Synthesis of MoS$_2$ and MoO$_2$ for their applications in H$_2$ generation and lithium ion batteries: a review

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Abstract

Scientists increasingly witness the applications of MoS$_2$ and MoO$_2$ in the field of energy conversion and energy storage. On the one hand, MoS$_2$ and MoO$_2$ have been widely utilized as promising catalysts for electrocatalytic or photocatalytic hydrogen evolution in aqueous solution. On the other hand, MoS$_2$ and MoO$_2$ have also been verified as efficient electrode material for lithium ion batteries. In this review, the synthesis, structure and properties of MoS$_2$ and MoO$_2$ are briefly summarized according to their applications for H$_2$ generation and lithium ion batteries. Firstly, we overview the recent advancements in the morphology control of MoS$_2$ and MoO$_2$ and their applications as electrocatalysts for hydrogen evolution reactions. Secondly, we focus on the photo-induced water splitting for H$_2$ generation, in which MoS$_2$ acts as an important co-catalyst when combined with other semiconductor catalysts. The newly reported research results of the significant functions of MoS$_2$ nanocomposites in photo-induced water splitting are presented. Thirdly, we introduce the advantages of MoS$_2$ and MoO$_2$ for their enhanced cyclic performance and high capacity as electrode materials of lithium ion batteries. Recent key achievements in MoS$_2$- and MoO$_2$-based lithium ion batteries are highlighted. Finally, we discuss the future scope and the important challenges emerging from these fascinating materials.

Keywords: MoS$_2$, MoO$_2$, H$_2$, generation, lithium ion batteries, electrochemistry

1. Introduction

1.1. Motivation

The development of modern society has largely relied on the consumption of fossil fuels (coal, oil, natural gas, etc.). Due to the non-renewable nature of such fossil fuels, energy shortage is now emerging as a central issue worldwide. Meanwhile, emissions along with the combustion of fossil fuels have also been a major source of pollution of our ecological circle, which is a serious threat to our life and safety. For these reasons, it is urgent to exploit renewable and environment-friendly energy resources to satisfy the ever-increasing global energy demand. The so-called renewable energy resources mainly include solar energy, wind energy, water energy, geothermal energy, tidal energy and so on. Among them, solar energy represents an endless and clean energy resource, generated from the nuclear fusion arising from the Sun’s core. Therefore, searching for the utilization pathway of solar energy is an attractive and thriving pursuit for many scientists.

Hydrogen is supposed to be a major energy carrier, which could provide high combustion heat. Hydrogen is not only an environmentally benign fuel for power generation,
but also a versatile reagent for chemical synthesis. Today, the industrial production of hydrogen is achieved by steam reforming of methane and water, in which the accompanying product is carbon dioxide. However, methane is not a renewable energy source and the CO₂ released may cause new problems. Reduction of water for H₂ production offers an alternative strategy, which is a potential replacement of methane reforming. Importantly, the abundant water on Earth provides an ideal resource for hydrogen production in a cheap and reliable way. In general, the production of hydrogen and oxygen from water, or ‘water splitting’, consists of two half cell reactions:

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + 0.5\text{O}_2, \]  
\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2, \]  
\[ \text{OH}^- \rightarrow 0.5\text{O}_2 + \text{H}^+ + 2e^- . \]

However, H₂O is stable and the water splitting for H₂ evolution usually requires highly efficient catalysts or lots of electrical power. Although electrolysis of water to produce H₂ is a facile method, the high cost of the consumed electrical power prevents its wide application. Therefore, producing H₂ in an economic and green way is highly desirable and becomes a scientific challenge. In the last few decades, many studies have focused on the photocatalytic H₂ production from water splitting by using semiconductor photocatalysts, which is an attractive issue of converting solar energy into chemical energy. In 1972, for the first time, Fujishima and Honda [1] reported photoelectrochemical water splitting on a TiO₂ modified electrode. This promising strategy offers a photocatalytic process for the clean, low-cost and environmentally friendly production of H₂ by utilizing solar energy. Since then, photoelectrochemical-induced water splitting has received much attention from researchers.

In the many studies reported so far, Pt-based materials were found to be well-performing catalysts, and they are used not only for electrochemical water reduction, but also for photoelectrocatalytic water splitting. The high activity of Pt-based catalysts toward water reduction indicates that the surface of Pt-based catalysts provides efficient active sites for catalytic H₂ evolution. However, the large-scale application of Pt-based catalysts has been limited by their low natural abundance and high cost. In recent years, extensive efforts have been devoted to looking for alternative catalysts containing only non-precious elements. Noteworthy, MoS₂ and MoO₂ nanoparticles have been identified as promising catalysts for electrocatalytic or photoelectrocatalytic hydrogen evolution. Molybdenum (Mo) is a transition metal that is relatively abundant and therefore much cheaper than platinum. Thus, its complexes offer significant advantages over noble metal catalysts as electrocatalysts or photoelectrocatalysts for H₂ production. However, for a long time, MoS₂ was not considered as an ideal catalyst for H₂ production because bulk MoS₂ shows very poor activity for the hydrogen evolution reaction (HER). In 2005, nanocrystallized MoS₂ was reported as a promising HER catalyst [2]. Since then, Mo and its related complexes have invoked wide research interest as electrocatalysts for water reduction, especially as photoelectrocatalysts for water splitting to produce H₂.

