1. Introduction

Ever-increasing demand for energy to address depletion of fossil fuels significantly require the development of renewable and sustainable energy storage and conversion systems[1-4]. Rechargeable and storage batteries or secondary cells, can be charged, and discharged into a load, and recharged many times for use, which are designed to deliver high energy and power densities in many energy applications[5-8]. The rechargeable batteries are used in portable electronics and power supplies, electric vehicles, and energy storage power stations, because of their high energy density, low cost, lightweight, size, and long lifetime. A lithium-ion battery is one of the most developed batteries, which consists of anode (e.g., graphite) and cathode (e.g., lithium metal oxide) separated by the electrolyte. Recently, in order to increase energy performance of Li-ion batteries and address limitation of lithium resources, sodium and magnesium-ion batteries have attracted a great deal of attention because of their low cost, natural abundance, and similar insertion mechanism to lithium ions[9-12]. Supercapacitors or electrochemical capacitors store electrical charges by typically two mechanisms: (1) formation of an electrical double layer between electrode and electrolyte and (2) reversible Faradaic reaction at the electrode/electrolyte interface[13,14]. Compared to rechargeable batteries, supercapacitors are capable of delivering higher power density, higher rate capability, and more stable cycle life. However, most supercapacitors suffered from lower energy densities than batteries[15-19].

Ultrathin and layered two-dimensional (2D) nanosheets, especially, graphene materials, have drawn tremendous attention and shown great promise for a wide range of applications[20,21]. Since graphene materials have shown a great potential for the application of energy storage systems, and other 2D materials, such as, metal oxides, hydroxides, dichalcogenides, and carbides have been extensively investigated[22-25]. Among them, molybdenum disulfide (MoS2) is widely interested in many applications because of its unique 2D morphology and phys-
icochemical properties[26-29]. The 2D morphology enables MoS2 to provide high specific surface area compared to its bulk counterpart. The ultrathin layers of MoS2 allow to high flexibility and strong mechanical strength in contrast to MoS2 bulk materials. The attractive merits of MoS2 have been demonstrated in many applications of electronics, sensors, and biomedicine. In particular, the high conductivity, large surface area, and active edge sites of MoS2 made it a promising electrode material for development of energy conversion and storage applications, such as, rechargeable batteries, supercapacitors, electrocatalytic reaction, and solar cells.

In this article, we reviewed unique structures and properties and preparation methods of MoS2 nanosheets. Various experimental techniques were introduced to investigate MoS2 nanosheets. We summarized the recent synthetic methods for preparation of MoS2 materials to achieve nanostructure, extraordinary properties, and enhanced electrochemical performances, including mechanical exfoliation, chemical intercalation and exfoliation, liquid phase exfoliation by direct sonication, electrochemical intercalation exfoliation, microwave-assisted exfoliation, mechanical ball-milling, and hydrothermal synthesis. Following that, the main applications of MoS2 materials are reviewed, involving energy storage systems of supercapacitors and rechargeable batteries.

2. Properties of MoS2

Natural MoS2 materials have a crystalline structure of trigonal prismatic or an octahedral Mo coordination[30]. Particularly, MoS2 has different polymorphs depending on the electron filling in the valence d-orbitals of Mo atoms, involving 3R of rhombohedral polymorph with three-layers and Mo atoms in trigonal prismatic coordination, 2H of hexagonal with two-layers and Mo atoms in trigonal prismatic coordination, and 1T of trigonal with one-layer and Mo atoms in octahedral coordination[31]. MoS2 shows diverse electrical and optical properties according to the different atomic arrangement of MoS2. The 2H MoS2 is naturally abundant and stable, and exhibits indirect bandgap of 1.29 eV for bulk state and direct bandgap of 1.90 eV for monolayer state[32]. The 1T MoS2 shows hydrophilic and metallic nature; the electrical conductivity of 1T is 10^2 times higher than 2H phase. The 1T MoS2 has a similar electrical conductivity with metallic materials of copper and gold. The attractive features of 1T MoS2 have made it as a promising electrode material in applications of energy storage and conversion.

