 Characterization of few-layer BN, metal selenides and metal tellurides nanosheets

Figure 4-25A exhibits the TEM morphology of BN nanomaterial. The selected area electron diffraction (SAED) pattern (inset of Figure 4-25A) and the HRTEM image exhibit the lattice structure of hexagonal, the lattice space is 2.2 Å, which is

attributed to (100) planes (Figure 4-25B) [100]. The folded edges of such BN nanosheets give thicknesses of ~ 3.3 Å for double (Figure 4-25C) or triple layers (Figure 4-25D). Which is in agreement of the theoretic value in bulk h-BN [100]. The TEM image of the obtained NbSe₂ nanosheet is shown in Figure 4-25E, together with the SAED pattern shown as the inset. The lattice spacing of 3.0 Å measured in the HRTEM image (Figure 4-25F) is consistent with that of the NbSe₂ (100) planes. The Photograph of BN and NbSe₂ solution are shown in Figure 4-25G and 4-25H.

Figure 4-25. (A) TEM image of a typical BN nanosheet. Inset: The SAED pattern of BN nanosheet. (B) HRTEM result for the few-layer BN nanosheet. (C-D) TEM images of the folded edges of few-layer BN nanosheets. (E) TEM result of a representative NbSe₂ nanosheet. The inset: The SAED pattern of NbSe₂ few-layer nanosheet. (F) HRTEM result for the few-layer NbSe₂ nanosheet. (G) Photograph of BN solution. (H) Photograph of NbSe₂ solution.

Figure 4-26 shows SEM and AFM images of individual BN nanosheets, deposited on Si/SiO₂ substrates, the nanosheets observed are hundreds of nanometers wide, with lateral sizes of 550 (Figure 4-26A) 670, (Figure 4-26B) and (Figure 4-26C) 730 nm. The corresponding AFM measurement of BN nanomaterials are exhibited in Figure 25D-F, The average thicknesses for these different sheets are 2.3 (Figure 4-26D), 4.0 (Figure 4-26E) and 8.0 nm (Figure 4-26F), confirming that few-layer BN nanosheets were successfully produced by our method. The clear and obvious SEM images and corresponding AFM images of our prepared BN nanosheets is much better than all these literatures [9, 36-38] that were based on solution process to exfoliate BN nanosheets, strongly convinced the high quality of our prepared BN nanosheets, which further confirm our method is much convinced and effective to exfoliate BN into 2D sheets.

Figure 4-26. SEM images of typical BN nanosheets, deposited on Si/SiO₂ substrates, with lateral sizes of (A) 550 (B) 670 and (C) 730 nm. AFM measurements of typical

BN nanosheets, deposited on Si/SiO₂ substrate, give average thickness of (D) 2.3 (E) 4.0 and (F) 8.0 nm, confirming that few-layer BN nanosheets were successfully produced by our method.

Figure 4-27 shows SEM and AFM images of typical NbSe₂ nanosheets, deposited on Si/SiO₂ substrates. From SEM images, we have prepared large lateral size (6.4 μ m, Figure 4-27A) and normal size 1.1 μ m, (Figure 4-27B) of NbSe₂ sheets. AFM measurements of NbSe₂ nanosheets corresponding to Figure 4-27A and 4-27B give average thicknesses of 2.6 (Figure 4-27C) and 2.4 nm (Figure 4-27D), confirming that few-layer NbSe₂ nanosheets were successfully produced by our method. One thing to emphasize, to the best of our knowledge, we for the first time give direct evidence of our prepared few layer NbSe₂ nanosheets by using AFM, which further prove the effectiveness of our method.

Figure 4-27. SEM images of typical NbSe₂ nanosheets, deposited on Si/SiO₂ substrates, with lateral sizes of (A) 6.4 and (B) 1.1 μm . AFM measurements of NbSe₂ nanosheets corresponding to Figure 6A and 6B give average thickness of (C) 2.6 (D) 2.4 nm.