On the other hand, lithium ion batteries (LIBs) have received much attention. As an advanced energy storage device, LIBs have many attractive properties including high operating voltage, large energy density, low self-discharge rate and long cycle life. Nowadays, LIBs have become the main power sources for consumer electronics, high-power tools and electric vehicles [3]. Normally, a LIB consists of an anode, cathode and electrolyte. In an ideal case, the cathode material should have high Li intercalation voltage, whereas the anode material should have low Li deintercalation voltage [4]. The anode of LIBs is usually made from carbon materials because of their flat potential profile versus lithium and good structural stability during cycling, and the graphite materials are extensively utilized as commercial materials. However, six carbon atoms are required to accommodate one Li ion. This leads to a low specific capacity (a theoretical value of 372 mAh g⁻¹) of graphite [5], which largely limits its performance as LIB anode material. Many transition metal oxides, such as Mn₃O₄ [6], Co₃O₄ [7], MnO₂ [8], TiO₂ [9] and NiO [10], are capable of functioning as LIB anode materials. Among them, MoO₂ is a promising candidate as LIB anode material with a theoretical specific capacity of 838 mAh g⁻¹ [11–13]. In recent years, many reports have been published on the MoO₂-based LIB anode material. Moreover, MoS₂ and its composites were also investigated as both LIB anode material and cathode material. MoS₂ is characterized as its layered structure with galleries held together by weak van der Waals forces [14], which endows it with a promising property for Li⁺ accommodation and transport. As cathode material, MoS₂ is limited by the low energy density because of its relatively low average voltage. Recent research progress shows that MoS₂ can be a good anode candidate as well, if fully discharged to low voltage. In LIBs, the performance of MoO₂ and MoS₂ is strongly associated with their morphology and structure. Therefore, the synthesis and characterization of MoO₂ and MoS₂ have been an attractive research direction for their applications as LIB electrode materials.

In this review, we summarize the synthesis of MoO₂ and MoS₂ for their applications in energy conversion and storage. To the best of our knowledge, only a few perspective papers were published relating to this topic. Merki and Hu [15] reviewed the advancement of MoS₂ as a photocatalyst for water splitting. Moreover, Laursen et al [16] summarized the recent progress of MoS₂ used for electro- and photoelectrocatalytic hydrogen evolution. However, considering the rapid progress and new achievements of MoO₂ and MoS₂ for their applications as catalysts for energy conversion and storage, a detailed review is highly desirable to fully cover this thriving field and motivate further scientific activities. This review will, in particular, focus on recent progress in preparation methods and doping strategies for MoO₂ and MoS₂. We emphasize the morphology control and its relationship with the catalytic activities of MoO₂ and MoS₂ towards electrocatalytic or photoelectrocatalytic H₂ production. We also highlight the advantages of MoS₂ and MoO₂ for their enhanced cyclic performance and high capacity as electrode materials of LIBs. In this regard, recent key achievements in MoS₂- and MoO₂-based lithium ion batteries are addressed. Finally, we present our viewpoints for
future research scope and important challenges emerging from these fascinating materials.

1.2. Structure of MoS$_2$

As a typical semiconductor material, MoS$_2$ is naturally noted as molybdenite featured with a layered hexagonally packed structure. A single layer is formed through the S–Mo–S bond, and layers are held together in stacks by van der Waals forces. Figure 1(a) illustrates the lamellar structure and S–Mo–S existing in the single layer of MoS$_2$, and a single-layer MoS$_2$ with a thickness of $\sim$0.7 nm is presented in the AFM image in figure 1(b) [14]. As an important semiconductor material, the unique layered structure endows MoS$_2$ with many promising properties, such as anisotropy, chemical stability and anti-photo corrosion. It is well known that the quantum confinement effect has a vital effect on the value of band gap in semiconductor materials. The band gap of MoS$_2$ can increase from $\sim$1.29 to $\sim$1.8 eV through peeling bulk to single layer [17]. These unique properties provide MoS$_2$ with promising applications in hydrogen storage [18], catalysis [19], double-layer capacitance [20], LIBs and photoelectrocatalytic water splitting (figure 2). The synthesis strategies of MoS$_2$ mainly include the hydrothermal method [21], the microwave plasma method [22], the arc process [23] and the electrochemical method [24].

Figure 1. (a) Three-dimensional schematic of the atomic structure of MoS$_2$. (b) AFM height profile of monolayer MoS$_2$; the inset is the corresponding AFM image. (Reproduced with permission from [14] © 2012, American Chemical Society.)

1.3. Structure of MoO$_2$

MoO$_2$ is a well-studied semiconductor catalyst and has superior properties, which have been extensively utilized in catalysis, sensors, recording media, supercapacitors, LIBs and photoelectrocatalytic water splitting (figure 2). MoO$_2$ mainly exists in three polymorphic forms: hexagonal phase (P63/mmc) [25], tetragonal phase (P42/mnm) [26] and monoclinic phase (P21) [27]. The tetragonal MoO$_2$ with a distorted rutile structure and the monoclinic one are common forms, while the hexagonal phase is unstable. Recent research efforts are directed toward the synthesis of nanosized MoO$_2$ through different routes, such as solid reduction [26–28], electrospinning [29], liquid reduction [27, 30] and rheological phase reaction [30]. The detailed introduction of its synthesis and applications as an electrode material will be given in the following section.

