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Application of MoS_2 in the cathode of lithium sulfur batteries

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Molybdenum disulfide (MoS_2) with a two-dimensional layered structure can effectively inhibit the shuttle effect of lithium–sulfur batteries (Li–S batteries). It contains metal–sulfur bonds and combines with polysulfides through electrostatic bonds or chemical bonds. In this paper, the structure and properties of MoS_2 are briefly introduced, and the research progress on the design, preparation, structure and properties of MoS_2 as a cathode material for Li–S batteries in recent years is reviewed. The effects of MoS_2 structure and its composition with carbon materials or metallic oxides on the performance of the electrode materials are analyzed. Finally, the existing problems and possible future research directions are pointed out.

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1. Introduction

With the development of social economy and the continuous increase of the population in the world, the total amount of energy consumed by humans and society is increasing. Traditional energy production and consumption has caused global warming and ecological environmental destruction. At the same time, according to current energy consumption patterns, global fossil energy will be exhausted in the future. Therefore, energy storage and transformation is the key to coping with the climate crisis and achieving sustainable development of human society.[1]

Li–S batteries are rechargeable and generally consist of a sulfur-based cathode, binder, separator, organic liquid electrolyte, lithium anode and current collector. A schematic diagram of a Li–S battery is shown in Fig. 1.[2]

The working principle of Li–S batteries is shown in Fig. 2.[3] During the discharging process, sulfur in the solid phase ($S_{8(s)}$) is firstly dissolved in the electrolyte and then transforms to $S_{8(l)}$. Then $S_{8(l)}$ is gradually reduced to high-order lithium

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polysulfides (Li_2S_n, $4 \leq n \leq 8$), which are easily soluble in the electrolyte and diffuse from the cathode to the electrolyte. As discharge continues, the high order lithium polysulfides are further reduced to low order lithium polysulfides (Li_2S_2 and Li_2S) which are less soluble in the electrolyte. During the charging process, the discharge products (Li_2S_2 and Li_2S) are gradually oxidized to high order lithium polysulfides and eventually oxidized to elemental sulfur.

Metallic lithium has very high electro-negativity while possessing the lowest density among all metals, leading to its highest specific capacity (3861 mA h g^{-1}).[4] Element sulfur has a theoretical specific capacity of 1675 mA h g^{-1}.[5] Thus, Li–S batteries can reach high theoretical gravimetric and volumetric energy densities of 2500 W h kg^{-1} and 2800 W h L^{-1}, respectively. Given a complete reaction to Li_2S, the energy densities are 3–5 times as high as those of commercial lithium-ion batteries.[6,7] Moreover, sulfur also has the advantages of low cost, non-toxicity and high storage capacity as compared with that of conventional lithium-ion batteries.[8] Furthermore, Li–S batteries have more possibility of commercialization than lithium-air batteries. Therefore, Li–S batteries have good application prospects in energy storage to reduce the use of fossil fuels and protect the environment.

2. Research situation of Li–S batteries

The development of Li–S batteries was initiated in 1962. Herbert[9] was the first person to have the idea to use sulfur as the cathode in Li–S batteries. General Motors also proposed to use sulfur as an active material for thermal batteries and put the batteries into early electric vehicle projects.[10] In 1976, Whittingham *et al.*[11] successfully researched Li–TiS_2 secondary batteries using layered TiS_2 as the cathode and metal lithium as the anode. However, it failed to be commercialized due to safety problems such as "lithium dendrites". In 2009, Nazar[12] with his team in Canada stimulated attention toward Li–S batteries when they successfully compounded high performance cathode materials of Li–S batteries with ordered mesoporous carbon CMK-3 and sulfur. At present, the representative manufacturers of Li–S batteries in the world are Sion Power, Poly plus and Moltech in the US, Oxis in the UK and Samsung in Korea, among which the US is expected to reach 500 W h kg^{-1} as the energy density of Li–S batteries in the coming years.

Although Li–S batteries have many advantages, there are many factors that have gravely hindered their commercialization, for example, the insulating nature of sulfur and the lower electronic and ionic conductivity of the discharging products result in poor electrode reaction kinetics,[13] and polysulfides formed in the cathode can be easily dissolved in the electrolyte and aggregate into the anode through the diaphragm during the charging and discharging processes. The redundant reaction is called the "shuttle effect" of polysulfides and results in capacity loss and cycling decay.[14–16] The volume expansion of sulfur during charging and discharging can be up to 80%. This causes

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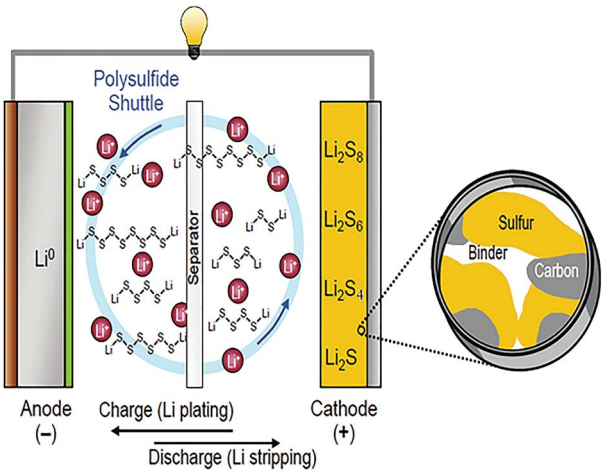

Fig. 1 Schematic diagram of a Li–S battery.[2]

the powdering and collapse of the electrode material and worsens the electrical contact between the electrode material and the collector. The decline of the lithium storage capacity will be accelerated to some extent as a result.[17]

There are two main research points in order to promote the commercialization of Li–S batteries. The first one is improving the conductivity of the cathode through compounding with high conductivity materials during the preparation of the initial electrode materials. The second one is adding materials that have high adsorption for polysulfides to inhibit the dissolution of polysulfides. Carbon materials have been paid more attention in recent years due to their excellent electrical conductivity, non-toxicity, and effective inhibition of the shuttle effect. However, the physically weak bonding between carbon and polysulfides is not strong enough to completely inhibit the shuttle effect. Instead, the application of transition metal sulfides can effectively solve this problem. The metal–sulfur bonds can combine with polysulfides through electrostatic or chemical bonds,[18] which can effectively inhibit the dissolution of polysulfides. The emergence of metal sulfides, such as MoS_2, has attracted researchers' attention.

