Advancement in Layered Transition Metal Dichalcogenide Composites for Lithium and Sodium Ion Batteries

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Abstract: With an ever increasing energy demand and environmental issues, many state-of-the-art nanostructured electrode materials have been developed for energy storage devices and they include batteries, supercapacitors and fuel cells. Among these electrode materials, L-TMD (layered transition metal dichalcogenide) nanosheets (especially, S (sulfur) and Se (selenium) based dichalcogenides) have received a lot of attention due to their intriguing layered structure for enhanced electrochemical properties. L-TMD composites have recently been investigated not only as a main charge storage specie but also, as a substrate to hold the active specie. This review highlights the recent advancements in L-TMD composites with 0D (0-dimensional), 1D, 2D, 3D and various forms of carbon structures and their potential applications in LIB (lithium ion battery) and SIB (sodium ion battery).

Key words: L-TMD based composites, energy storage devices, nanocomposites, LIBs and SIBs.

1. Introduction

With the fast depletion of current energy sources on the *pushed* end, coupled with the increasing energy demands at the *pulled* end, it is not difficult to understand that the World will need new power sources of nearly 30 TW (10^{12}) by 2050 [1]. This humongous new energy demand, together with the rising consumption of non-renewal fossil fuels (coal, oil, gas, etc.) and the difficult and often, conflicting environmental issues have created enormous pressures for the World to develop clean and sustainable technologies to rapidly provide for huge amounts of energy. It is necessary to develop renewable energy sources in order to fulfill the demands of modern society and eliminate environmental issues. In this regard, solar cells, fuel cell, wind and biomass-based energy are playing a vital role. To fully utilize these renewable energy resources, highly efficient, low cost, and environmental benignity energy storage systems

are required. Among various energy storage systems, batteries (e.g. LIBs/SIBs) are attractive candidates for renewable energy storage due to their low cost, high energy density and environmental benignity [2-5]. Nevertheless, many challenges are still big hurdle in their real application due to lower power density and poor cyclic life. For example, most of electrode materials used in batteries have low conductivity, which affect the storage of ions and rate performance. In addition, large volume expansion during charging/discharging processes produces the strains in electrode materials, which can cause the delamination of active materials from current collector, resulted in severe capacity fading and poor cyclic stability. Besides, during volume expansion or in morphological and structural changes in most of electrode materials, causes the formation of newly SEI (solid electrolyte interface film), consequences the irreversible loss of capacity [2]. Therefore, electrode materials with high specific surface areas, high conductivity which could provide large sites for intercalation of ions for both insertion and conversion processes are required,

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eventually providing opportunities to tailor high energy density and power density devices for practical applications.

In recent years, 2D layered materials have attracted enormous attention due to their unique physical, chemical and electronic properties [6-8]. Among various layered structures, graphene with its excellent properties (conductivity, large surface area, flexibility, and the ability to functionalize with other molecules) is probably the most popular as it possesses great potentials in Li-based batteries, supercapacitors, photovoltaic devices, fuel cells etc. [9-15]. With motivation from graphene, other layered inorganic nanomaterials, particularly L-TMD (layered transition metal dichalcogenides) such as MoS_2 , MoSe_2 , WS_2 , SnS_2 , SnSe_2 , etc. have also received wide attention from scientific communities [16-20]. They are compounds with the formula MX_2 , where M is a transition metal element of group IV-B (Ti, Zr, Hf, etc.), V-B (V, Nb, Ta, etc.), VI-B (Mo, W, Sn, etc.), and X is a chalcogen of the VI-A group (S, Se, etc.). In these materials, the interlayer atoms are strongly held together by covalent bonds, while the individual layers are weakly held in place by the van der Waal interaction to form a sandwich-like X-M-X structure, [21-23] where the M atom layer is sandwiched between the two X layers. These compounds have crystalline structure that varies from the hexagonal (MoS_2 and WS_2) to the orthorhombic (MoTe_2 and WTe_2). Such compounds are very important in industry and from scientific point of view, they are interesting. For instance, owing to their layered structure, MoS_2 and WS_2 have been utilized as dry lubricants in industry as they can withstand higher temperatures than graphite [24, 25]. In addition, L-TMD offers unique electronic, physical or chemical properties compared to its bulk counterparts and this makes it attractive for various applications [26, 27]. Moreover, due to their higher surface area and being active electronically and chemically, these 2D nanomaterials have been used in electronic/optoelectronic devices, sensors,

electrocatalysis, energy storage devices and many other applications [28, 29]. However, there are some challenges associated with these L-TMD NSs (nanosheets) in energy storage due to their inherent limitations [30]. For example, the low electronic conductivity of L-TMD NSs will affect their electrochemical performance, and they also suffer from large mechanical stress and volume change during charging/discharging, which can induce pulverization and aggregation of active electrode materials, resulting in poor cyclic stability.