2. Synthesis and applications of MoS$_2$ and MoO$_2$ for electrocatalytic H$_2$ production

2.1. Synthesis of MoS$_2$ as an electrocatalyst for H$_2$ production

In the 1970s, Tributsch and co-workers reported work on electrochemical hydrogen evolution on natural crystals of MoS$_2$ [31]. Jaramillo et al [32] investigated the mechanism, and found that the edges of the planes of the MoS$_2$ layers, and in particular the sulfur vacancies that are formed in the edge sites, contribute to the electrocatalytic activity of MoS$_2$. Therefore, they suggested that increasing the edge active sites by the morphology controllable synthesis process may enhance remarkably the electrocatalytic activity of MoS$_2$ in electrochemical HER. Toward this goal, different methods have been utilized to prepare MoS$_2$ with a novel structure, such as MoS$_2$ nanotubes [33], MoS$_2$ nanorods [34], MoS$_2$ nanofibers [35] and MoS$_2$ nanoflakes [36]. The reported
results clearly demonstrate that the catalytic activity of MoS$_2$ toward the HER is closely associated with the nanostructure and morphology of the prepared samples.

Merki et al [37] prepared amorphous MoS$_2$ thin films by a cyclic voltammetry technique in a simple and rapid manner at room temperature and atmospheric pressure. The obtained MoS$_2$ thin film is a mixture of MoS$_3$ and MoS$_2$. They utilized x-ray photoelectron spectroscopy and optical absorption to analyze the product of the electrocatalytic reaction. Results show that the MoS$_2$ phase was identified as the major active material responding for the electrocatalytic reduction of water. Such amorphous MoS$_2$ gives significant geometric current densities toward the water reduction at low overpotentials (e.g. 15 mA cm$^{-2}$ at $\eta = 200$ mV) and also shows good compatibility in a wide range of pHs (e.g. 0–13). The Tafel slope of amorphous MoS$_2$ was measured as 40 mV dec$^{-1}$, which was different from those of MoS$_2$ crystals [32] (55–60 mV dec$^{-1}$) or MoS$_2$ nanoparticles [38] (120 mV dec$^{-1}$). According to the classical theory, a Tafel slope of 40 mV dec$^{-1}$ indicates that the surface coverage of adsorbed hydrogen is less than 10%, and hydrogen production follows a fast discharge reaction mechanism (equations (4)–(6)).

\[
\text{discharge reaction} \quad \text{H}_2\text{O}^+ + e^- + \text{cat} \leftrightarrow \text{cat} - \text{H} + \text{H}_2\text{O}, \quad (4)
\]
\[
\text{ion}^\text{+} \text{atom reaction} \quad \text{H}_2\text{O}^+ + e^- + \text{cat} - \text{H} \leftrightarrow \text{cat} + \text{H}_2 + \text{H}_2\text{O}, \quad (5)
\]
\[
\text{combination reaction} \quad \text{cat} - \text{H} + \text{cat} - \text{H} = 2\text{cat} + \text{H}_2. \quad (6)
\]

All the results demonstrated that amorphous MoS$_2$ exhibits higher activity than the nanoparticles of MoS$_2$.

Elemental doping provides an alternative route to enrich the edge active sites and therefore improves the electrocatalytic activity of MoS$_2$ toward water reduction. Co and Ni are the most studied doping elements for MoS$_2$. The incorporation of cobalt or nickel into the MoS$_2$ structure can be realized by co-impregnation of two solutions (e.g. C$_6$H$_5$Co$_2$(OH)$_2$) [38] or by adding the appropriate metal ion (e.g. (Co)(acetate)$_2$) [39] to the impregnation solution. Bonde et al [38] investigated the effect of Co doping on the structure of MoS$_2$, and thereby on the electrocatalytic activity of MoS$_2$. It was found that the introduced cobalt is located at the edge of MoS$_2$, more specifically, the so-called S-edge (1110).

In addition to the increasing amount of sulfur active edge sites of MoS$_2$ plates [16, 35], improving the electrical contact between the active sites and the underlying electrode is also important in the catalytic process. Carbon materials, such as graphene and carbon nanotubes (CNTs), are good candidates as support catalysts due to their unique physicochemical properties. Carbon materials are usually relatively cheap and stable. Importantly, they have good electrical conductivity, high activity and a wide electrochemical window. Some groups evaluated MoS$_2$ performance as a catalyst for electrocatalytic water reduction by combining MoS$_2$ with graphene, graphite and CNTs. By the introduction of mesoporous carbon nanospheres (MCNs), Bian et al [40] synthesized MoS$_2$/MCN nanocomposites using an in situ reduction method. The MCNs were firstly prepared according to a novel low-concentration hydrothermal route [41] and the Mo/C molar ratios of the prepared MoS$_2$/MCNs were controlled by a one-step hydrothermal method [42]. The resulting morphologies suggest that the addition of MCNs greatly prevents the serious aggregation of MoS$_2$ nanospheres, and facilitates a uniform distribution of MoS$_2$ on MCNs (figure 3). Therefore, the introduction of MCNs not only improves the electronic conductance, but also promotes the catalytic performance by creating more edge active sites of MoS$_2$. They further compared the catalytic activity for hydrogen evolution upon MCNs, pure MoS$_2$, a simple mixture of MoS$_2$ and MCNs, and the obtained MoS$_2$/MCNs materials. From figure 4 we could find that MoS$_2$/MCNs exhibit the best electrocatalytic activity for hydrogen evolution with the lowest overpotential and the highest current density. The observed onset potential of MoS$_2$/MCNs for HER was approximately $-0.1$ V (versus reversible hydrogen electrode) at high current densities of $\sim 7$ and $\sim 30$ mA cm$^{-2}$ with overpotentials of 150 and 200 mV.