3. Research situation of MoS_2 as a cathode material of Li–S batteries

MoS_2 is a kind of typical graphene-like two-dimensional layered transition metal sulfide. It has a high theoretical storage capacity of 670 mA h g^{-1} when it reacts with Li^+ according to the conversion reaction ($MoS_2 + 4Li^+ + 4e^- \rightarrow Mo + 2Li_2S$), which is much higher than that of graphene (372 mA h g^{-1}).[19] Each layer is composed of S–Mo–S by covalent bonding in a hexagonal sandwich-like structure. In other words, each layer of Mo is sandwiched between two layers of S atoms, and the layers are connected by weak van der Waals forces.[20] A schematic diagram of the structural unit is shown in Fig. 3.[21]

This special structure makes the interaction forces inside the layer strong, while the interaction between layers is relatively weak, and this makes it easy for external substances to be embedded.[22] At the same time, double-layer MoS_2 also has good storage capacity of charge, and the Mo atoms have an oxidation state from 2 valence to 6 valence. High theoretical lithium storage capacity is produced by these characteristics.[23] When used as the cathode material of Li–S batteries, the electrochemical reactions between MoS_2 and Li^+ are shown as follows:[24–26]

$$MoS_2 + xLi^+ + xe^- \rightarrow Li_xMoS_2, \quad (1)$$

$$Li_xMoS_2 + (4 - x)Li^+ + (4 - x)e^- \rightarrow Mo + 2Li_2S, \quad (2)$$

$$Li_2S \rightarrow S + 2Li \quad (3)$$

The strong adsorption of MoS_2 can prevent polysulfide groups from dissolving in Li–S batteries. Thus, it can ensure lower volume expansion and better cycling stability over several thousands of charge/discharge cycles. Fig. 4 illustrates the polysulfide immobilization and conversion processes on the surface of nitrogen-doped carbon@MoS_2 (NC@MoS_2). It is found that MoS_2 can accelerate the redox reaction kinetics through strong adsorption of polysulfides, fast electron transfer and catalysis for fast redox.

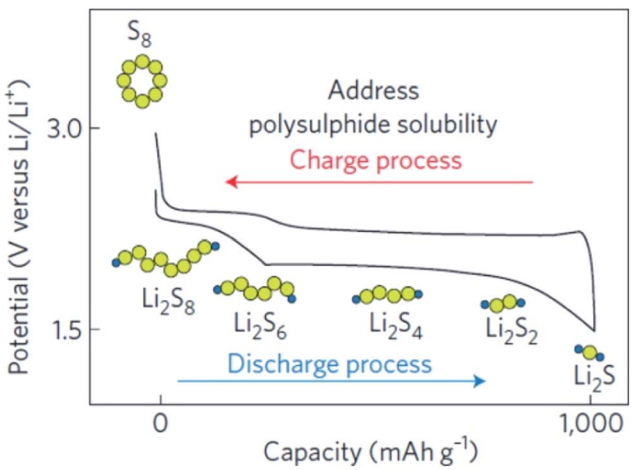

Fig. 2 Voltage profiles of a Li–S battery.[3]

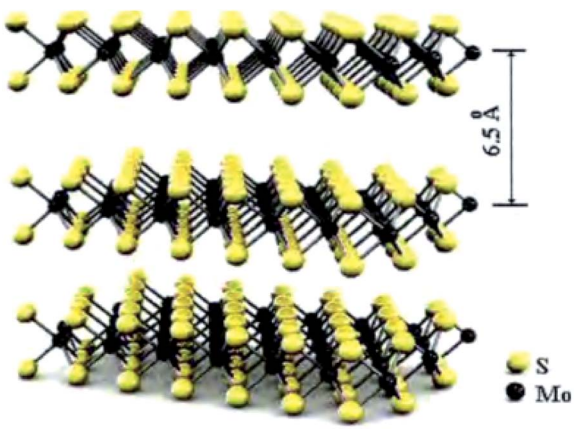

Fig. 3 Structural unit diagram of MoS_2.[21]

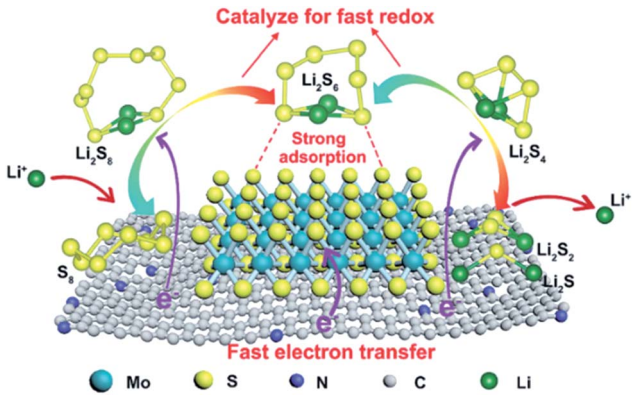

Fig. 4 Polysulfide immobilization and conversion processes on the surface of NC@MoS_2.[27]

Wu[27] proposed density functional theory (DFT) calculations to explore the catalytic effect of NC@MoS_2 on polysulfide demobilization and conversion. Soluble long-chain polysulfide Li_2S_6 was chosen as the prototype for calculations. Fig. 5(a–c) display the optimized geometries of Li_2S_6 adsorption on carbon matrix, NC, and MoS_2 (001) surfaces. The adsorption energies for NC and MoS_2 are −0.66 and −0.57 eV respectively, which are larger than that of a pure carbon matrix. This indicates a stronger polysulfide adsorptivity. Therefore, MoS_2 possesses superior anchoring ability for polysulfides.