To overcome the weakness of individual counterparts, the hybridization of two or more nanomaterials is an intriguing approach to engineer target materials with multifunctionalities, and improved properties for practical applications [31, 32]. Similar to 2D graphene, L-TMD NSs have also been incorporated into a number of materials to improve their electrochemical properties. With an ever-increasing demand for energy storage devices and increasing interest in L-TMD from the scientific community, we aim to give a mini-review of this immensely important and rapidly growing research field. First, we will elaborate various approaches for the preparation of L-TMD nanocomposites with 0D, 1D, 2D, 3D and others as shown schematically in Fig. 1. Then, we will highlight the promising application of these L-TMD composites in LIBs and SIBs. Hopefully, this article

Fig. 1 Schematic illustration of L-TMD composites with 0D, 1D, 2D, 3D.

will be beneficial to researchers and materials scientists.

2. Different Approaches to Prepare L-TMD-Based Composites

The charge storage capabilities of the electrode materials depend strongly on the exposed surface of the active materials. Owing to largely exposed external surface of TMD layers, the L-TMDs present unique materials (similar to graphene in some extent) with high surface area, which benefits from their ultrathin sheets and 2D morphology. However, the adjacent 2D layers can be easily restacked together under van der Waals interaction during cycling processes in batteries that resulted in a loss of the 2D structure and significant decreases of their active surface area. Hybridization of L-TMD with other functional material is an effective strategy to retain their inherent structure and hence, the inherent specific surface area for improved electrochemical response. Recently, there have been a lot of developments on the hybridization of L-TMD NSs with 0D (NPs (Nanoparticles)), 1D, 2D and 3D structures.

2.1 Composites of L-TMD with 0D (NPs) Structures

The electrochemical applications of L-TMD are undermined by poor conductivity and restacking (limiting effective surface area) during the reversible charge storage. A possible way to tailor the L-TMD materials with enhanced conductivity and good control over the surface area during cycling is to incorporate the 0D moieties (noble metal, and metal/metal oxide (NPs) etc.) in the layered structures which can provide charge carriers for enhanced conductivity and effectively limit the restacking of L-TMDs [33-38]. Such incorporation acts as a spacer to support the material, making the active surfaces of L-TMD accessible for electrolyte penetration lithiation/de-lithiation process improving electrochemical response of the LIBs. Recently, the incorporation of noble metals (Au, Ag, Pt, Pd) [38-41]

has been identified as a possible solution to improve the inherent conductivity of L-TMDs. For instance, Pan et al. [38] anchored the Ag NPs on MoS₂ NSs through coordination by using multifunctional organic ligand. Ag NPs not only improve the conductivity (due to the higher intrinsic conductivity of noble metals) but also, act as a spacer and inhibit the restacking or agglomeration of MoS₂. Further, due to the high inflexibility and low deformability of Ag NPs effectively preserve the composite structure [38]. Similarly, Chen et al. used ultrasmall (~3.5 nm) Fe₃O₄ NPs to decorate the MoS₂ NSs by a 2-part hydrothermal process. Authors argue that due to elastic and flexible nature, the MoS₂ NSs are more active electrochemically than reduced graphene oxide (rGO) and act as a better substrate for the growth of Fe₃O₄ NPs and accommodate the strain. The ultrasmall Fe₃O₄ NPs also act as spacer between the sheets of MoS₂ and prevent the composites from collapsing during charging and discharging in an LIB, whereas the L-TMDs without spacer tended to crumpled and agglomerate (Figs. 2a and 2b) [33], severely limiting the reversible capacity and cycling performance of the LIB. In similar attempts, metal NPs have also been decorated on MoS₂ NSs. For instance, Sn NPs were embedded in layered MoS₂ by two step hydrothermal method. The MoS₂-C hybrids were fabricated from Na₂MoO₄·2H₂O, NH₂CSNH₂ and glucose as source material by hydrothermal method with subsequent heat treatment in Ar atmosphere. The resultant product was then subjected to another hydrothermal reaction in presence of Sn precursor followed by final calcination in Ar [37].

Keeping in mind the individual advantages of noble metals and other metal nanostructures, the co-doping of noble metal along with electrochemical active metal nanostructures could effectively provide dual advantage of better conductivity and reversible capacity [34]. Recently, Pan et al. proposed the development of ternary heterostructures (Ag/Fe₃O₄/MoS₂) by one step, in which as prepared

Fig. 2 (a) TEM images and schematic illustration of pristine MoS₂; (b) Fe₃O₄/MoS₂ before and after 1180 cycles of charge/discharge [33]. (a, b) Reproduced with permission of John WILEY & Sons, Inc.; (c) Schematic illustration of Exfoliation of MoS₂ powder into NSs, mixing of exfoliated MoS₂ with Fe₃O₄ and Ag NPs and deposition of NPs on MoS₂ NSs through van der Waals interactions [34]. Reproduced with permission of The Royal Society of Chemistry.