Besides, other carbon materials such as CNTs [43] and reduced graphene oxide (GO) sheets [42] have also been incorporated with MoS$_2$ to enhance the performance of electrocatalytic HER. Compared with only MoS$_2$, the introduction of carbon materials can significantly elevate the catalytic activity of MoS$_2$, which contributes not only to enhanced electronic conductance but also to the reduced sizes.
of MoS$_2$. In this way, more edge active sites are available for the reduction of water and evolution of H$_2$.

### 2.2. Synthesis of MoO$_2$ as an electrocatalyst for H$_2$ production

Lačnjevac _et al_ [44] reported a Ni-doped MoO$_2$ composite electrode by an electrodeposited route using a suspension containing 3 g dm$^{-3}$ of MoO$_2$ powder particles in 0.2 M NiCl$_2$ + 2 M NH$_4$Cl solution, in which the pH value of the suspension was adjusted to 3.8 by adding HCl. The obtained Ni–MoO$_2$ electrode consisted of a Ni-rich part and a MoO$_2$-rich part (figure 5). This might be caused by the specific hydrodynamic conditions established on a substrate of the characteristic geometry (mesh) during deposition, leading to the incorporation of MoO$_2$ particles increasing at some positions and decreasing at others. The catalytic activity of the Ni–MoO$_2$ electrode was examined and a steady-state polarization curve for the HER characterized with a Tafel slope of $-122$ mV dec$^{-1}$ was observed. The electrochemical impedance spectroscopy plots were recorded at overpotentials corresponding to the Tafel region to determine the rate constants of individual steps and understand the mechanism of the HER. The true catalytic effect of the Ni–MoO$_2$ combination, since the Ni–MoO$_2$ coating possesses an order of magnitude higher intrinsic activity for the HER in comparison with that of a flat Ni electrode.

### 3. Synthesis and applications of MoS$_2$ for photoelectrocatalytic H$_2$ production

Photoelectrocatalytic HER has received much attention since photo-induced water splitting was reported on a TiO$_2$ electrode [1]. To realize photoelectrocatalytic HER, photocatalysts are required to have a suitable band gap. Moreover, the conduction band bottom edge should be more negative than the reduction potential of H$^+$/H$_2$. The principle of photoelectrocatalytic water splitting on a photocatalyst is illustrated in figure 6.

Common semiconductor materials, such as TiO$_2$ [45], CdS [46] and Cu$_2$O [47], can be used for photo-induced water splitting. However, all of these materials have their own drawbacks. For example, due to the wide band gap, TiO$_2$ absorbs only a small fraction of the sunlight. Photoerosion, which leads to a remarkable reduction in photocatalytic activity, is a common phenomenon during the working of semiconductors such as CdS and Cu$_2$O. In order to overcome these problems, much effort has been devoted to the modification of photocatalysts or doping the photocatalysts with noble metals.

Similar to most semiconductor catalysts, the conduction band of MoS$_2$ is more positive than the reduction potential of H$^+$/H$_2$, which does not meet the requirement of photocatalytic HER. However, MoS$_2$ has been demonstrated as an efficient co-catalyst for photocatalytic HER. For example, one promising strategy is to combine MoS$_2$ with traditional semiconductors, such as CdS [46], CdSe [48] and TiO$_2$ [45], to form a novel nanocomposite for efficient photoelectrocatalytic generation of hydrogen.

Frame and Osterloh [48] studied the photocatalytic property of CdSe and found that bulk CdSe is catalytically inert for HER under visible light irradiation. As a comparison, it was shown that CdSe nanoribbons photocalyze H$_2$ evolution from an aqueous sodium sulfite/sulfide solution with a quantum efficiency of 9.2% at 440 nm. However, they further demonstrated that the performance of CdSe nanoribbons can be improved with the addition of MoS$_2$ as a co-catalyst. The MoS$_2$ nanosheet was obtained by exfoliation of bulk MoS$_2$. The CdSe–MoS$_2$ nanocomposites were prepared by a simple mixture process in solution. The successful attachment of MoS$_2$ to CdSe was characterized by transmission electron microscopy (TEM), in which the linkage was supposed to involve van der Waals interactions and covalent interactions between the soft selenide and the molybdenum ions or a combination of both. They investigated the effect of concentration of MoS$_2$ on the activity of CdSe–MoS$_2$.