The oxidation states of the BN nanosheets were characterized by X-ray photoelectron spectroscopy (XPS, Figure 4-28A-B). The B1s spectrum can be fitted by two energy bands at 189.1 and 190.4 eV, The N1s peak can be fitted with two sub-bands located at 396.3 and 397.5 eV, which may be assigned to B1s and N1s oxidation states in Li_δBN (δ means residual amount of Li ions on BN nanosheet) [58,101] and BN, respectively [58,102,103]. The XPS spectra of Nb3d and Se3d core peaks are shown in Figure 4-28C-D. The doublet with components at 203.8 and 206.5 eV is attributed to Nb^{(4- ϵ)⁺} in Li _{ϵ} NbSe₂ (ϵ means the residual amount of Li ions on NbSe₂ nanosheet) [101,104]. The two bands at 204.4 and 207.2 eV are assigned to Nb⁴⁺ in NbSe₂. Those at 208.1 and 210.9 eV are attributed to Nb⁵⁺ in the oxidized species of Nb₂O₅ (37 atomic %) [104]. For the evolution of the Se3d core peak, the doublet (54.6 - 55.5 eV) corresponds to Se²⁻ in NbSe₂, indicating that selenium is not oxidized [104,105].

Figure 4-28. (A) B1s and (B) N1s XPS spectra of the prepared BN nanosheets deposited on Si/SiO₂ substrate. (C) Nb3d and (D) Se3d XPS spectra of prepared NbSe₂ nanosheets deposited on Si/SiO₂ substrate.

In comparison with the n-butyllithium insertion approach, which requires high reaction temperature and takes long time [12], our electrochemical lithium intercalation way is well processed and finely controlled without high temperature [99]. However, unlike our previously reported transition metal sulfide crystals (for example, MoS₂, TiS₂ and WS₂) which exhibited the distinct discharge plateaus during the electrochemical lithiation process, the h-BN, metal selenides or tellurides exhibit the continuously descending discharge curve without an obvious plateau. This makes it difficult to determine the cut-off voltage (i.e. the voltage to stop the discharge) to obtain the optimized insertion of Li amount. Therefore, in the present work, in order to apply the lithiation method to BN and NbSe₂, as well as the other layered materials,

we determined the optimized cut-off voltage by carrying out a series of control experiments at different discharge capacity, and systematically examined the obtained products.

Taking h-BN as an example, its galvanostatic discharge curve (i.e. open circuit voltage *vs.* x , where x is the value in Li_xBN) shows that the discharge voltage decreases from 1.8 V to 0.4 V (at $0 < x < 0.058$) without an obvious discharge plateau (Figure 4-29A). The optimized cut-off voltage is 0.4 V. If the discharge was stopped at a voltage higher than 0.4 V, for example, 0.5 V, only thick BN flakes were obtained. On the other hand, if the discharge was continued till 0.3 V, the chemical decomposition of BN crystals was observed (Figure 4-30). Discharge curve with a similar profile was also observed for NbSe_2 crystals (Figure 4-29B). Based on our systematic study, the optimized intercalated lithium amount (x) in NbSe_2 for preparation of high quality exfoliated NbSe_2 nanosheets was 3.2, corresponding to the discharge voltage of 0.7 V, where the lithiation process stopped. Importantly, in order to further improve the quality of the produced nanosheets, based on our systematical investigation, we set the discharge current at 0.025A, which is lower than 0.05A used in our previous procedure [99]. It can avoid the structure degradation induced by a large discharge current. Furthermore, we also applied a deoxygenation procedure by bubbling N_2 to the water dispersion of Li-intercalated compounds, to alleviate the excessive surface oxidation under sonication.

Figure 4-29. Galvanostatic discharge curves for (A) BN and (B) NbSe₂.

Figure 4-30. SEM images of exfoliated BN crystals prepared at a discharge cut-off voltage of 0.3 V.

Most importantly, our current method based on the aforementioned technical improvement can be not only used for fabrication of BN and NbSe₂ nanosheets, but also applied to a wide range of layered materials, such as WSe₂, Sb₂Se₃ and Bi₂Te₃. For example, Figure 4-31A-B shows the SEM images of WSe₂ powder and a WSe₂ nanosheet after exfoliation. Similarly, the SEM images of Sb₂Se₃ and Bi₂Te₃ before and after exfoliation are shown in Figure 4-31C-D and Figure 4-31E-F, respectively. As observed, the Sb₂Se₃ and Bi₂Te₃ bulk materials are crystals, while the exfoliated

materials exhibit the sheet morphology, and appear darker in contrast to the Si/SiO₂ substrate in the SEM images, indicating the better electrical conductivity of the semiconducting nanosheets compared to Si/SiO₂.