The transformation of 2H into 1T phase in MoS2 can be characterized by various analytical techniques, such as, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), Raman, photoluminescence (PL), extended X-ray absorption fine structure (EXAFS), and ultraviolet-visible (UV-vis)[30]. The measurement of XRD using bulk 2H MoS2 and 1T MoS2 samples provides exfoliation states and crystalline structure of MoS2. The exfoliated 1T MoS2 compared to 2H MoS2 exhibits reduced (002) peak with blue shift, indicating expansion of the interlayer spacing and low crystallinity. In addition, most XRD peaks of 1T MoS2 are reduced when MoS2 sheets are exfoliated. Raman spectroscopy provides a clear evidence for the formation of 1T phase MoS2. The 2H MoS2 shows characteristic peaks of 380 cm-1 (E^1 g mode associated with opposite vibration of two S atoms with respect to the Mo atom) and 400 cm-1 (A^1 g mode associated with the vibration of only S atoms in opposite directions)[30]. Compared to 2H MoS2, the 1T MoS2 shows prominent peaks at around 150, 220, 280, 330, and 400 cm-1, corresponding J1, J2, E^g, J3, and A^g modes, respectively. As the 1T phase increases, E^g, and A^g decrease, while J1, J2, and J3 modes increase[30]. This observation in Raman spectroscopy indicates the presence of the as-synthesized 1T phase in MoS2 sheets. The atomic arrangement of Mo and S between the triangle prismatic and octahedral coordination structures differ from each other. Hence, Mo 3d and S 2p XPS investigation is one of the most promising way to detect 1T phase of MoS2. In addition, peak fitting of Mo 3d and S 2p XPS provides accurate 1T contents of MoS2. The different atomic structures of MoS2 result in different optical properties, and thus UV-vis absorption spectrum of 2H MoS2 and 1T MoS2 are a good indicator to distinguish phases of MoS2. Typically, 2H MoS2 shows three peaks at 440 (attributed to the quantum effect of small lateral-sized MoS2 sheets), 610, and 650 nm (attributed to the energy split large lateral dimensions)[33]. The formation of 1T phase removes the characteristic peaks of 2H MoS2, indicating metallic properties of 1T MoS2.

3. Preparation of MoS2

Tremendous efforts have been attempted to synthesize MoS2 nanosheets in terms of production cost and scalability. Various methods have been employed to prepare MoS2 in order to achieve nanostructure, special properties, and superior performance, including mechanical exfoliation, chemical intercalation and exfoliation, liquid phase exfoliation by direct sonication, electrochemical intercalation exfoliation, microwave-assisted exfoliation, mechanical ball-milling, and hydrothermal synthesis[34-46].

3.1. Top-down approaches for preparation of MoS2

Similar to graphene materials, MoS2 nanosheets can be obtained from mechanical exfoliation of bulk layered MoS2 powers. Novoselov and co-workers successfully exfoliated MoS2 into single-layer MoS2 nanosheet with a high quality of crystalline structure and micro-sized lateral size, but the very small quantities are limited to many practical applications[36]. In order to enhance production rate of MoS2 nanosheets, lithium ion-intercalation and exfoliation methods have extensively been developed[38,39]. Typically, this process is carried out in an atmosphere protected by inert gas, such as, an argon-filled glove box, using n-butyl-lithium at a certain temperature for a certain time of 5~70 h (Figure 1). The lithium-ion intercalation can be accelerated by the assistance of sonication, microwaves, and ball-milling. And also, a lithium-ion battery system was attempted to intercalate Li-ion into layered MoS2 sheets, in which bulk MoS2 and lithium foil were used as the cathode and anode, respectively[37]. By discharging, Li-ion effectively intercalates into bulk MoS2 sheets, thereby achieving efficient exfoliation of MoS2. Other alkali metals have been employed to exfoliate MoS2. The use of alkali metals as the intercalants are basically
electron donors, and thus inducing strain force by the electron transfer from the intercalant. The strain force leads to facilitate the phase transition of MoS\(_2\) from 2H to 1T[34]. Compared to 2H MoS\(_2\), 1T MoS\(_2\) exhibits higher electrical conductivity, larger spacing distance, and more abundant active site surfaces. These features of 1T MoS\(_2\) are especially favorable to the electrochemical applications that require high electron and ion conductivity. The 1T phase of MoS\(_2\) was confirmed by various analytical instruments, such as, TEM, XRD, Raman, STEM, and XPS.