Then, symmetric cells with a Li_2S_6 catholyte were assembled to study the transition kinetics of polysulfide conversion. As shown in Fig. 5(d), CP-NC@MoS_2 electrodes exhibit a decreased charge-transfer resistance, implying enhanced reaction kinetics of polysulfide conversion. Fig. 5(e) shows the CV curves of Li_2S_6 symmetric cells recorded at 50 mV s^{-1} within a voltage window of −1.0 V to 1.0 V. The CP-NC@MoS_2 electrode shows significantly increased redox currents, further confirming faster redox kinetics in the soluble region.

Remarkably, the effective polysulfide adsorption ability and high electronic conductivity of MoS_2 enable fast redox of Li–S batteries. Therefore, MoS_2 plays a dominant role in the redox reaction kinetics of polysulfide conversion.

Fig. 6 shows the energy profile of polysulfide conversion on a MoS_2 (001) surface.[28] It was confirmed that MoS_2 participates in the polysulfide conversion and accelerates the kinetics of the polysulfide redox reactions in Li–S batteries. The polysulfide conversion on the MoS_2 (001) surface undergoes a "lithiation-cleavage–lithiation-cleavage–lithiation-cleavage" mechanism from the reactant S_8@MoS_2 to the product Li_2S@MoS_2. The polysulfides need to coordinate with the MoS_2 surface to accelerate electron transfer, and the system energy decreases significantly after reduction. The fast conversion of the soluble

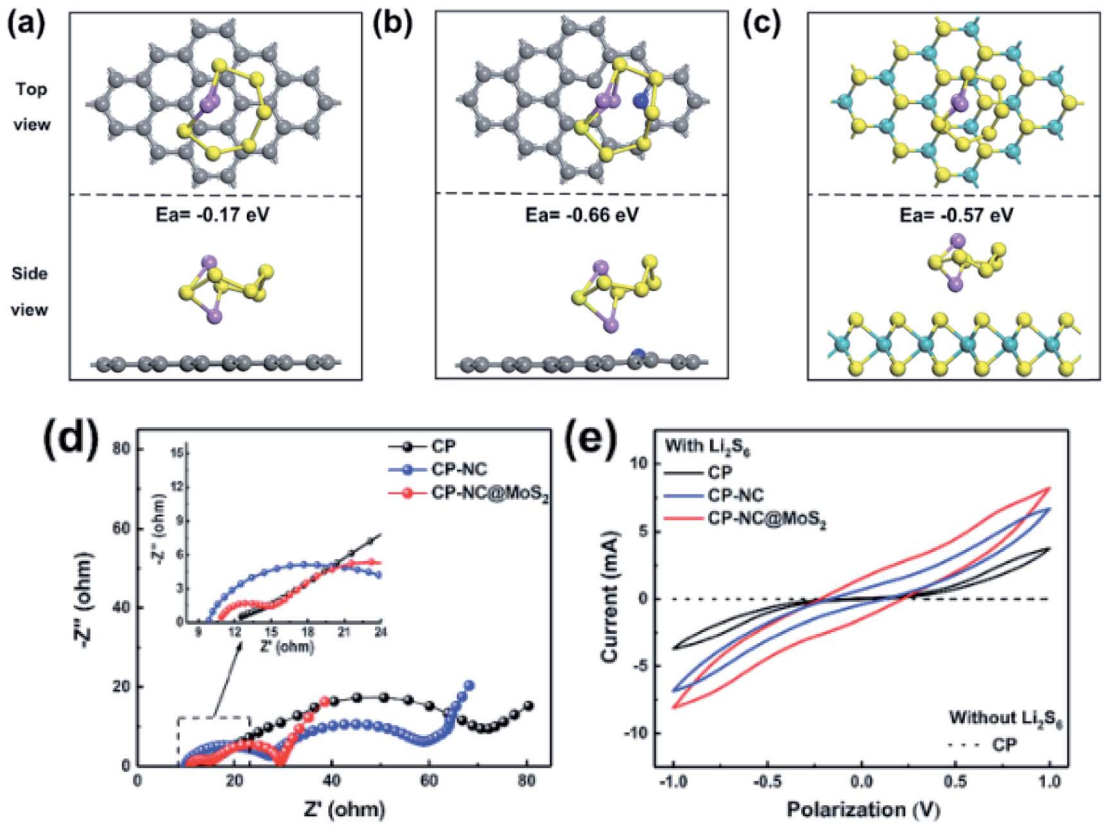

Fig. 5 Optimized geometries of Li_2S_6 on (a) carbon matrix, (b) NC, and (c) MoS_2 (001) surfaces, in which grey, yellow, blue, purple, and green spheres represent C, N, S, Li, and Mo, respectively; Nyquist plots (d) and CV (e) curves of Li_2S_6 symmetric cells employing CP, CP-NC, and CP-NC@MoS_2 as working electrodes.[27]