Figure 4-31. SEM images of (A) The WSe₂ starting powder and (B) typical WSe₂ nanosheet. (C) The Sb₂Se₃ starting powder and (D) typical Sb₂Se₃ nanosheet. (E) The Bi₂Te₃ starting powder and (F) typical Bi₂Te₃ nanosheet deposited on Si/SiO₂ substrates.

4.2.4 Few-layer NbSe₂ nanosheets film for thermoelectric measurement

Thermoelectric materials are important in both power generation and energy conservation. Thermoelectric device can directly convert thermal energy into electric energy. One important phenomenon for thermoelectric materials is “Seebeck effect”, which is the generation of an electrical voltage cause by a temperature gradient through the material. The thermoelectric properties of NbSe₂ nanosheets were

measured. Figure 4-32A shows the temperature-dependent Seebeck coefficient (or the thermoelectric power) for the NbSe₂ nanosheets and bulk crystals. The bulk NbSe₂ gives the negative Seebeck coefficient, indicating its n-type behavior. However, the Seebeck coefficient of NbSe₂ nanosheets is positive, suggesting that they are p-type semiconductor [54,63]. This is consistent with the results reported previously, i.e. the nanosheets obtained from the Li-intercalation and exfoliation are p-type semiconducting [54,106]. For detailed explanation, the ideal system is the n-type bulk NbSe₂ without lithium intercalation, the band structure is d² system or d^{2+x} system. After lithium intercalation with subsequent exfoliation, the distorted system is half filled for d² and more than half filled for d^{2+x}, which results in the p-type metallic behavior [54]. The NbSe₂ nanosheets gave much higher absolute Seebeck coefficient (Figure 4-32A) and increased electrical conductivity (Figure 4-32B) compared to the bulk counterpart, resulting in an improved overall thermoelectric transport property, in terms of power factor, i.e. $S^2\sigma$, (S = Seebeck coefficient, σ = electrical conductivity, Figure 4-32C). The result is quite promising, since the great challenge nowadays is how to increase the Seebeck coefficient of a material without depressing the electrical conductivity [107]. Fortunately, we accomplished this two goals by exfoliating the lithium intercalated NbSe₂ into few layer nanosheets. These enhanced properties can be ascribed to the change of carrier concentration and mobility of NbSe₂ after lithiation and exfoliation [63], most likely caused by the extra electrons introduced into the half filled Nb dz² band [54,106]. Furthermore, according to the Mott equation [107], the Seebeck coefficient (S) is a measure of the variation in electronic conductivity σ above and below the Fermi surface. The thermopower of a material is a

measure of the asymmetry in electronic structure and scattering rates near the Fermi level. Thus, the aim should be to produce complexities in either or both the electronic structure and scattering rates within a small energy interval near E_F . In our experiment, we prepared lithium intercalated and exfoliated NbSe₂ nanosheets with features of complex structures and compositions, also with nanoscale feature, which will produce emergent electronic structures with considerable complexity. As a result, the complex structure of our prepared NbSe₂ nanosheets film showed the enhanced power factor [107]. Finally, I would like to say the complex electronic structure originating from the lithium intercalation and the nanoscale features of the exfoliated 2D nanosheets are quite important to enhance the power factor for the prepared thermoelectric materials. These effects can generally applied to other transition metal chalcogenide nanosheets, such as MoS₂ and WS₂ [54], MoSe₂ and WSe₂ [63]. The reason is that these transition metal chalcogenides are all layered structures with similar electronic and band structures [108].

Figure 4-32. Temperature-dependent Seebeck coefficient (A), electrical conductivity (B) and powder factor (C) for NbSe₂ nanosheet and bulk material.