As co-catalysts, 0.58 wt% of MoS$_2$ enhances the activity of CdSe–MoS$_2$ by elevating the H$_2$ evolution amount up to 3.7 times that of the nano-CdSe. However, when the concentration of MoS$_2$ is further increased, the activity of CdSe–MoS$_2$ decreases, which is probably due to the adsorption of photons by MoS$_2$ (figure 7). In comparison, they found that platinum is not an effective co-catalyst for CdSe, which is likely due to the sulfide poisoning of surface active sites. Figure 8 shows linear sweep voltammetry (LSV) curves of the CdSe–MoS$_2$ nanocomposite in different solutions, revealing its flatband potentials. The enhanced activity of CdSe by the MoS$_2$ co-catalyst is ascribed to the partial reduction of the CdSe surface that flatband potential has shifted both in the methanol and Na$_2$S/Na$_2$SO$_3$ solution, which has a direct relationship with the catalytic activity.

As mentioned above, carbon materials play important roles in improving the interfacial charge transfer between MoS$_2$ catalysts and the electrode substrate. Xiang _et al_ [45]...
Figure 5. SEM images of the Ni–MoO$_2$/Ni mesh electrode surface: (a) the backscattered electron analysis performed at low magnification (90×) showing two characteristic parts, (b) the MoO$_2$-rich part of the coating (1000×) and (c) the Ni-rich part of the coating (5000×). (Reproduced with permission from [44] © 2012, Elsevier.)

Figure 6. Principle of photoelectrocatalytic water splitting on a photocatalyst.

synthesized a layered MoS$_2$/graphene (MG) hybrid and incorporated it with TiO$_2$ to form a new composite material. The TiO$_2$/MG composite performs well as a photocatalyst used for the photocatalytic water splitting to produce H$_2$. The TiO$_2$/MG composite photocatalyst was synthesized by a two-step hydrothermal process. The layered MG hybrid was

Figure 7. Variation of initial H$_2$ evolution activity with MoS$_2$ loading (mass %). Inset: photos of nano-CdSe–MoS$_2$ and nano-CdSe. (Reproduced with permission from [48] © 2010, American Chemical Society.)
firstly prepared by the hydrothermal reaction of Na$_2$MoO$_4$ and H$_2$CSNH$_2$ in an aqueous solution of GO at 210 °C for 24 h. During this process, GO was reduced to graphene simultaneously with the dispersion of graphene-like MoS$_2$ nanosheets on graphene sheets. Subsequent hydrothermal treatment of Ti(OC$_2$H$_5$)$_4$ and the MG hybrid in an ethanol/water solvent led to crystallization of TiO$_2$ and formation of the TiO$_2$/MG composite.

As shown in figure 9, under light irradiation, electrons transfer from the valence band of TiO$_2$ to the conduction band of TiO$_2$. Subsequently, one part of the electrons was directly delivered to MoS$_2$, while the other part of the electrons flows to MoS$_2$ through graphene. The edge sites of MoS$_2$ can effectively reduce water to H$_2$. The introduction of graphene material can remarkably improve the charge transport and hinder the recombination of electrons with holes.

The results show that the photocurrent density of TiO$_2$/graphene and TiO$_2$/MoS$_2$ is higher than that of pure TiO$_2$, indicating that conduction band electrons of TiO$_2$ can be injected into the graphene sheets in the TiO$_2$/graphene system or the MoS$_2$ sheet of the TiO$_2$/MoS$_2$ system. Among all samples, the TiO$_2$/MoS$_2$/graphene composite shows the highest photocurrent density, indicating the charge transportation from TiO$_2$ to graphene and/or MoS$_2$, and then to the improved working electrode surface (figure 10).

Stability is a vital parameter for photocatalysts, which has a relationship with the working life. Among all TiO$_2$/MoS$_2$/graphene samples with different proportions, T/95M5.0G does not exhibit any significant loss of activity during the recycling experiments, indicating that the catalysts are stable in the process of photocatalytic H$_2$ production (figure 11).

The other promising application of MoS$_2$ relies on combining them with a photosensitizer to form a novel catalyst for H$_2$ production. Under light irradiation, the photosensitizer injects the electrons to MoS$_2$ and water is reduced to H$_2$ at the edge active sites of MoS$_2$. Zong et al [49] reported Ru(bpy)$_2^+$ (bpy = 2, 2'-bipyridine) as a photosensitizer combined with MoS$_2$ catalyst for photo-induced H$_2$ evolution (figure 12). A colloidal MoS$_2$ nanoparticle was synthesized by a simple solvothermal method. The solubility of colloidal MoS$_2$ was greatly enhanced, leading to an increase in edge active sites of MoS$_2$. 

Figure 8. Photocurrent spectra (chopped light) (A) in 1.0 M aqueous KCl solution containing 20% (v/v) methanol and (B) in 0.1 M Na$_2$S/0.1 M Na$_2$SO$_3$ solution (pH = 9.3). Scan speed = 10 mV s$^{-1}$, scan direction = cathodic (right to left). (Reproduced with permission from [48] © 2010, American Chemical Society.)