Fe₃O₄, Ag NPs and exfoliated MoS₂ NSs were mixed in THF (tetrahydrofuran) by magnetic stirring and these NPs were spontaneously decorated onto naked surfaces of MoS₂ by van der Waals interactions (Fig. 2c) [34]. Here, Ag NPs enhance the intrinsic conductivity of composites while Fe₃O₄ stores lithium reversibly. Despite considerable efforts, it is a big challenge to obtain single layer as it is difficult to control the layer number by hydrothermal process and could be a topic for future research as it will not only provide the insertion and conversion sites for lithium storage, but also numerous interfacial Li storage sites.

2.2 Composites of L-TMD with 1D Structure

1D nanostructures have also been used to hybridize with L-TMD NSs to improve the reversible charge storage of electrode materials. As an attractive 1D nanostructure, single wall and/or MWCNT (multiwalled carbon nanotubes) have received a great

deal of attention due to their excellent mechanical and electronic properties. The 1D nature of the CNTs provides pathways for conduction during cycling, which make them excellent substrates for the growth of L-TMD NSs for Li storage [42-46]. Further, due to their high flexibility, CNTs also help to accommodate volume expansion of electrode materials during charging/discharging. Several efforts have been made to tailor efficient 1D electrode materials using CNTs as seed to grow L-TMD NSs. Ding et al. [42] used a simple hydrothermal approach for the growth of MoS₂ NSs on the surface of CNT from sodium molybdate hexahydrate and thiourea precursor in the presence of glucose. The synthesis method not only ensured homogeneous growth of MoS₂ on CNT surface but also, a good conductive network formed from pyrolysis of glucose, which ensured the excellent contact between CNT backbone and MoS₂ NSs. Recently, many nanostructured materials have been prepared by using

biomolecular-assisted synthetic approaches [43, 47]. Among numerous biomolecules, L-cys (L-cysteine) is very promising due to its special structure, which contains many functional groups ($-NH_2$, $-SH$, and $-COO$) and has been utilized as sulfur source and reductant in hydrothermal synthesis approaches. A simple hydrothermal method was used to synthesize CNTs-MoS₂ hybrid by reaction between sodium molybdate dehydrate and L-cys in the presence of acid treated CNTs with subsequent annealing treatment [43]. The electrostatic interaction between the negatively charged MWCNT and Sn⁴⁺ ion played a critical role for the decoration of SnS₂ NSs on MWCNT, followed by the nucleation and 2D growth of SnS₂ as shown in Fig. 3a. Besides, TMD-coated hybrid nanocomposites, single- or multi-layered MoS₂-embedded carbon nanotube/nanofibers or nitrogen doped CNF (carbon nanofibers) have also been reported [48-50]. Kong et al. [49] fabricated MoS₂ NSs embedded-graphitic nanotubes structure in which graphene rolled up into hollow nanotubes and thin MoS₂ NSs were standing on the inner surface of graphitic carbon. Recently, the electrospinning method has been identified as an excellent way to obtain single layers of L-TMD NSs and this is demonstrated by the electrospun single layers of WS₂ nanoplates that were homogeneously embedded in NCNFs (nitrogen-doped carbon nanofibers) [50].

Additionally, L-TMD NSs have also been decorated on the non-carbon based 1D structure. For example, several layers of MoS₂ NSs were decorated on TiO₂ nanotubes/nanowires/nanobelts by the hydrothermal/solvothermal approach [51-53]. Li et al. fabricated a hierarchical nanocomposite, in which MoS₂ NSs were coated on 1D TiO₂ nanowires by a cost-effective glucose-assisted hydrothermal route as illustrated in Fig. 3b. The robust nature of TiO₂ served as the effective template for the growth and nucleation of the layered-MoS₂ NSs. Both the roughness of TiO₂ and glucose played an important role in homogenous coating of MoS₂ NSs in the composite [52]. However,

Fig. 3 (a) Schematic representation for the synthesis process of the SnS₂ NS@MWCNTs coaxial nanocables [45]. Reproduced with permission of American Chemical Society; (b) Schematic description of the growth process of the TiO₂@MoS₂ nanocomposite [52]. Reproduced with permission of The Royal Society of Chemistry.

uniform and controllable deposition of MoS₂ on TiO₂ surface is still a big challenge due to its poor affinities and chemical reactions.

2.3 Composites of L-TMD with 2D Structure

The excellent properties of L-TMDs have been further exploited by growing them on flexible 2D substrates. Graphene constitutes an excellent substrate material with exceptional electrochemical properties due to the extended π -conjugation and honey comb-like structure. It is also the most conductive form of carbon with excellent mechanical properties and good flexibility spread over a large surface area. Incorporation of graphene with L-TMD NSs can enhance the electrochemical performance of L-TMD by improving the (i) electrochemical surface area; (ii) electrode/electrolyte interface; (iii) inherent conductivity by providing pathways for electronic conduction; (iv) ease of mass diffusion, etc. Surfactant assisted hydrothermal/wet chemical method is the most common approach for the preparation of single- or multi-layered L-MoX₂ (X = S, Se)-graphene composites [47, 54-60]. For instance, Chang et al. presented a novel approach for the growth of layered MoS₂/graphene hybrids by an L-cys-assisted solution-phase technique; using sodium molybdate,