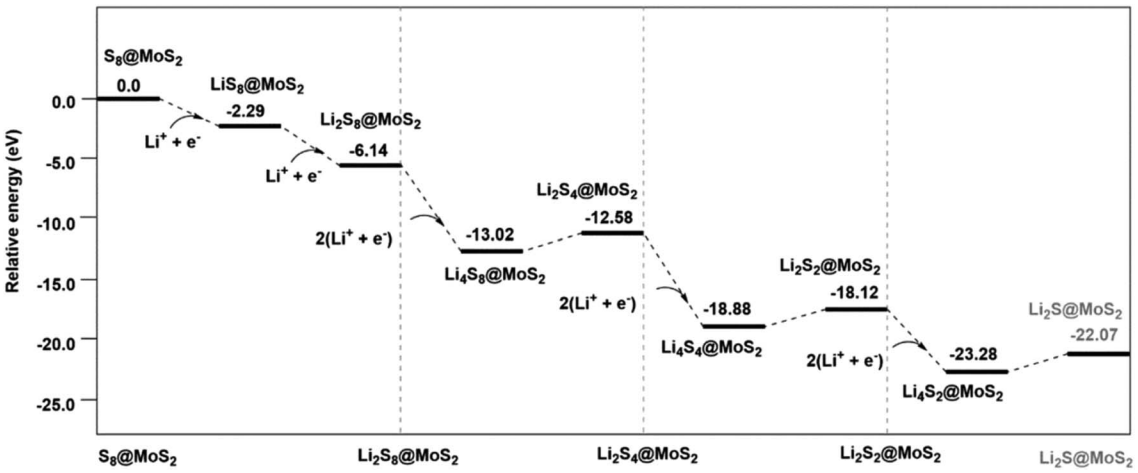

Fig. 6 Energy profile of the polysulfide conversion mechanism on the MoS_2 (001) surface.[28]

polysulfides decreases their accumulation in the sulfur cathode and inhibits their subsequent loss from the cathode. The suppression of this loss mechanism leads to a more sustained cyclability.[29,30]

3.1 Effect of MoS_2 structure on electrical properties

A change in the MoS_2 structure has a great influence on the capacity and cycling stability of electrode materials.[31] Therefore, optimizing the structure of MoS_2 nanomaterials can effectively improve the electrochemical performance of Li–S batteries. There are three main types: one-dimensional MoS_2 like nanotubes, two-dimensional MoS_2 like nanosheets, and three-dimensional MoS_2 like nanoparticles, nanoflowers and other special nano-structured cathode materials.

3.1.1 One-dimensional MoS_2 nanomaterials. Qiu[32] synthesized tubular MoS_2/S composites with a template method. The tubular structure has double the surface area and is favorable for the fixation and infiltration of sulfur into the MoS_2 nanotubes as shown in Fig. 7. The initial capacity of the tubular MoS_2/S composites can reach 650 mA h g^{-1} at 100 mA g^{-1}. However, the reversible specific capacity decreases to 450 mA h g^{-1} after 50 cycles. The electrochemical properties are not good. MoS_2 and sulfur can be compounded to some extent, but sulfur cannot well penetrate into the tube to form a MoS_2/S composite, and only mixing of the two phases can occur.

However, Qiu did not point out the mechanism of inhibiting the shuttle effect of MoS_2 nanotubes in Li–S batteries. There are few reports on the application of one-dimensional MoS_2 nanomaterials in Li–S batteries at present, and further study in this area is required. If MoS_2 nanotubes with a mesoporous structure can be synthesized, the loading rate of sulfur and the cyclic properties of the electrode materials will be greatly improved. This structure contributes to the inflow of sulfur through the micropores of the MoS_2 nanotubes at 155 °C (at 155 °C, the S_8 is mainly short linear sulfur chains, and the viscosity of molten sulfur is the lowest[33]). On the one hand, MoS_2 nanotubes have double the surface area, so the loading of sulfur is increased, and more reactive sites are provided for the electrochemical reaction. On the other hand, in the process of electrochemical reaction, molybdenum polysulfides can be controlled or adsorbed inside the MoS_2 nanotubes, which can inhibit the shuttle effect of Li–S batteries.

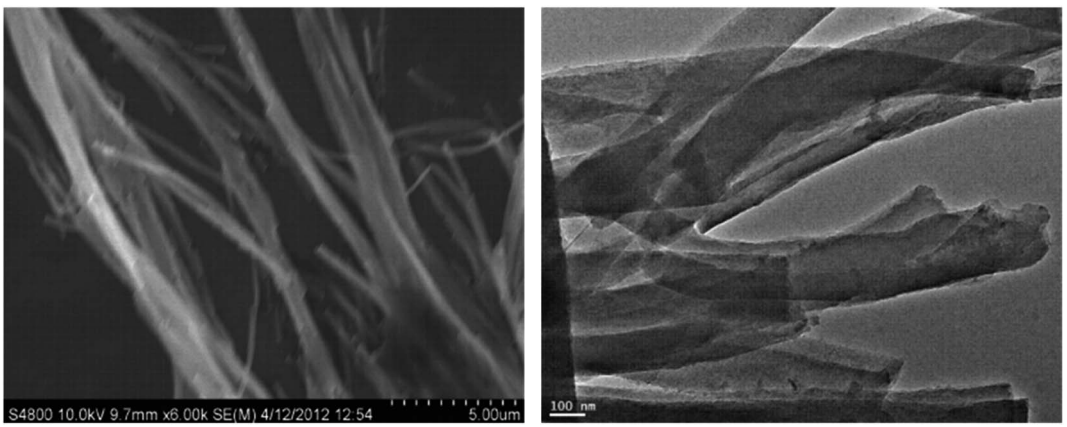

Fig. 7 TEM image of MoS_2 tubes.[32]