4.2.5 Short summary

This section presents that few-layer BN, NbSe₂, WSe₂, Sb₂Se₃ and Bi₂Te₃ nanosheets have been prepared from their layered bulk precursors by using an electrochemical lithiation process. The lithiation conditions, such as cut-off voltage and discharge current, have been systematically studied and optimized, so that the high-quality BN and NbSe₂ nanosheets have been successfully produced, evidenced by SEM, TEM and AFM. In addition, the NbSe₂ nanosheets showed both the enhanced Seebeck coefficient and electrical conductivity with p-type semiconducting behavior, suggesting their potential application in thermoelectric devices.

4.3 Fabrication of graphene nanomesh (GNM) devices and their applications

4.3.1 Introduction

Graphene, has been widely studied due to their comprehensive applications in electronics [16,17], composites, chemical and bio-sensors [109-111], solar cells [85], electric and optical devices [112]. Single nanoribbons showed the low conductance for FET devices [69]. To increase the conductance, the preparation of ordered, dense nanoribbon arrays are realized by the e-beam lithography [71,72]. But, this process is restricted due to its low throughput and high cost. On the other hand, Bai et al fabricated GNM with the neck width as narrow as 5 nm utilizing the block copolymer lithography [21]. The driving current of these GNM transistors are 100 times the conductance of the single nanoribbon for graphene transistor. Later, Sinitskii fabricated porous metal film by using nanosphere lithography, the porous metal film was engaged as the etching mask for preparation of GNM [20]. However, these literatures depended on the ion etching utilizing reactive toxic gases, e.g. CF_4 and CHF_3 , to remove SiO_2 , they will also corrode Si/ SiO_2 wafer and produce cavities [20] on SiO_2 dielectric layer, that may influence the back gate modulation. Furthermore, HF was utilized to corrode SiO_2 mask [20,21], it could also corrode the dielectric layer of Si/ SiO_2 wafer. Then, Liang et al. integrated the nanoimprint lithography and self-assembly of block-copolymers to obtain GNM with the width of neck as narrow as 10 nm, however, the fabrication procedure of template is really complicated [22]. Later, Akhavan prepared GNM using the photodegradation with UV-assisted, the ZnO

nanorods was used as the photo corrosive catalyst [75], but the low hole's density and the large adjacent hole's distance is difficult to increase the GNM's band gap.

Noted the draw backs of these previous works, we are inspired to fabricate the large-area, high-quality GNM by using a facile method. In this section, we are focusing on the preparation of GNM by utilizing the AAO as a template. As the adhesion layer, poly(methyl methacrylate) (PMMA) was deposited between AAO and rGO. rGO was deposited on a Si/SiO₂ wafer by LB method. After process the O₂ plasma etching, a uniform, large-area GNM was prepared, the neck width and pore size of the GNM can be adjusted using different AAO membranes. For the application, a field-effect transistor (FET), fabricated by GNM with neck width of ~15 nm and pore size of ~85 nm as the electrode, was prepared, which showed a p-type semiconducting property.

4.3.2 Fabrication of graphene nanomesh (GNM)

The prepared AAO template is utilized as etching template for fabrication of GNM. The scheme is shown in Figure 4-33. The sheet like GO were deposited on a Si/SiO₂ wafer utilizing the LB method [82], their reduction were accomplished in vapor condition of hydrazine at temperature of 60 °C for about 12 hours [85] (Figure 4-33A). Then, 8 nm-thick poly(methyl methacrylate) (PMMA) was spin-coated onto the rGO sheets (Figure 4-33B), followed by placing the AAO template on the surface of PMMA film (Figure 4-33C). One thing need to mention is that to replicate the nanosized feature from AAO to the rGO sheets, it is necessary to make them closely contacted, this good contact could not be realized only by laying AAO template onto the rGO deposited Si/SiO₂ substrate, owing to the rigid property of the prepared AAO.