On the other hand, other top-down approaches have been developed. The mechanical ball-milling process can be used to prepare MoS\(_2\) nanosheets without any additives or any other additional treatment for several hours. In particular, the milling time influenced the size of MoS\(_2\) and phase transition (2H to 1T)[40]. The use of microwaves was also reported by Reshmi et al. for exfoliating MoS\(_2\) and phase conversion of 2H into 1T[41]. Recently, supercritical CO\(_2\)-assisted exfoliation method has been also developed by Xu and coworkers (Figure 2)[42]. The use of supercritical CO\(_2\) gas effectively exfoliated bulk MoS\(_2\) into mono- or few-layer MoS\(_2\) nanosheets. The pre-dispersion of MoS\(_2\) flakes in a mixture of ethanol and water was treated in supercritical CO\(_2\) gas condition at 80 °C and 16 MPa under stirring for 6 h. The introduction of CO\(_2\) gas induced strain forces into MoS\(_2\) sheets, and thus leading to phase transform of the 2H into the 1T phase of MoS\(_2\). Because the 1T phase of MoS\(_2\) is important in applications of electrochemical devices, numerous methods have been developed to control the phase of MoS\(_2\). The phase transition of 2H and 1T can be occurred by mechanical tensile and compressive strains onto the MoS\(_2\) surfaces. Chi et al. reported that high pressure up to 81 GPa induced sufficient strain forces into MoS\(_2\) sheets, and thus leading to 1T phase by mechanical layer sliding[43]. However, this compressive pressure is extremely high and the process is very low throughput, which is hard to realize. In order to induce phase transition of 2H into 1T, electron injection, argon-plasma treatment, and chemical vapor treatment have successfully developed. More recently, our group reported scalable and straightforward process for exfoliating MoS\(_2\) materials using fluid dynamins into metallic MoS\(_2\) sheets, resulting in an impressive yield performance of 76.9% and a high concentration of 20 mg/mL[35]. In this process, ionic liquid was used as additives for stabilizing MoS\(_2\) dispersion and 1T phase.

3.2. Bottom-up approaches for preparation of MoS\(_2\)

Hydrothermal and solvothermal reactions are common for preparing MoS\(_2\) nanosheets[44-46]. A mixture of ammonium molybdate tetrahydrate ((NH\(_4\))\(_6\)Mo\(_7\)O\(_{24}\) \(\cdot\) 4H\(_2\)O) and thiourea was used as the precursors for the Mo and S elements. The precursors were thermally treated at 200 °C for 20 h. The typically obtained MoS\(_2\) sheets have a lateral size of 200 nm with 2~5 layers. In addition, 1T phase of MoS\(_2\) was also obtained with 1T contents of < 70%. In order to increase 1T contents, the temperature-assisted phase transform of MoS\(_2\) has been developed. The hydrothermal treatment at 180 °C for 24 h induced metallic phase up to 92.4%. The high temperature above 200 °C caused to the formation of dominant 2H phase (> 90%). The composition ratio of precursors is also critical factor for control the phase of MoS\(_2\). Liu et al. reported that changing the precursor ratio significantly influenced metallic contents of MoS\(_2\)[45].

4. Applications of MoS\(_2\)

Since the 2H MoS\(_2\) was synthesized for many applications, the 1T MoS\(_2\) has also synthesized and now been widely used in various application fields, such as, electrocatalysts (Figure 3), electronic devices, photovoltaic, sensors, and energy storage and conversion systems[27,34].