L-cys and GO (graphene oxide) as a precursor with a subsequent heat treatment [47]. Similarly, wet-chemical routes have been used to synthesize single layered MoS₂/GNS hybrid materials by CTAB (cetyltrimethylammonium bromide) assisted with a reduction of (NH₄)₂MoS₄ and GO sheets by hydrazine, followed by a heat treatment in an N₂ atmosphere [56]. Other cationic surfactants such as dodecyltrimethylammonium bromide, DTAB; octocyltrimethylammonium bromide, OTAB; tetrabutylammonium bromide TBAB have also been used for the synthesis of layered MoS₂/GNS hybrids [57, 58]. The use of surfactant helps to control the morphology of the resulting product, which in turn results in a better control of the performance of the

hybrid materials. In addition, the use of different cationic surfactants and their concentration in synthesis can be used for controlling the number of layers of MoS₂ [57].

Recently, NG (nitrogen doped graphene) has received greater attention as a suitable substrate for the growth of nanomaterials for nanostructured electrodes due to their high roughness and wrinkled surface with large number of defect sites and vacancies. Chang et al. developed MoS₂/NG composite by a facile two step mechanism where L-cys was used as S source and doped in NG by heating at an elevated temperature followed by *in-situ* MoS₂ NSs, as depicted in Fig. 4a [61]. Besides wet chemical/hydrothermal routes, a scalable liquid phase exfoliation approach was used to

Fig. 4 (a) Schematic representation of synthesis process of MoS₂/NG composite [61]. Reproduced with permission of John WILEY & Sons, Inc.; (b) Schematic representation of MoS₂ nanoflowers (MoS) and MoS₂/rGO composite (MoSG) [62]. Reproduced with permission of Nature Publishing Group; (c) Schematic description of the growth mechanism and applications of SnS₂-RGO sheet-on-sheet nanostructure [64]. Reproduced with permission of American Chemical Society.

synthesize MoS_2 -rGO composite, in which the PVP assisted MoS_2 NSs were first prepared by a low temperature hydrothermal method and the flower like MoS_2 -rGO composite prepared by ultrasonic exfoliation technique (Fig. 4b) [62]. Further, a layered by layered MoS_2 /rGO composite was synthesized via chemical lithiation and exfoliation methods with less stacked MoS_2 layers with 1~3 layers [63].

Other L-TMDs such as SnX_2 ($\text{X} = \text{S}, \text{Se}$) materials have also been composited with graphene to enhance their electrochemical performance. Similar to MoX_2 , wet-chemical-methods have also been most common approaches to synthesize nanocomposites of SnX_2 with graphene [65-69]. For example, L-cys assisted FL- SnS_2 /G (few-layer SnS_2 /graphene) composites were synthesized by solution-chemistry method, in which L-cys was used as sulfur source, complexing and reducing agent [66]. Another technique was also used to fabricate sheet-on-sheet SnS_2 /RGO via a 1-step microwave assisted method for enhanced electrochemical performance and photocatalytic applications, as shown in Fig. 4c [64]. A CVD approach has also been used for SnS_2 -graphene composites. The 2-step approach was used to synthesize 2D graphene- SnS_2 composites, with the SnO_2 NPs anchored in the graphene NSs and then, converted into the metal disulfide nanoplates via a solution method followed by a simple CVD process [70]. In addition, graphene supported WS_2 nanocomposites have also been synthesized and investigated to improve the electrochemical performance of WS_2 because of its higher conductivity than MoS_2 [71-74]. A solution-phase method was reported for the synthesis of few-layer WS_2 supported on RGO (reduced graphene oxide) by reduction of GOS dispersion with hydrazine hydrate under reflux [71].

2.4 3D Porous Structures with 2D Graphene/Porous CNF

Although the nanocomposites of L-TMD with

graphene showed much better performance, but these L-TMD NSs are affected by strong aggregation upon successive cycling because of non intimate contact between graphene layers and L-TMD, and later suffers from large contact resistance among numerous active NSs. Recently, 3D porous architecture of MoX_2 ($\text{X} = \text{S}, \text{Se}$) with graphene and porous CNF have been reported [75-79]. For instance, a bottom-up approach is developed to synthesize with 3D porous architecture from exfoliated MoS_2 -GNS (MoS_2 NSs and GO NSs) as building block and afterwards hydrothermal reaction (Fig. 5a) [75] in which MoS_2 NSs were confined in the matrix of graphene as shown in Fig. 5b. Recently, both graphene and o-MWCNT (oxidized MWCN) together combined with MoS_2 , to synthesize the 3D f- MoS_2 (flower-like MoS_2) hierarchical structure (f- MoS_2 /RGO/o-MWCNT) [77]. Addition of o-MWCNT in the composites resulted in the formation of flower-like morphology and also inhibited the stacking of RGO. Besides MoS_2 , first time 3D mesoporous MoSe_2 /rGO foam was synthesized by hydrothermal method, which was used as anode in LIB [78]. Additionally, L-TMD NSs such as the SnS_2 and WS_2 have also been combined with the 3D porous structure to improve their electrochemical performance [80-84]. Recently, a facile two-step route to synthesize 3D interconnected graphene frameworks embedded with homogeneously distributed SnS_2 nanoplates (SSG) by using GO NSs, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and L-cys as source materials has reported. Firstly SnO_2 NPs decorated on GO NSs via water bath strategy [85] and then directly transformed into SnS_2 by hydrothermal treatment with L-cys as reducing agent and sulfur source [81]. Additionally, Huang et al. [82] reported a layered composite WS_2 with 3D-graphene interconnected networks by hydrothermal method at relatively low temperature for LIB and hydrogen evolution reactions.