The interspaces at the interface of AAO/rGO can generate inhomogeneously corroded holes on rGO. As a result, a PMMA layer, which located in the middle of AAO and rGO, was used in the fabrication process. On the other hand, to make a good connection for the AAO template and the layer of PMMA, to decrease the AAO's rigidity, a 1 μm thick AAO was fabricated. After the multilayer structures of $\text{SiO}_2/\text{rGO}/\text{PMMA}/\text{AAO}$ was prepared, one more Si/SiO_2 substrate was compressed on thin AAO template, so that the interspaces in the interfaces of $\text{rGO}/\text{PMMA}/\text{AAO}$ were decreased to minimum (Figure 4-33D). The $\text{rGO}/\text{PMMA}/\text{AAO}$ multilayer between two substrates of Si/SiO_2 was heated in vacuum condition at temperature of 180 $^{\circ}\text{C}$ for 2 hours. As a result, the template of AAO stuck closely on the adhesion layer of PMMA. On removing top Si/SiO_2 wafer, plasma etching using O_2 was employed to create pores on thin film of PMMA and generate holes on sheet like rGO (Figure 4-33E). In the end, the adhesion layer of PMMA and AAO membrane were eliminated by utilizing acetone and NaOH , respectively (Figure 4-33F).

Figure 4-33. Schematic illustration of the process to fabricate GNM.

In this work, the AAO membrane was prepared by anodizing aluminum foil with purity of 99.999% in acidic condition via a two-step anodizing process [76,77]. The pore size is ~ 80 nm and the thickness of AAO cell wall [113] is ~ 20 nm for the as-prepared AAO (Figure 4-34A). The cross-section of the prepared AAO template is shown in Figure 4-34B, the membrane thickness is ~ 1 μm .

Figure 4-34. (A) SEM image for the prepared AAO template, the size of pore is ~ 80 nm, the thickness of cell wall is ~ 20 nm. (B) Cross-section of the AAO membrane, the thickness of membrane is 1 μm .

In a typical experimental condition, with the PMMA adhesion layer was 8 nm-thick, the O_2 plasma etching time was 30 s, GNM was produced, the pore size is ~ 67 nm and the width of neck is ~ 33 nm (Figure 4-35). AFM characterization (Figure 4-36A) further verified that the GNM's neck width is 32.9 ± 4.9 nm (Figure 4-36B). The result is in accordance with the SEM result (Figure 4-35). Furthermore, the longer the etch time, the smaller the neck width. For example, Figure 4-36C exhibits the AFM image of the prepared GNM. The plasma etching time using O_2 is 40 s, the GNM's neck width is 14.7 ± 2.4 nm (Figure 4-36D).

Figure 4-35. Large-area GNM exhibited in SEM image. Top right inset: the size of pore is ~67 nm and the width of neck is ~33 nm, as shown in magnified SEM image.

Figure 4-36. (A) The size of pore is ~ 67 nm and the width of neck is ~ 33 nm, as shown in AFM image. (B) GNM with neck width (average) in (A) is 32.9 ± 4.9 nm. (C) The size of pore is ~ 85 nm and the width of neck is ~ 15 nm, as shown in AFM image. (D) GNM with neck width (average) in (C) is 14.7 ± 2.4 nm.

In addition to the O_2 plasma etching time, another factor to determine the quality of the prepared GNM is the PMMA thickness. The PMMA thickness is decided by PMMA concentration in anisole, this solution is used for spin coating at a speed of 4,000 rpm and time of 90 s. For example, When the concentration of PMMA solutions were 1, 0.5 and 0.25 wt%, the thickness of the prepared PMMA films were 45, 15 and 8 nm, respectively. The best PMMA thickness is ~ 8 nm, in this case, the obtained GNM have best quality and large scale of $100 \mu m^2$ (Figure 4-37A). When the PMMA thickness increased to 15 nm, after plasma etching process using O_2 for 40 s, the holes could be generated in rGO. However, the quality of etched rGO sheet is bad and the density of generated holes is low (Figure 4-37B). When elongating the etching time (e.g. 60 s), the hole density increased a lot. But the problem is, some areas have enlarged and fused holes, while some areas were not etched in rGO sheets (Figure 4-38A). The possible reason is, it takes longer time to etch through the thicker layer of PMMA, and the variation of PMMA thickness case the inhomogeneous etching of rGO sheets. Besides, the O_2 plasma etching process is an isotropic etching, which generates both laterally and vertically. As a result, the longer etch time leads to the lateral etching obvious in the film of PMMA. Therefore, the holes on rGO sheets become irregular and enlarged. Actually, for the thicker PMMA film (e.g. 45 nm), when O_2 plasma etching time is 120 s, some areas on rGO sheets were totally

removed, but the other parts were still intact (Figure 4-38B). Base on the experimental results, to get high-quality GNM, the thickness of PMMA layer and the time for O₂ plasma etching need to be optimized.