4.1. Supercapacitor

Supercapacitors, also called ultracapacitors or electrochemical capacitors, are power supply devices to bridge the gap between batteries and capacitors[1-10]. By separating electrolyte ions, supercapacitors can store electrical charges and provides high power density. The desirable supercapacitors can operate at high charge and discharge rates within a few seconds during long-term. Recent issue of supercapacitors is how to increase energy densities, which is generally low than lithium-ion batteries. Since the discovery of graphene materials, ultra
thin-layered 2D materials are promising electrode materials to achieve a high capacitance, resulting in high energy density of supercapacitors [5]. Various 2D materials, including MXenes, metal oxides, metal hydroxides, and disulfide family, have been extensively attempted to enhance electrochemical performances of supercapacitors [5]. Among them, MoS₂ has been attracted a great deal of attention for development of supercapacitors because of its high theoretical capacitance value and unique structural properties of MoS₂. The porous MoS₂ thin films were prepared by Choudhary and coworkers based on a direct magnetron sputtering method [47]. The MoS₂ film electrode showed a high gravimetric capacitance of 330 F/g at 10 V/s (high rate capability) and a good cycling stability of 97% retention over 5,000 cycles of charging/discharging measurement. Karade et al. synthesized ultrathin and layered MoS₂ nanosheets by a chemical deposition method, and demonstrated as energy storage electrodes by a high specific capacitance of 576 F/g at 5 mV/s and an excellent cycle life (82% retention over 3000 cycles) [48]. However, 2H MoS₂ electrodes limited to practical supercapacitor electrodes because of their poor electrical conductivity. In contrast, the metallic MoS₂ electrodes provide more advantages of high electrical conductivity, a high hydrophilicity, and a large interlayer space. Acrce and coworkers successfully fabricated 1T MoS₂ film electrodes by a chemical intercalation-exfoliation and post vacuum filtration methods [49]. The 1T MoS₂ film electrode had a thickness of 5 μm and film packing density of 2.5 mg/cm², in which 1T content is approximately 70%. The 1T MoS₂ film electrode showed an extremely high volumetric capacitance of 400~650 F/cm³ at a scan rate of 20 mV/s. In addition, this MoS₂ film electrode had high specific capacitance at high scan rate of 200 mV/s. Hence, high energy and power densities were achieved to 0.11 Wh/cm³ and 1.1 W/cm³, respectively. Other researchers have focused on synthesis of 1T MoS₂ materials and applied them into supercapacitor electrodes. Thi et al. reported that synthesized 1T MoS₂ nanoflower-based electrodes show a high specific capacitance of 259 F/g at 5 mV/s with a good long-term stability during 1,000 cycles [50]. On the other hand, MoS₂/carbon composite electrodes have been developed in order to address intrinsically low electrical conductivity of MoS₂. Various nanocarbon materials have been employed, including carbon nanofibers, graphene, carbon nanotubes, carbon spheres, and conducting polymers. Huang and coworkers synthesized composite electrodes consisted of carbon aerogel/MoS₂, showing 260 F/g at 1 A/g with a good cycle life of 92.4% capacitance retention over 1,500 cycles [51]. The MoS₂/graphene-incorporated into multiwalled carbon nanotube electrodes have been also prepared, showing a high specific capacitance, a high rate capability, and a good long-term stability. To increase ion and electron transport properties in electrode materials, three-dimensional (3D) MoS₂/graphene aerogel composites were synthesized by a self-assembly of graphene oxide under hydrothermal treatment. As-synthesized 3D MoS₂/graphene electrodes showed a high capacitance of 231 F/g with high energy (26 Wh/kg) and power (6,443 W/kg) densities [52]. Zhang and coworkers fabricated a rambutan-like composite electrode of MoS₂-incorporated into carbon spheres [53]. This composite electrode exhibited a high specific capacitance of 411 F/g at an applied current density of 1 A/g and a good long-term stability of 93.2% capacitance retention during 1,000 cycles. The conducting polymers have been also attempted to enhance the electrical conductivity of MoS₂. For instance, poly(3,4-ethylenedioxythiophene) was in situ polymerized onto the MoS₂ surface. The coated conducting polymer enhanced the electrochemical performance of composite electrodes, showing a high specific capacitance of 405 F/g and an excellent capacitance retention of 90% over 1,000 cycles [54]. Yang et al. synthesized core-shell structured electrode consisted of polyaniline shell and 1T MoS₂ core. This unique structured electrode exhibited an impressive specific capacitance of 678 F/g at 1 mV/s with a good capacitance retention of 80% during 10,000 cycles [55]. The polypyrrole was polymerized onto the MoS₂ surface, showing a high specific capacitance of 700 F/g at a scan rate of 10 mV/s and a good cycling stability of 85% capacitance retention during 4,000 cycles [56]. The controlled morphology of conducting polymer/MoS₂ composite electrodes showed enhanced electrochemical performances for supercapacitor applications. The Mn₃O₄ was incorporated into MoS₂ using a hydrothermal and chemical precipitation method. This hybrid electrode showed a high specific capacitance of 119.3 F/g after 2,000 cycles at an applied current density of 1 A/g with a capacitance retention of 69.3% [57]. The ultrathin layered 2D hybrid films of graphene/MoS₂ was fabricated by vacuum filtration method, showing an extremely high volumetric capacitance of 1,292.0 F/cm³ at 1 A/g and an excellent cycle life [58].