Besides the 3D architectures of MoS_2 with carbonaceous materials, recently 3D networks of MoS_2 have also been prepared with TiO_2 microspheres to

enhance the electrochemical performance of LIBs [86]. For instance, a firework shaped TiO_2 (3D F- TiO_2) microspheres have been used as template, in which 3D F- TiO_2 microspheres were embedded with MoS_2 NSs by two step hydrothermal methods [86].

2.4.1 Composites of L-TMD with 3D Bulk Materials

In addition to developing 3D architectures from 2D graphene, 3D graphene has itself been employed to tailor the electrode materials. CVD is used successfully to grow 3D graphene network (3DGNs) which is used as substrate to grow nanomaterials resulting in functional composites [87, 88]. The 3DGNs not only offer high surface area, but also preserve the excellent conductivity of graphene. In a synthesis strategy, MoS_2 flakes were coated on 3DGNs through CVD using $(\text{NH}_4)_2\text{MoS}_4$ dissolved in DMF (dimethylformamide) as a precursor [89]. Similarly, MoS_2 NSs can also be deposited on ACF (activated carbon fiber) cloth. Wang et al. [90] reported a two step method to grow ultrathin MoS_2 NSs on the surface of ACF cloth using $(\text{NH}_4)_2\text{MoS}_4$ dissolved in DMF (dimethylformamide) as source material in the presence of pre-annealed ACF cloth with subsequent annealing treatment in 5% H_2/Ar atmosphere. The formation of MoS_2 is described by the following equation [91].

2.5 Composites of L-TMD with Various Other Forms of Carbon

The amorphous form of carbon has also been used for templates and matrices for growing the L-TMD [92-98]. For example, Chang et al. [92] developed MoS_2 /amorphous carbon composites using simple hydrothermal process followed by high temperature calcination. Similarly a facile and simple solution-phase method was used to synthesize the sheet-like MoSe_2/C composite from $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, Se powder and glucose as the precursor and following with heat treatment. The carbon in the composite maintains structural integrity and also inhibits the stacking of NSs [96]. Recently, different carbon hollow

structures such as nitrogen doped hollow carbon nanobox and PHCS (porous hollow carbon spheres) have also been used for the growth of L-TMD NSs. These hollow carbon structures increase the conductivity of nanocomposites and also inhibit the aggregations of L-TMD NSs during cycling [94, 95]. The composite of N-doped carbon nanobox with MoS_2 mainly involve 4 steps as shown in Fig. 5c. This carbon shell greatly improved the conductivity of the composite, accommodated the strain and effectively prevented the aggregation of MoS_2 NSs during cycling processes.

Fig. 5 (a) Schematic representation for the growth mechanism of 3D MoS_2 -graphene architectures; (b) Photographs and SEM of 3D MoS_2 -graphene architectures, respectively [75]. (a, b) Reproduced with permission of WILEY & Sons, Inc. (c) Schematic representation of synthesis process for $\text{C}@\text{MoS}_2$ nanobox [94]. Reproduced with permission of WILEY & Sons, Inc.

3. Prospective Applications of L-TMD Composites

With an ever increasing energy demand and resource depletion crisis, the storage of green and sustainable energy has become a major challenge for materials scientists and researchers. In recent years many new energy materials have been synthesized to meet these challenges. Due to improved physical and electrochemical properties, L-TMD nanocomposites appear to lead the way for many advanced applications in the development of energy storage devices. In this section, we will briefly review the potential applications of the nanocomposites for high performance LIB and SIB batteries.

3.1 LIBs (Lithium Ion Batteries)

Rechargeable LIBs are now used extensively as a power source for portable electronic devices (such as laptops, notebooks, mobile phones, etc.), EVs (electric vehicles) and HEVs (hybrid electric vehicles) and this can be attributed to the many merits of LIBs; the principal ones are: high energy density, durable cycle life and no memory effect [2, 5, 99]. As an anode material in LIBs, graphite has been widely employed; however, due to its low specific capacity (372 mAhg^{-1}) and relatively poor rate capability, it cannot fulfill the demand of EVs and HEVs. L-TMD NSs have relatively high specific capacity compared to graphite, shortened path lengths for Li^+ ion and large exposed surface area, which plays an important role in enhancing the performance of LIBs. However, they have poor cycle life and rate capability as a result of the low intrinsic conductivity and easy restacking during Li^+ insertion/de-insertion [100]. The hybridization of L-TMD with different morphologies such as 0D (noble metals, metal/oxides NPs), 1D (CNT, CNF, TiO_2 nanotubes/nanowires/nanobelts), 2D (graphene, TiO_2 nanosheets), 3D (3D graphene, ACF, 3D porous architectures) and other forms of substrates is one of the most promising approaches to enhance the reversible capacity, cycle ability and rate performance

of LIBs.