3.1.2 Two-dimensional MoS_2 nanomaterials. Two-dimensional nanomaterials have been extensively studied due to their special structures and excellent physical properties, such as high specific surface area. Two-dimensional structures can form networks through overlapping and stacking. They also have a large surface area which can provide more reactive sites and an open pore structure. These properties are very helpful for enabling effective anchoring of polysulfides and enhancing the reaction kinetics.[34]

Zhao[35] proposed a MoS_2/mesoporous carbon hollow sphere (MCHS) structure as an efficient sulfur cathode in order to deal with the shuttle effect, avoid active material loss and prevent performance decay of Li–S batteries. Ultrathin multi-layer MoS_2 nanosheets are uniformly distributed in the mesoporous carbon hollow spheres, enhancing the physical adsorption and chemical entrapment functionalities towards the soluble polysulfides. Polar MoS_2 can trap polysulfides *via* strong chemical bonds, so the polysulfides are largely fixed and remain inside the conductive MCHS as shown in Fig. 8. Benefiting from these structural advantages, the sulfur-impregnated MoS_2/MCHS cathode presents remarkable electrochemical performance.

Zhao[36] studied MoS_2 nanosheets by liquid phase exfoliation. As shown in Fig. 9, the layered MoS_2 nanosheets can achieve a good coordination with graphene and control polysulfides on graphene. Yu[37] deposited an ultrathin layer of MoS_2 (10–40 nm) nanoflakes by a liquid-based self-assembly method in the cathode of Li–S batteries. The results show that the reversible specific capacity reaches 1010 mA h g^{-1} at 0.5C, and the capacity fading is 0.11% per cycle over 400 cycles. The MoS_2 interlayer inhibits polysulfide diffusion across the separator and remarkably improves the battery performance. Moreover, the MoS_2 films with a high density of catalytic active edges can achieve high areal sulfur loading.

There are still many researchers studying the application of two-dimensional MoS_2 in Li–S batteries.[38–41] Many properties of two-dimensional MoS_2 are highly sought after for application in batteries. Two-dimensional MoS_2 has a large surface area, while maintaining a low size, especially thin-layer MoS_2, which can provide more active sites, and the electrode materials and electrolyte can fully contact each other. This is helpful to realize fast electrochemical reaction kinetics. In addition, the thin layer of MoS_2 can achieve a good match with graphene, improving the capacity of the electrode materials.[42] At the same time, it can effectively inhibit the shuttling of polysulfides. At present, the preparation methods of thin layer MoS_2 mainly include the stripping method,[43] high temperature solid phase method,[44,45] template method[46] and hydrothermal method.[47] The MoS_2 layers are connected with each other by weak van der Waals forces, and delamination can be realized in theory. However, the prepared MoS_2 in most actual exploration processes is a small amount of thin layer only in the liquid state. Therefore, it is difficult to realize a large number of thin layer products of MoS_2, which has become the main difficulty in their exploration.

3.1.3 Three-dimensional MoS_2 nanomaterials. For three-dimensional nanomaterials, electrons can move freely in all three dimensions. Different morphologies, such as nanoparticles and nanoclusters, have diverse properties.

At present, the design of nano-core-shell structures has become a research hotspot. This is because the core structure can provide supportive materials for the synthesis of MoS_2 shell structures, which can fix polysulfides inside the shell, effectively inhibiting the dissolution of polysulfides, and improving the material's reversible cycling performance. Cheng[48] synthesized a core–shell structured MoS_2@S cathode material through a chemical route using $MnCO_3$ as a template, as shown in Fig. 10. A picture of the core–shell structured MoS_2@S is shown in Fig. 11. The initial discharge capacity of the material is 800.6 mA h g^{-1} at 1C rate, and the capacity retention rate is 79% after 200 cycles. For comparison, a MoS_2/S cathode was also synthesized. It is found that the electrochemical performance of the core–shell structures MoS_2@S cathode is much improved as compared with the MoS_2/S composite. The high capacity and cycling stability of MoS_2@S cathode materials are attributed to the mechanical inhibition and chemical combination of the polar MoS_2 shell with lithium polysulfides, which further illustrates that the core–shell structure of MoS_2@S can effectively inhibit the shuttling of polysulfides.

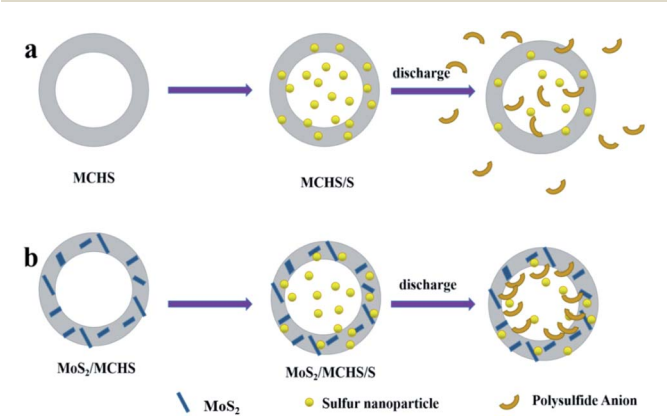

Fig. 8 Proposed adsorption mechanism of polysulfides for the (a) MCHS/S and (b) MoS_2/MCHS/S electrodes.[35]

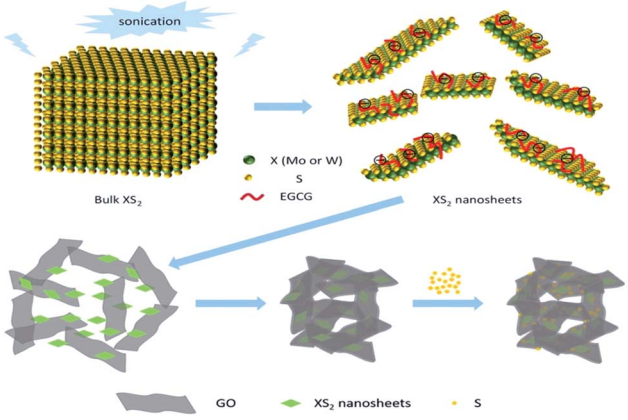

Fig. 9 Proposed adsorption mechanism of polysulfides for XS_2 (Mo or W).[36]