Figure 4-37. (A) AFM image of the large-area (10 $\mu\text{m} \times 10 \mu\text{m}$) GNM obtained with PMMA thickness is 8 nm, the O₂ plasma etching time is 30 s. (B) AFM image of large-area GNM obtained with PMMA thickness is 15 nm, the O₂ plasma etching time is 40 s.

Figure 4-38. (A) AFM image of large-area GNM obtained with PMMA thickness is 15 nm, the O₂ plasma etching time is 60 s. (B) AFM image of the etched rGO layer obtained with PMMA thickness is 45 nm, the O₂ plasma etching time is 120 s.

4.3.3 The electrical transport characteristics of graphene nanomesh (GNM) and rGO

On obtaining the GNM, it was utilized to prepare FET device on the heavily doped Si substrate, a 300 nm SiO₂ layer was used as the gate, a pair of metal pads (Ti/Au) were used as the drain and source electrodes (Figure 4-39A). Figure 4-39B shows the SEM image of an FET device by using a rectangular shaped GNM as the testing channel, with the GNM width of 5.8 μm and channel length of 2 μm . The neck width and pore size of this GNM are ~ 15 and ~ 85 nm, respectively (Figure 4-36C). The electronic result of this FET device was conducted at ambient environment. The typical electrical transport curves are shown in Figure 4-39C-D. The recorded curve of drain current (I_d) versus drain-source voltage (V_d) at gate voltage with different values (Figure 4-39C), and the plot of I_d versus gate voltage (V_g) (Figure 4-39D) both exhibit the typical p-type conducting behavior for the prepared GNM. The p-type conducting behavior may originate from the edge oxidation of rGO, which is generated from the O₂ plasma treatment, or from the physical adsorbed oxygen coming from the ambient [20,21]. The ON/OFF ratio of current for the prepared GNM-based FET is 4.2 (Figure 4-39D), the result is in accordance with graphene nanoribbon or graphene nanomesh with widths of ~ 15 nm [20,21,67,68]. In a control experiment, we prepared the rGO-based FET device and tested its transport characteristics. As shown in Figure 4-40, the device exhibited a weak p-type conducting behavior. The current ON/OFF ratio is 1.2.

The result further proved that our prepared GNM show enhanced semiconducting behaviors compared with the original rGO. The key reasons for improved electrical properties of graphene nanomesh as compared to pure graphene or other graphene-based structures (e.g. nanoribbons) are attributed to a variety of factors, such as lateral quantum confinement, a localization effect originating from the variable edge roughness or oxygen-content introduced by O_2 plasma process [21]. Based on the research work of Bai et al [21], The on-off ratio of graphene nanomesh (GNM) is inversely proportional to the neck width.

Figure 4-39. (A) Schematic plot of GNM-based FET. (B) SEM image of GNM-FET device (pore size = 85 nm, neck width = 15 nm). (C) Curve of drain current (I_d) versus drain-source voltage (V_d) for the fabricated GNM - FET. (D) Plot of drain current (I_d) versus gate voltage (V_g) for the fabricated GNM - FET in (b) at $V_d = 20$ V.

Figure 4-40. (A) Curve of I_d versus V_d for the rGO - FET. (B) Plot of I_d versus V_g of the unpatterned rGO - FET at $V_d = 10$ V. The ON/OFF ratio of current for the device is 1.2. Inset: SEM image of the measured unpatterned rGO-based FET device.

4.3.4 Short summary

This section demonstrates a simple and effective method to prepare GNM with AAO template as the etch mask and utilizing O_2 plasma etching process. The GNM with narrow neck width and regular pore size has been prepared. For the application, a GNM-based FET is prepared, which shows a p-type conducting property. Such continuous semiconducting GNM with large-area might have applications in electronics and sensors.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this thesis, we are focusing on the preparation and characterization of 2D inorganic nanosheets, such as transition metal dichalcogenides, graphene and BN. For the application of 2D nanosheets, we fabricated single layer and thin film devices for the application of field effect transistor, gas sensor and thermoelectric properties.