In this regard, composites of L-TMD NSs with 2D graphene are the most studied nanomaterials for LIBs [47, 54-60, 63-72, 74]. As a typical example, layered MoS_2/G ($\text{MoS}_2/\text{graphene}$) composite was reported by solution-phase approach, when this composite was used as anode in LIBs, it exhibited a high specific capacity of about $1,100 \text{ mAhg}^{-1}$ at 0.1 Ag^{-1} current density with an excellent cycling stability (100 cycles). It also showed good rate capability with the specific capacity at about 900 mAhg^{-1} , even at 1.0 Ag^{-1} current density [47]. The enhanced electrochemical performance of the composites was attributed to the synergistic effect between L-TMD and GNS. GNS not only preserved the electronic conductivity of the composites, but it also, reduced the contact resistance of the electrode. Further, the flexible nature of GNS absorbed the stress peaks induced during the cycling processes. In addition, many composites of WS_2 , SnS_2 , and SnSe_2 with graphene for the improved performance of LIBs have been reported [64-72, 74]. Doping is another strategy used to further increase the conductivity of graphene, which resulted in high lithium storage capacity. N-G (nitrogen-doped graphene), the more conductive form of GNS has also been used for synthesizing MS_2 ($\text{M} = \text{Mo}, \text{W}$)/N-GNS composites [61, 73]. Due to N-doping, the defect sites and vacancies for Li^+ ions active sites extend gradually during cycling process and resulted in high performance in terms of capacity and cyclic stability. (Fig. 6a) [61]. For example, $\text{MoS}_2/\text{N-G}$ composite possesses better reversible capacity than MoS_2 , MoS_2/G and good rate capability for LIBs as shown in Figs. 6b and 6c which clearly demonstrated that defect sites or vacancies are gradually extending and facilitating more Li^+ ions for insertion in N-G structure during charging/discharging.

3D porous interconnected architectures of L-TMD with varying carbon structures of 2D graphene and porous CNF have been used as an anode for LIBs [75-82, 84]. These porous structures not only provide a

Fig. 6 (a) Schematic description of N-G during cycling: the defect sites or vacancies are extending gradually, facilitating more intercalation of Li⁺ ions, blue balls represent Li⁺ ions; (b) Cycling behaviors of MoS₂, MoS₂/G and MoS₂/N-G samples at a current density of 0.1 mA/hg⁻¹; (c) Cycling performance of MoS₂/N-G electrode with different current densities [61]. Reproduced with permission of John WILEY & Sons, Inc.

larger surface area, increased channels for easy electrolyte access and continuous pathways for rapid charge transfer, but they also, provide a cushion for the volume expansion of L-TMD nanosheets during the charging/discharging. As a result, the high specific capacity, excellent cyclic performance and ultrahigh-rate capability are achieved using 3D porous interconnected architectures. For instance, 3D porous graphene architecture coated with MoS₂ by the hydrothermal method for high performance of LIB has been reported with improved capacity retention (1,200 mAhg⁻¹ after 3,000 cycles), and excellent rate capability with capacity of 270 mAhg⁻¹ at 140 C [76]. Also, the CVD method is used to deposit MoS₂ on 3D graphene network (MoS₂/3DGN) and when used as an anode in LIB, this 3D architecture yields a specific capacity of 665 mAhg⁻¹ at current density of 0.5 Ag⁻¹ after 50 cycles with a good rate performance; even at 4 Ag⁻¹, the reversible capacity is still an impressive 466 mAhg⁻¹ [89]. The deposition of L-TMD NSs on the surface or within the CNT, [42-45] carbon nanotube/fibers [48-50] and amorphous/other form of

carbon [92-97] have also been reported as an anode for LIBs. Just like the graphene, the good conductivity of these carbonaceous materials and high specific surface area of L-TMD deposited on them yield enhanced reversible capacity, excellent cyclic stability and improved rate performance compared to their individual counterparts. Kong et al. demonstrated that MoS₂ NSs embedded in graphene nanocables (MoS₂@G) could provide high reversible capacity with excellent cyclic stability (1,150 mAhg⁻¹ at 0.5 Ag⁻¹ after 160 cycles) and extraordinary rate capability (700 mAhg⁻¹ at 10 Ag⁻¹). Surprisingly, this hybrid structure delivered high capacity of 900 mAhg⁻¹ at 5 Ag⁻¹ with long cycle life (700 cycles) [49].