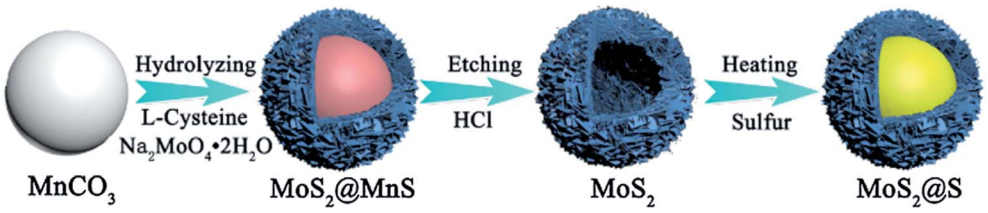

Fig. 10 Schematic of the synthesis route of the core–shell structured MoS_2@S spherical cathode.[48]

Other researchers have also[49–53] devoted their attention to the application of core–shell structured MoS_2 nanocomposites. The double-layer core–shell structure has good prospects. This special structure can effectively alleviate the shuttle effect of batteries. On the other hand, it can improve the sulfur loading rate and buffer the volume expansion of sulfur during the charging and discharging processes. However, the sulfur load is hard to improve, because the infiltration of sulfur is often not sufficient and uniform. And in the process of experiments, superior formation conditions of the core–shell structure need to be explored when the repeatability is not high.

Flower-like nanomaterials have a large surface area because of their unique and complex morphology. Therefore, the application of flower-like nanomaterials in the cathode of Li–S batteries can effectively improve the loading rate of sulfur and the capacity of the batteries. Tang[54] synthesized MoS_2 nanoflowers consisting of many irregular MoS_2 nanosheets with an average diameter of about 1–2 μm by a facile CTAB-assisted hydrothermal method at 180 °C for 24 h. Zhang[55] successfully synthesized high-purity MoS_2 nanoflowers by a hydrothermal method. The particle diameter is around 300 nm, consisting of tens of hundreds of MoS_2 petals, and the thickness of each layered petal is about 10 nm. Through gradient experiments, it was found that silicotungstic acid played an important role in the formation of the nano-flower MoS_2. Xiong[56] fabricated hierarchical porous MoS_2/C flower-like microspheres as shown in Fig. 12. The initial discharge capacity of the porous MoS_2/C flower-like microsphere electrode was 1125.9 mA h g^{-1}. The discharge capacity remained at 916.6 mA h g^{-1} after 400 cycles at 200 mA g^{-1}. This is attributed to the unique porous composite structure of MoS_2/C effectively improving the contact area between the active substances and electrolytes. This also provides more channels for the rapid transmission of electrons and ions during charging and discharging, contributing to a fast kinetic reaction and effectively improving the electrochemical performance of the batteries.

Flower-like nanomaterials have been studied a lot among all kinds of battery materials, because the flower structure has a large specific surface area, which can effectively improve the loading of active materials. Compared with the core–shell structure, the synthesis process is relatively mature, and has been widely studied.[57,58]

Therefore, different structures of MoS_2 have great impacts on the electrochemical properties of materials. In the current research, three-dimensional MoS_2 is widely researched as the cathode material of Li–S batteries, while the research of two-dimensional MoS_2 is mostly conducted in the diaphragm. Few research studies have paid attention to the application of one-

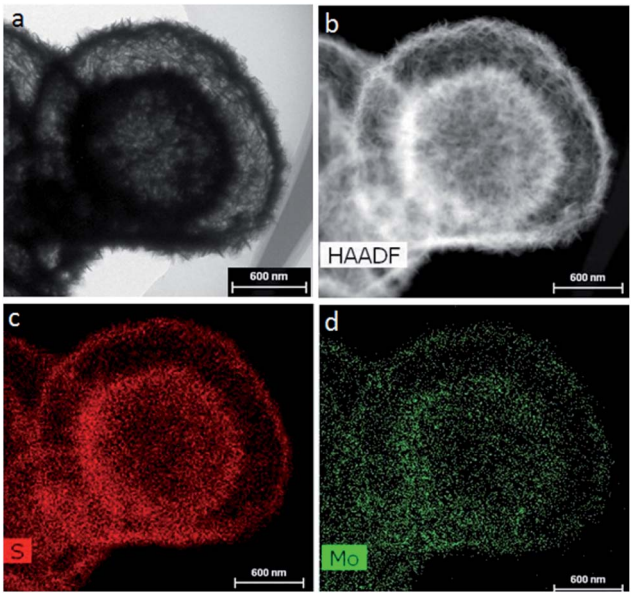

Fig. 11 (a) TEM image, (b) HAADF image, and (c) S and (d) Mo element mapping of the MoS_2 shells.[48]