An electrochemical lithiation approach to controlled fabrication of high-production single-layer transition metal disulfides and graphene nanosheets, is developed. By using the bulk material of layered compounds, for example, MoS₂, TiS₂, WS₂, ZrS₂, TaS₂ and graphite, which are assembled in a simulated cell as cathode, the insertion of lithium in the layered compounds is exactly controlled by carrying out a galvanostatic discharge procedure. On sonicating the lithiated materials in DI water (in some case is pure ethanol), high-production single-layer nanomaterials are obtained. A single-layer MoS₂ FET is fabricated, because electrons from some amount of lithium were transferred to MoS₂ upon lithium intercalation, which generates a more than half-filled band in the band structure of MoS₂, as a result, it shows *p*-type conducting behavior. The MoS₂ based TFT is also fabricated for NO detection, the detection limit is lower than that of graphene-based TFTs, indicating its promising sensing applications.

We extend the controllable lithiation process into BN, metal selenide and metal telluride, by systematical study and optimization of the lithiation conditions. The optimization processes are: the use of low cut-off voltage to increase the

inserted lithium ions; the use of a low discharge current to prevent the high-current-induced structure degradation, and the deoxygenation of lithiated compound solutions to alleviate the surface oxidation of the nanosheets during sonication. Based on these processes, few-layer BN, NbSe₂, WSe₂, Sb₂Se₃ and Bi₂Te₃ nanosheets are prepared, as evidenced by SEM, TEM and AFM. The thermoelectric property of the obtained NbSe₂ nanosheets film is tested, which shows the enhanced Seebeck coefficient and electrical conductivity with the p-type semiconducting behavior, suggesting the potential application in thermoelectric device.

We demonstrate a simple and effective method to prepare GNM with the AAO template as etch mask and use O₂ plasma etching process. The GNM with narrow neck width and regular pore size is fabricated. For the application, a GNM-based FET is prepared, which shows enhanced semiconducting properties as compared with the original rGO. Such continuous, large-area semiconducting GNM might have applications in electronics and sensors.

5.2 Recommendations for Future Work

The present work has realized high yield preparation of single-layer inorganic nanosheets using an effective electrochemical lithiation process. Use the fabricated two-dimensional nanomaterials for electronic applications. These methods can be further optimized and extended to synthesize high purity nanosheets. Hence the following future works are recommended:

First, grow noble metal nanostructures (i.e. Pt, Pd and Au) on 2D semiconducting nanosheets via the solution-phase synthesis method. The Pt-MoS₂ hybrid nanomaterial with a lower Pt content compared to the commercial Pt

catalyst can be used as catalyst for the hydrogen evolution reaction (HER), to investigate the electrocatalytic activity. The solution synthesis of noble metal nanostructures with the preferred orientation and alignment on the dispersible semiconductor nanosheets can provides a new strategy for the facile and high-yield preparation of novel functional materials.

Second, generalize the 2D semiconducting nanosheets for thin film devices. Make use of the very high work function exhibited by the 2D nanosheets MoS₂ and NbSe₂, which reduces the barrier for the injection of hole into the polymer. By means of simple oxidation for the TMDC, a blocking barrier layer is introduced. This oxide layer prohibits electron extraction from the electronic device and the consequential build up of space charge. The high work function of the underlying MoS₂ layer and the Mo d-orbital characteristics of the oxide valence band facilitate hole tunneling through the barrier. The device structure suggested is general in PLED devices comprising MoS₂, NbSe₂, WS₂, TaS₂, and their corresponding oxides. The range of the electronic properties of the TMDC/TMO materials may offer a unique route to optimize device performance through selection of suitable inorganic and polymeric materials in the hybrid devices.

Third, study the electrochemical performance of single-layer, two-dimensional WS₂, TaS₂ and TiS₂ nanosheets, Test their redox peak using cyclic voltammetry in NaCl aqueous solution. The conductivity and electron transfer rate can be obtained in the [Fe(CN)₆]^{3-/4-} and [Ru(NH₃)₆]^{2+/3+} redox systems. The 2D nanosheets can be used for glucose detection. Moreover, they can selectively detect dopamine in the presence of ascorbic acid and uric acid. We believe that these novel materials are good electrode candidates which can be used for electrochemical sensing applications.

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