The performance of nanostructured electrodes in LIBs is largely undermined by two key issues which are (1) low conductivity and (2) high volume expansion. Although, a very high initial charge and discharge capacity can be attained by most of the nanostructured electrodes but the rapid capacity fade limits their practical utilization for longer durations. The loss of capacity is a direct result of the large volume expansion during SEI layer formation as a result of lithiation/de-lithiation in the electrode materials. Such limitations could be addressed by tailoring the electrode materials to (1) accommodate the strains and lower the barrier of ion intercalation by synthesizing single layered TMD and (2) composites of TMD with various carbon or other material structures which are flexible in nature and can accommodate strains. Single-layered TMD offers remarkable advantages over multi-layered TMD in terms of large surface area and additional interfacial lithium storage, shortened diffusion pathway to Li⁺ ion, and accommodate the volume change [48, 50]. Zhu et al. prepared single-layered ultrasmall MoS₂ nanoplates uniformly embedded in carbon nanofibers by electrospinning process and this composite showed extraordinary performance for LIBs. Authors further applied TEM modeling to demonstrate that composites were made of single layered and ultrasmall, which were embedded in

CNFs as shown in Fig. 7a. The composite showed high discharge ($1,712 \text{ mAhg}^{-1}$) and charge ($1,267 \text{ mAhg}^{-1}$) capacities at 0.1 Ag^{-1} (Fig. 7b) and outstanding rate performance with specific capacities of 637, 548, and 374 mAhg^{-1} at current density increases from 10, 30, to 50 Ag^{-1} respectively. The cyclic stability was also excellent as the capacity was 661 mAhg^{-1} at 10 Ag^{-1} after 1,000 cycles [48]. Obviously, the enhanced electrochemical performance of these CNFs can be attributed to several factors: (1) Single-layered TMD nanosheets not only provided the insertion and conversion sites for lithium storage, but also numerous interfacial storage sites; (2) The carbon matrix inhibits the restacking of single-layered TMD and aggregation of nanoparticles after cycling; (3) These carbon networks not only solve the volume expansion problem,

but also provide easy access to Li^+ ion due to 1D character of CNF; (4) Conductivity of carbon networks further increase due to N-doping in CNFs.

Besides carbonaceous materials, composites of noble metal, metal/metal oxide NP-decorated with MoS_2 have also been explored for fabricating anodes in LIBs with an enhanced performance [33-38]. The large surface area, elastic and flexible nature of MoS_2 NSs act as an ideal template to inhibit NP aggregation and cushion the volume changes during charging/discharging. The NPs anchored on or in between MoS_2 NSs serve as spacer, preventing the restacking of MoS_2 during cycling processes and thus improving the capacity retention. Besides, NPs ensure short Li^+ ion diffusion pathways resulting in superior capacities and rate capabilities [38]. Recently, composites of 1D TiO_2 nanotubes/nanowires/nanobelts [51-53] with MoS_2 have also been prepared and considered as alternative anode for LIB with remarkable cycling stability and rate capacity due to their low volume changes during the cycling process and the higher operating voltage of 1.7 V (compared to Li^+/Li). Nevertheless, 1D TiO_2 and MoS_2 nanostructures are interconnected with each other by loose surface contact, which result in self aggregation upon charging/discharging, and hence their performances are still limited. Moreover, 3D porous hollow structures have also been prepared of $\text{TiO}_2/\text{MoS}_2$ as anode in LIB, in which MoS_2 homogenously deposited on TiO_2 surface with remarkably improved structural stability and effectively shortened the diffusion path length of both electrons and Li^+ ions. As a consequence, 3D $\text{TiO}_2/\text{MoS}_2$ showed a stable cycling performance and superior rate capability [86, 101]. For example, a 3D core shell nanostructure was prepared by coating few layers (<4 layers) MoS_2 on TiO_2 NSs (3D FL- $\text{MoS}_2@\text{TiO}_2$) as an anode for LIB [101]. It exhibited stable cycling performance after 100 cycles with capacity of 713.7 mAhg^{-1} at 0.1 Ag^{-1} .

Fig. 7 (a) Schematic illustration based on TEM modeling study. The large black sphere, small black sphere, and white sphere correspond to Mo, C, and S, respectively; (b) Charge and discharge voltage profiles for the first three cycles at 0.1 Ag^{-1} of the MoS_2 -carbon fiber composite [48]. Reproduced with permission of John WILEY & Sons, Inc.