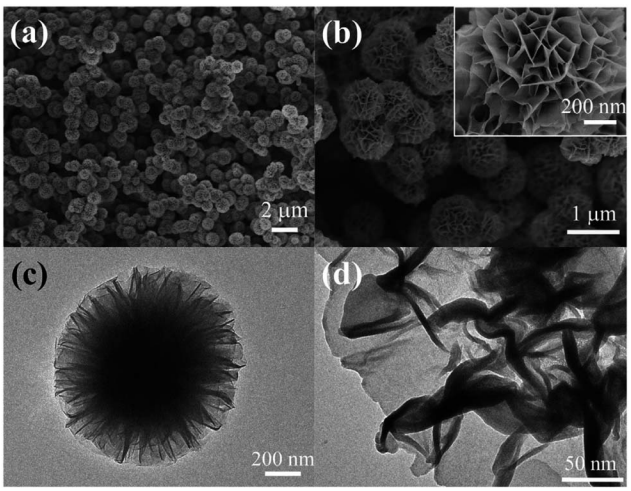

Fig. 12 Morphological and structural characterization of the MoS_2/C flower-like microspheres: (a and b) FESEM images with low and high magnification, respectively; (c and d) TEM images with low and high magnification, respectively.[56]

dimensional MoS_2 in Li–S batteries, which is worth exploring. Nano-mesoporous materials have the advantages of high specific surface area, well-ordered channels, high porosity and good thermal stability. As a battery material, they can retain high porosity and uniform aperture distribution on adjusting the size of the material. So the design of mesoporous MoS_2 nanomaterials can improve the reversibility, rate performance of discharge and cycling life of electrode materials.[59–62]

3.2 Preparation and properties of MoS_2/carbon composite cathode materials

In spite of many advantages, MoS_2 has another serious disadvantage: poor conductivity which cannot guarantee rapid electron transfer in the process of electrode reaction. Therefore, simple structure design of MoS_2 is not enough for high-rate performance. At present, conductive nanoporous MoS_2 cathode materials with excellent electrochemical properties have been put forward, such as MoS_2/carbon nanocomposites.[63,64] Carbon materials that have an interconnected conductive network structure can effectively improve the conductivity and dynamic performance of electrodes.[65] It has been found that the strong chemical and electronic coupling between MoS_2 nanoparticles and graphene nanosheets could allow rapid electron transportation through the conductive graphene substrate.[66,67]

At present, the synthesis methods of MoS_2/carbon composites in Li–S batteries are mainly based on chemical methods. They include vapor phase synthesis, like chemical vapor deposition, and liquid phase methods, such as hydrothermal methods, solvothermal methods, template methods, thermal decomposition and precipitation methods, *etc.*

3.2.1 Chemical vapor deposition. Chemical vapor deposition (CVD) is a direct synthesis method to obtain a uniform MoS_2 coating on targeted carbon substrates. Namjo *et al.*[68] obtained a uniform MoS_2 coating on the surface of porous carbon structures with nano-sized pores by chemical vapor deposition. Mugyeom *et al.*[69] synthesized MoS_2–SRGO composites by one-pot deposition of MoO_2 on SRGO and simultaneous reduction of GO to SRGO in supercritical methanol followed by sulfurization. The obtained MoS_2–SRGO composites contain an 11–14 layer crystalline MoS_2 phase.

However, the deposition temperature of CVD is relatively high, generally at 900–1200 °C, which is not conducive to the preparation of inorganic materials. In recent years, with the improvement of industrial production requirements, the process and equipment of CVD have been continuously improved. Not only are a variety of new heating sources used, but also auxiliary methods such as plasma, laser and electron beam are used to reduce the reaction temperature, making its application scope wider.[70,71]

3.2.2 Hydrothermal methods. Hydrothermal methods are a common method for material preparation. Ren[72] prepared multi-dimensional N-doped porous carbon/MoS_2/CNT nanostructures by a facile hydrothermal process. The synergistic action of polar MoS_2 and porous carbon imbedded with electroconductive acid–CNTs could construct a conductive network for the rapid transfer of ions/electrons. As the cathode of Li–S batteries, N-doped porous carbon/MoS_2/CNT nanostructures deliver a high discharge capacity of 1313.4 mA h g^{-1} at 0.1C and good cycling stability with an average capacity fade of 0.059% per cycle after 500 cycles at 1.0C. This can significantly strengthen the chemical attraction with polysulfides. Chen[73] prepared graphene-like-MoS_2/graphene (GL-MoS_2/G) composites by a hydrothermal method assisted with cetylammonium bromide cationic surfactant and subsequent heat treatment. You[74] prepared a three-dimensional porous MoS_2/rGO foam based sulfur cathode by a facile hydrothermal method. Few-layer MoS_2 nanosheets with mixed 1T and 2H phases were developed on reduced graphene oxide, forming a continuous 3D porous network.

Solvothermal reactions are a development of hydrothermal reactions, where the reaction occurs in an organic solvent or non-aqueous solvent (such as organic amine, alcohol, ammonia, carbon tetrachloride or benzene, *etc.*).

Huo[75] prepared S/N co-doped reduced graphene oxide modified with MoS_2 by a one-pot solvothermal method with L-cysteine mixed in ethylene glycol. The specific surface area of this compound gel was estimated to be 151.41 m^2 g^{-1}. Its large specific surface area can promote the contact between the electrode and electrolyte, and the porous structure provides transport channels for electrons and ions. Electrochemical tests revealed that the capacity retention of the electrode was 91.32% after 500 cycles. The size and morphology of the phase particles can also be controlled by a solvothermal method, and the product also has good dispersion.

Hydrothermal methods can directly obtain powders with high purity, good dispersity and good crystal shape, with no need for burning treatment at high temperature, and the preparation process is relatively simple and the production cost is relatively low.[76] However, solvothermal reactions are not as safe as hydrothermal reactions according to practical experience. So it would be better to avoid reactions that produce large quantities of gases and heat in solvothermal reactions.