### 4.2. Rechargeable batteries

Increasing energy demands in modern society has required the development of the high energy and power density of energy devices. Lithium-ion batteries have offered high energy densities for commercially available electronic products, such as, personal mobile phones, notebooks, portable electronics, and electric or hybrid vehicles [59]. They can store electrical charges by the electrochemical reactions between anode and cathode materials. Graphite is one of the most promising anode materials in commercial Li-ion batteries. However, the intrinsically low theoretical capacity of graphite (372 mAh/g) limited to application of Li-ion batteries. In this regard, MoS₂ has been attracted

![Figure 3. (a) Cyclic voltammograms of various solutions. (b) Schematic illustrations for the evolution process of the 1T phase based on Mo (Reprinted with permission form ref. 46. Copyright (2017) American Chemical Society).](image-url)
The availability of MoS₂ sheets with the intercalation of alkali metal ions allowed them to accumulate sodium ions among the MoS₂ sheets, resulting in fabrication of Na-ion batteries. The graphene/MoS₂ composite electrodes exhibited a high rate capability of 284 mAh/g at a high rate of 20 A/g with an excellent cycle life of 95% retention after 250 cycles[70]. In addition, expanding MoS₂ sheets with polyethylene oxide led to a high specific capacity of 225 mAh/g and maintained 148 mAh/g after 70 cycles[71]. Because the magnesium can accumulate charges two times higher than those of sodium and lithium metal, magnesium-ion batteries have been attracted a great deal of attention as potential rechargeable energy storage devices. Liang and coworkers reported that MoS₂/polyethylene oxide composite electrodes exhibited a specific capacity of 75 mAh/g at 5 mA/g[72]. In addition, Liu et al. fabricated graphene/MoS₂ composite electrode, showing a high discharge capacity of 115.9 mAh/g and a good cycle life of 82.5 mAh/g after 50 cycles[73].

5. Conclusions

We summarized the properties, preparation methods, and energy storage applications of MoS₂ materials. Particularly, the properties of MoS₂ depend on morphologies and phase. Thus, various synthetic methods of MoS₂ were introduced involving top-down and bottom-up approaches. Supercapacitors and rechargeable batteries (i.e., lithium-ion, magnesium-ion, and sodium-ion batteries) using MoS₂ electrode materials were described. The metallic MoS₂ nanosheets have shown a promising potential in energy storage applications, because of their high electrical conductivity, hydrophilicity, high active surface area, and expanded interlayer distance. Although MoS₂ materials has been employed as advanced electrode materials in energy storage field, there still are many challenges in terms of mass production, fine control of phase and morphology, and unit cost production.

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