Figure 9. Schematic illustration of the charge transfer in TiO$_2$/MG composites. The proposed mechanism for the enhanced electron transfer in the TiO$_2$/MG system under irradiation assumes that the photoexcited electrons are transferred from the CB of TiO$_2$ not only to the MoS$_2$ nanosheets but also to the C atoms in the graphene sheets, which can effectively reduce H$^+$ to produce H$_2$. (Reproduced with permission from [45] © 2012, American Chemical Society.)

Figure 10. Stabilization test of T/95M5.0G sample for recycling experiments.
In addition, no H$_2$ was evolved when only Ru(bpy)$_3^{2+}$ or colloidal MoS$_2$ was used. However, when both Ru(bpy)$_3^{2+}$ and MoS$_2$ were employed, a large amount of H$_2$ can be produced.

4. MoO$_2$ and MoS$_2$ as promising electrode materials for LIBs

At present, LIBs are extensively used as a power source for portable electronic devices due to their high power density, high safety and long cycle life. Research efforts have recently focused on increasing energy density and reducing cost while maintaining a high rate performance. In spite of the fact that several lithium-insertion compounds as cathodes have been developed, the commercialization of rechargeable lithium batteries is still being hindered by the poor cycle performance of the metallic lithium anode [50].

One possible method to solve this problem is to use the insertion compounds as the LIB anode. In recent years, many materials have been developed as anode materials to improve the performance of LIBs, including core–shell structured Si nanocomposites [51], TiO$_2$ nanocomposites [52] and CNT-coated SnO$_2$ nanowires [53]. Notably, MoO$_2$ and MoS$_2$ have also been investigated for their applications as novel LIB anode materials. Their layered structure, as well as low electrical resistivity, high electrochemical activity and high stability, makes them promising anode materials for LIBs.

4.1. Synthesis of MoS$_2$ and its application as an electrode material for LIBs

As a typical conducting material, MoS$_2$ has a distinctive layered structure that makes it favorable for reversible Li$^+$ intercalation/deintercalation. Furthermore, the weak van der Waals force between MoS$_2$ layers allows Li$^+$ ions to diffuse without a significant increase in volume expansion. These properties make MoS$_2$ an ideal electrode material for advanced LIBs [54, 55].

The first patent of the MoS$_2$-based LIB was published in 1980 [56]. A series of MoS$_2$ samples with different morphologies were prepared and carefully studied for their use in LIBs. The electrochemical performance of MoS$_2$ as a LIB electrode was believed to be significantly influenced by morphology, structure and particle size. Considering that the Li diffusion path could be significantly shortened in the nanostructured MoS$_2$, thus improving the performance, many research efforts have been directed to prepare nanostructured MoS$_2$ for LIB applications. For instance, Feng et al [57] synthesized MoS$_2$ nanoflakes by using a hydrothermal method and the MoS$_2$ obtained afforded a high capacity of about 1000 mAh g$^{-1}$. Moreover, MoS$_2$ nanoflowers and nanotubes have also been studied as anode materials and have been proven to have high capacity [58, 59]. However, it should be noted that the cycling stability for these nanostructured MoS$_2$ is still poor and strongly hinders their further applications.

Carbon materials are the most common LIB anodes. Among them, graphite is easily available and cheap. Unfortunately, the theoretical capacity of graphite is only 372 mAh g$^{-1}$ calculated by forming the compound of LiC$_6$. The low capacity cannot meet the ever-increasing demand for LIBs. Nevertheless, owing to their high electrical...
conductivity, carbon materials, such as graphite, CNTs and graphene, are expected to combine with MoS$_2$ to generate novel composite materials for use as a LIB anode.

Zhang et al. [60] reported the synthesis of carbon-coated MoS$_2$ (C-MoS$_2$) nanorods. Uniform C-MoS$_2$ nanorods are obtained by chemical vapor deposition of a thin carbon layer on the MoS$_2$ nanorods. The one-dimensional structure is well retained during the synthesis process. When used as an anode material for LIBs, the C-MoS$_2$ nanorods exhibit improved reversibility and cycling performance compared with the non-coated MoS$_2$ nanorods. After 80 cycles at a current density of 200 mA g$^{-1}$, a high capacity of 621 mAh g$^{-1}$ can be retained, suggesting that the thin carbon layer effectively improves the stability of the MoS$_2$ nanorods. This fact might be ascribed to the increase in the electronic conductivity and to less aggregation of the resulting sample.

CNTs have unique properties associated with their small dimensions, high anisotropy and intriguing tube-like structures. The fabrication of semiconductor/CNT nanocomposites with very small particle sizes for energy conversion and storage devices seems to be very attractive. Wang and Li [61] demonstrated that overlayered MoS$_2$ supported on coaxial CNTs performs well as an LIB anode material. The unique nanoarchitecture of these samples has been confirmed to contribute to the reversible capacity (approaching 400 mAh g$^{-1}$) and their excellent cyclability.