3.2.3 Template methods. Template methods are a very important technique to synthesize nanocomposites. Jiang[77] synthesized nitrogen-doped hollow mesoporous carbon spheres (NMCS) using SiO_2 as a template. Wang[78] synthesized TiO_2 nanotubes using MnO_2 nanowires as templates and coated them with nitrogen-doped carbon (NC). Ultra-thin MoS_2 nanosheets were grown on them by a hydrothermal method to obtain layered nanostructures of TiO_2@NC@MoS_2. Yin[50] firstly prepared MoS_2 and carbon on the surface of SiO_2 nanoparticles as a sacrificial template by a sol–gel method with CTAB. Then, MoS_2/carbon hollow microspheres wrapped with petaloid MoS_2 lamellae and amorphous carbon were prepared by alkali liquor etching of the silica microsphere matrix. The average diameter of the MoS_2/C hollow microspheres was approximately 200–300 nm. As the cathode material of a lithium battery, the first charge–discharge capacity was more than 1400 mA h g^{-1} at a current density of 100 mA g^{-1}. This technique has the following advantages: simple experimental device, high flexibility, accurate control (size, morphology and structure), and

effective prevention of agglomeration. Therefore, it has attracted wide attention.[79]

3.2.4 Thermal decomposition methods. Li[80] successfully studied MoS_2-decorated coaxial nanocable carbon aerogel composites (MoS_2/CNCA) by phenolic reaction and treatment at high temperature in a sulfur atmosphere. The MoS_2-decorated carbon aerogel (CA) with carbon nanotubes as fine wires presented a narrow distribution of pore size, an interconnected structure and high conductance. The discharge capacity was 1314 mA h g^{-1} at 0.2C with the capacity retention of 81% after 200 cycles. These improved results can be attributed to MoS_2 as a network entangled structure. However, the reaction is usually endothermic as heat is required to break chemical bonds in the compound. If decomposition is sufficiently exothermic, it can easily lead to thermal runaway and possibly an explosion.

In summary, hydrothermal methods and template methods are widely applied at present in the synthesis of Li–S battery cathode materials. Hydrothermal methods can synthesize nanomaterials in different dimensions in one step, such as nanotube structures, two-dimensional nanosheet structures, three-dimensional nanoflower-like structures, and hierarchical porous structures. The template method is more conducive to synthesizing core–shell structures, and it provides a good idea for solving the shuttle effect of Li–S batteries. In addition to the above methods, physical methods such as stripping and vacuum condensation, and chemical methods such as precipitation are also commonly used to prepare nanomaterials. However, these methods are less used to prepare MoS_2 cathode composites for Li–S batteries.

3.3 Preparation and properties of MoS_2/metal oxide composite cathode materials

Metal oxides, which have chemical bonds or electrostatic adsorption with polysulfides, can effectively inhibit the shuttling of polysulfides and improve the charge–discharge performance of materials as cathode materials of Li–S batteries. Zhang[81] synthesized MoS_2/SnO_2 nanocomposites by a two-step hydrothermal method, and SnO_2 was uniformly loaded on the surface of the MoS_2 nanosheets. After loading SnO_2 nanoparticles, the diffusion of lithium polysulfides was greatly inhibited, and the conductivity of the material was also improved by embedding Mo atoms. Xu[82] first prepared TiO_2@PNT coaxial nano-materials by a sol–gel method. Porous TiO_2 nanotubes were obtained by roasting the PNT template in air. Furthermore, MoS_2 nanosheet@TiO_2 nanotube structures were successfully prepared by a solvothermal method. Porous TiO_2 nanotubes as supporting materials slow down the agglomeration of MoS_2 and make it distribute more uniformly. This intelligent design has remarkable lithium storage performance.

The use of metal oxides in cathode materials of Li–S batteries is of great significance. However, excessive introduction of metal oxides will affect the overall energy density of the batteries because of the high density of metal oxide. Moreover, their conductivity cannot meet the needs of cathode materials. Therefore, there are few studies on the application of MoS_2 and metal oxides in Li–S battery cathode materials, and most of the current studies are on lithium-ion battery electrode materials.

4. Conclusions

As the cathode material of Li–S batteries, MoS_2 can accelerate the redox reaction kinetics during the discharge/charge process through strong adsorption of polysulfides, fast electron transfer and catalysis for fast redox. It has great potential advantages for Li–S batteries.

(1) Strong adsorption of polysulfide lithium: as the cathode material of Li–S batteries, MoS_2 has a great advantage in reducing the "shuttle effect" that has gravely hindered their commercialization. MoS_2 has strong adsorption for sulfur-containing groups, thus preventing polysulfides from dissolving. Thus, it can ensure better cycling stability over several thousands of charge/discharge cycles.

(2) Graphene-like two-dimensional layered structure: MoS_2 is a kind of typical graphene-like two-dimensional layered transition metal sulfide. Each layer of Mo is sandwiched between two layers of S atoms, and the layers are connected by weak van der Waals forces. This special structure makes the interaction forces inside the layer strong, while the interactions between layers are relatively weak, and this makes it easy for external substances to be embedded, especially those having a good match with graphene.

(3) Good storage capacity: MoS_2 has a high theoretical storage capacity of 670 mA h g^{-1} when it reacts with Li^+, which is much higher than that of graphene (372 mA h g^{-1}). The Mo atom has an oxidation state from 2 valence to 6 valence. These characteristics determine its high theoretical lithium storage capacity. It can effectively solve the insulating nature and lower electronic and ionic conductivity of sulfur.

Many methods have been developed for the synthesis of MoS_2 nanocompounds, and hydrothermal methods and template methods are widely applied at present. Hydrothermal methods can synthesize nanomaterials in different dimensions in one step, such as nanotube structures, two-dimensional nanosheet structures, three-dimensional nanoflower-like structures, and hierarchical porous structures. Template methods are more conducive to synthesizing core–shell structures, and provide a good idea for solving the shuttle effect of Li–S batteries. The progress of these methods has made great contributions to the development of Li–S batteries.

Conflicts of interest

There are no conflicts to declare.

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