3.2 SIBs (Sodium Ion Batteries)

Although LIBs provide a potential solution to meet the rising demand of global energy for portable electronic devices, EVs and an emerging market for electrical energy storage, we must think about the availability of lithium in the earth's crust. The relative abundance of lithium is still a non-renewable resource and still relatively expensive. On the other hand, Na (sodium) is a low cost and earth abundant element. In addition, Al (aluminum) is used as a current collector in SIB, which does not make binary alloy with Na. On this basis, a rechargeable SIB seems to be a more promising alternative to an LIB [102-104]. However, SIBs possess lower theoretical gravimetric and volumetric capacity, because of the poor electrochemical activities compared with LIBs. This is due to 2 intrinsic shortcomings of Na: firstly, Na^+ ions are heavier than Li^+ ions, leading to a sluggish diffusion of Na^+ ions in bulk of electrode and larger volume expansion, which resulted in low cyclic stability and rate capability, and secondly, the ionization potential of Na is lower, leading to lower operating voltage, which results in a lowering the gravimetric and volume energy densities. To overcome these deficiencies unique porous crystalline structures with large insertion channels to facilitate sodiation/desodiation have been developed. Recently, a tremendous effort has been made to explore the possibility of using an SIB as an anode. Among them L-TMD NSs based composites have received a lot of attention in recent years. Similar to LIBs, composites of L-TMD with graphene in SIBs have also been investigated as an anode material with or without a binder [55, 62, 69, 83, 105]. For instance, Zhang et al. reported hierarchical MoSe_2 /Graphene composite being used as anode in SIB, after 200 cycles, the specific capacity of 430 mAhg^{-1} and 380 mAhg^{-1} at current densities of 0.5 Ag^{-1} and 1 Ag^{-1} were achieved, respectively. This high electrochemical performance was ascribed to synergistic interaction among MoSe_2 and GNS [55]. L-TMD composites supported on other

carbonaceous materials have also been investigated for application in SIB [46, 48, 95, 98]. Likewise, Zhu et al. fabricated the single-layered MoS_2 nanoplates embedded in CNFs and investigated its electrochemical performance. When used as an anode in SIB, it showed an excellent rate capability and cyclic stability. At current densities of 0.1, 0.5, 1, 5, 10, 20, 30, and 50 Ag^{-1} , the specific capacities obtained were 854, 700, 623, 436, 331, 224, 155, and 75 mAhg^{-1} , respectively. It delivered specific capacities of 484 mAhg^{-1} and 253 mAhg^{-1} , at 1 Ag^{-1} and 10 Ag^{-1} current densities after 100 cycles. This good performance can be attributed to the ultrasmall single-layered MoS_2 . This is the best reported anode material among all of them for SIB [48]. In another report, PHCSs (porous hollow carbon spheres) were directly decorated by MoSe_2 NSs by three steps and tested for electrochemical performance of SIB [95]. At current density of 0.2 Ag^{-1} , an outstanding specific capacity (580 mAhg^{-1}) was achieved over a prolonged cycle life (100 cycles) and at high current density of 1.5 Ag^{-1} , the specific capacity was still maintained to 400 mAhg^{-1} . MoSe_2 NSs and PHCS accommodated the stress during charging and discharging. Also PHCS offered the conductivity environment to the composite, while MoSe_2 NSs shortened the electronic Na^+ ion path [95]. In addition, the composites of MoS_2 with carbon [98] and MoSe_2 with MWCNT [46] have also been demonstrated as anode for SIB with good performance.

4. Conclusion and Outlook

Batteries (LIBs/SIBs) are being the future energy storage devices to fulfill the dream by continuously supplying the power to portable electronics and short EVs. Recent advances have shown that L-TMDs are promising materials for LIB and SIB applications, due to their unique physical and chemical properties. When used as an anode in an LIB or SIB, L-TMD NSs are found to be more effective compared to their bulk counterparts because of the higher specific surface area, longer cycle life, higher electronic conductivity and

shortened path length for ions. Moreover, their performance as measured by the capacity, cyclic stability and rate capability can be further enhanced by hybridization with functional nanomaterials.

In summary, composites of single- and multi-layer TMD have been prepared with 0D (noble metal, metal/oxides NPs), 1D (CNT, CNF, TiO₂ nanotubes/nanowires/nanobelts), 2D (graphene, TiO₂ nanosheets), 3D (3D graphene, ACF) structures and various other forms of carbon and have shown excellent performance in LIB and SIB. However, most of L-TMD composites with these structures are multilayers instead of single layer, resulting in reduced surface area for lithium and sodium storage. The excellent performance in terms of cycling stability and rate capabilities for LIBs/SIBs have exhibited by single-layered TMD embedded in CNF via electrospinning process. Besides, 3D graphene backbone hybrid porous structures with MoS₂ as binder free anode for LIBs have exhibited extraordinary cyclic performance and high rate capacities. Nevertheless, a good performance has been achieved, but some problems are still matter of great concern. The aggregation of TMD during electrode fabrication and degradation of structure during ultralong charging and discharging process (especially at high current density) are inexorable and responsible to their low performance. Moreover, the synthesis of TMD composites with these structures must be scalable before these nanocomposites can be considered for deployment in LIBs/SIBs. To overcome the current challenges, continuous research development is still required to fabricate and explore new L-TMD based composites that yield higher lithium and sodium storage capacity, longer cycle life and higher rate capability.

In future, just like 3D carbon based materials (3D graphene, CNT sponge) offer relatively large surface area, high conductivity and porous structure, 3D macroscopic structures of L-TMD can also be fabricated, and explore their unique properties and a

variety of applications. The 3D L-TMDs with large voids can provide the required spaces for fast mass transfer and reversible Li storage for enhanced capacity without any structural degradation. In addition, the yolk-shell structures of L-TMD can be synthesized, which can further provide spaces for reversible Li and Na storage with enhanced capacity.

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