Graphene was also investigated as potential conducting material for MoS$_2$ support. Graphene is a two-dimensional planar sheet of sp$^2$ bonded carbon atoms. The packed honeycomb crystal lattice endows it with a number of interesting properties such as ultrahigh specific surface area, high room temperature carrier mobility and excellent thermal conductivity. In particular, the extremely high electron mobility is expected to be beneficial for electrochemical applications. Hence, it is reasonable to believe that the incorporation of graphene can efficiently improve the performance of MoS$_2$. Chang and Chen [62] reported a facile process for the synthesis of layered MoS$_2$/graphene (MoS$_2$/G) composites by an L-cys-assisted solution-phase method. The resulting MoS$_2$/G composites basically retain the layered crystallinity. It was shown that the MoS$_2$/G composite electrodes exhibit much higher specific capacities and more cyclic stability than bare MoS$_2$ electrodes. The ratio of MoS$_2$ to G was optimized and the sample with a 1:2 ratio exhibited the highest specific capacity of $\sim$1100 mAh g$^{-1}$ at a current density of 100 mA g$^{-1}$ and no capacity fading after 100 cycles (figure 13).

In addition to the incorporation of conducting carbon materials in MoS$_2$, it was suggested that some polymers may also improve the performance of MoS$_2$ by increasing the lithium ion transfer in the interlayer space of MoS$_2$ thanks to the lithium ion coordination properties of these polymers. It is believed that these problems may lead to an increase of capacity in the restacked MoS$_2$. For example, Xiao et al. [63] prepared the MoS$_2$/PEO (polyethylene oxide) nanocomposites, in which PEO was thought to improve the ionic conductivity and stabilize the disordered structure of exfoliated MoS$_2$. As a result, MoS$_2$/PEO was demonstrated to have high capacities and excellent long-term reversibility. Graphene was further added into this hybrid material. The PEO/MoS$_2$/graphene showed potential applications as an LIB anode material. It was suggested that a new electro-interaction between lithium and molybdenum metal that only occurs in the nano-regime could be enhanced by PEO additions. The addition of 2 wt% of graphene to the nanocomposites greatly increased the rate capability with rates as high as 10 000 mA g$^{-1}$, recovering to >600 mAh g$^{-1}$ at 50 mA g$^{-1}$ (figure 14).

In some early studies, MoS$_2$ was investigated as a cathode material for LIBs based on the intercalation reaction. However, the relatively low average voltage and energy density make MoS$_2$ cathodes less attractive. Addressing these issues, Li et al. [64] systematically investigated the adsorption and diffusion of the Li atom in MoS$_2$ bulk, bilayer, monolayer and zigzag MoS$_2$NRs (Z-MoS$_2$NRs) by means of density functional theory calculations and explored the potential of using the MoS$_2$ monolayer and Z-MoS$_2$NRs as cathode materials of LIBs.

Furthermore, MoS$_2$ was demonstrated to act as a useful doping compound of other LIB electrode materials. Iron trifluoride (FeF$_3$) is the most typical transition metal fluoride, and the electrochemical performance was first studied by Arai et al. [65]. Wu et al. [66] prepared MoS$_2$-doped FeF$_3$ through mechanical milling and studied its performance as an LIB electrode material. The obtained FeF$_3$/MoS$_2$ sample displayed typical orthorhombic structure. The electrochemical
tests showed that, for pure FeF₃, the capacity was only 58.5% after 30 cycles, while for FeF₃/MoO₂, the initial capacity of FeF₃/MoO₂ was 169.6 mAh g⁻¹, and after 30 cycles the discharge capacity was still 141.0 mAh g⁻¹ and the capacity retention ratio was 83.1%, which was ascribed to the MoO₂ doping and improvement of FeF₃ electronic conductivity.

4.2. Synthesis of MoO₂ and its application as an electrode material for LIBs

MoO₂ has been considered as a promising anode electrode material for Li ion batteries because of its high theoretical capacity. MoO₂ has a higher mass density of 6.5 g cm⁻³ than that of graphite (2.3 g cm⁻³), which enables MoO₂ to store more energy with the same size of the battery. The theoretical capacity of MoO₂ as LIB anode material is calculated to be 838 mAh g⁻¹ [11-13]. Unfortunately, the low storage capacity of the bulk MoO₂ material results from the lithiation of the bulk MoO₂ electrode that is limited to the addition-type reaction with only one-electron reduction at room temperature. Moreover, the morphological properties are found to play an important role in their lithium-intercalation activity and cycling stability.

In the last few years, a wide variety of approaches have been pursued to synthesize different nanostructured MoO₂. It was found that different nanostructures of MoO₂ may lead to different diffusion lengths and different stored amounts of Li⁺. The earliest report is on the application of activated MoO₂ powder as LIB electrode material [67]. Since then, the ordered mesoporous metallic MoO₂ materials [26], hollow core–shell MoO₂ microspheres [68] and MoO₂ nanorods [69] have been extensively investigated. These nanostructured MoO₂ were reported to show apparently enhanced performance as LIB electrode materials. Ku et al [66] reported that the activated MoO₂ powder electrode delivers a reversible specific capacity that is close to the theoretical four-electron capacity (838 mAh g⁻¹) with an excellent cycle performance at room temperature. After that, Shi et al [26] found that mesoporous MoO₂ material exhibits a reversible electrochemical lithium storage capacity as high as 750 mAh g⁻¹ at C/20 after 30 cycles, rendering it a promising anode material for LIBs.

The research of MoO₂ as a LIB electrode material is not limited to creating a novel structure or to controlling the morphology. The elemental doping provides a favorable way of improving the performance of MoO₂. Nitrogen and carbon are the mostly applied elements for doping the MoO₂ electrode. N doping is usually realized in a simple way, in which NH₃ is added as the nitrogen source during the synthesis of MoO₂. The resulting samples were characterized and the presence of molybdenum nitride (γ-Mo₂N and δ-MoN) and molybdenum oxynitride (MoO₂Nₓ) was clearly demonstrated [70]. It was found that the N-doped MoO₂ has good cyclic performance and stability. The improved electrochemical performance of the N-doped MoO₂ is attributed to the high electrical conductivity provided by nitrogen doping/or substitution in the oxygen octahedral site of the MoO₂ structure. C doping has also been widely studied and different carbon sources have been exploited. For instance, glucose was used as a favorable carbon source and the doping was realized by sintering the glucose–MoO₂ mixture at high temperature [71].

Graphene is also an ideal candidate for incorporation with MoO₂ to improve the electrochemical performance of the LIB anode. Sun et al [72] reported the process of MoO₂/graphene in a facile solution-based method combined with a subsequent reduction process, as shown in

**Figure 14.** Comparison of the rate capabilities for pure exfoliated MoS₂, MoS₂–P and MoS₂–PG composites. (Reproduced with permission from [63] © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

**Figure 15.** (a) Schematic representation of the fabrication process of the MoO₂/graphene hybrid. (b) Discharge and charge curves at a current density of 1000 mA g⁻¹ in the range of 0.01–3 V versus Li. (Reproduced with permission from [72] © 2011, American Chemical Society.)
Figure 15(a). They finally obtained the large-scale fabrication of unprecedented self-assembled hierarchical MoO2/graphene nanoarchitectures.

Figure 15(b) shows the discharge and charge curves for the MoO2/graphene hybrid. In the first cycle, no obvious potential plateau appears. From the second cycle on, the capacity of the electrode does not decay, and over 70 cycles, it reaches 597.9 mAh g\(^{-1}\) with a Coulombic efficiency of \(\sim 98\%\).

The electrode made of the MoO2/graphene hybrid exhibits excellent cyclic performance at current densities of 500, 1000 and 2000 mA g\(^{-1}\). In particular at the current density of 500 mA g\(^{-1}\), the capacity is as high as 848.6 mAh g\(^{-1}\) after 70 cycles, even higher than the theoretical capacity of both bulk MoO2 (838 mAh g\(^{-1}\)) and graphite (372 mAh g\(^{-1}\)).

5. Outlook

In this review, we have summarized the recent progress of MoS2 and MoO2 for their applications in the fields of hydrogen generation and LIBs. In particular, we have described the recent advances of structure control, elemental doping and synthesis methods for preparing MoO2 and MoS2. Mo is a relatively abundant metal and much cheaper than Pt, and the Mo compounds may play important roles for developing low-cost, highly efficient, green and reliable catalysts in future. Here, we emphasize their potential advantages as an advanced energy material in energy conversion and storage.

Due to the remarkable potentials of electrocatalytic and photoelectrocatalytic hydrogen production from water, much effort has been focused on finding cheap and efficient catalysts for HER. Both MoO2 and MoS2 could function as electrocatalysts for HER, in which the active sites are believed to also be active in photocatalytic HER. However, the photocatalytic properties of MoO2 and MoS2 have been relatively poorly understood over the past few years. MoS2 has been utilized to effectively remove pollutants through a photocatalytic oxidation. In spite of this, very few studies have reported on the direct use of MoS2 as a photocatalyst for HER, where the low activity is considered to be the major limitation. However, a major breakthrough is the application of MoS2 as a co-catalyst of other semiconductor catalysts for photocatalytic HER and several impressive results have been reported in recent years. For these newly developed catalysts, it should be noted that further studies are required to clarify the mechanism of photocatalytic processes and understand the detailed functions of MoS2. In addition, more elaborate studies are necessary to design the structure and control the morphology of MoS2. MoO2 is well studied as an electrocatalyst for HER, while its photocatalytic property has been overlooked. To the best of our knowledge, there is no report on photocatalytic water splitting by using the MoO2 catalyst. As the analogue of MoS2, it is believed that MoO2 may be further explored for photocatalytic water splitting after elemental doping or structure design to control the band gap.

MoO2 and MoS2 have been demonstrated to have significant advantages as LIB electrode materials. As anode materials, the high capacity and good cyclic stability of MoO2 and MoS2 make them possible replacements for commercialized graphite material. However, further studies are needed to improve their electric conductivity, decrease volume expansion during Li\(^+\) insertion/extraction and optimize synthesis methods before they could be considered for commercialization. To further explore these issues, it is assumed that the introduction of conductive components, doping with metal elements and search for new synthesis routes are the most likely choices for research into MoS2 and MoO2 as LIB electrode materials.

In conclusion, MoS2 and MoO2 have been experiencing a renaissance in recent years, largely owing to the demand for renewable hydrogen production and energy storage. Both MoS2 and MoO2 are emerging as excellent candidates to meet these applications. Although experimental results on a laboratory scale have been reported, the real application of MoO2 and MoS2 as catalytic or electrode materials is still challenging. This means that more encouraging studies are highly desirable in this field.

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