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Abstract

Molybdenum and tungsten chalcogenides have attracted tremendous attention in energy storage and conversion due to their outstanding physicochemical and electrochemical properties. There are intensive studies on molybdenum and tungsten chalcogenides for energy storage and conversion, however, there is no systematic review on the applications of WS₂, MoSe₂ and WSe₂ as anode materials for lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs), except MoS₂. Considering the importance of these contents, it is extremely necessary to overview the recent development of novel layered WS₂, MoSe₂ and WSe₂ beyond MoS₂ in energy storage. Here, we will systematically overview the recent progress of WS₂, MoSe₂ and WSe₂ as anode materials in LIBs and SIBs. This review will also discuss the opportunities, and perspectives of these materials in the energy storage fields.

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Review

Molybdenum and tungsten chalcogenides for lithium/sodium-ion batteries: Beyond MoS₂

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ABSTRACT

Molybdenum and tungsten chalcogenides have attracted tremendous attention in energy storage and conversion due to their outstanding physicochemical and electrochemical properties. There are intensive studies on molybdenum and tungsten chalcogenides for energy storage and conversion, however, there is no systematic review on the applications of WS₂, MoSe₂ and WSe₂ as anode materials for lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs), except MoS₂. Considering the importance of these contents, it is extremely necessary to overview the recent development of novel layered WS₂, MoSe₂ and WSe₂ beyond MoS₂ in energy storage. Here, we will systematically overview the recent progress of WS₂, MoSe₂ and WSe₂ as anode materials in LIBs and SIBs. This review will also discuss the opportunities, and perspectives of these materials in the energy storage fields.

Keywords: MoSe₂; WS₂; WSe₂; Lithium-ion batteries; Sodium-ion batteries

1. Introduction

Being confronted with global energy crisis and environmental issues, the exploring of clean and renewable energy materials as well as their devices is urgently demanded [13]. Lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) have shown the unique potential and various advantages with good cycle life, high energy density, and low self-discharge features [49]. The achieving of excellent performance for an energy storage device is closely related to the properties of electrode materials [1015]. Layer-structured transition-metal dichalcogenides (TMDs) are characterized with relatively weaker M–X (M = transition metal, X = chalcogen) ionic bonds, van der Waals interaction dominated interlayers, and large surface-to-volume ratio. All these features endow them with kinetically favorable performances and have attracted intensive interest due to their immense potential for energy storage and conversion amongst various promising applications [1621]. Tungsten sulfide (WS_2), molybdenum and tungsten chalcogenides (MoSe_2 , WSe_2) have recently attracted great attention as anode materials for Na-ion batteries and Li-ion batteries beyond the well-studied two-dimensional (2D) MoS_2 analogue, owing to their unique physicochemical characteristics including higher intrinsically electrical conductivity and larger interlayer spacing [2228]. They share the same layered structure with 2D MoS_2 , and their structural similarities inspire the researchers to develop similar synthetic strategies for WS_2 , MoSe_2 and WSe_2 and explore their potential applications in electronics, sensors, and energy conversion/storage [16,17,2942]. For example, it is found that MX_2 (M = Mo, W; X = S, Se) as anode materials for LIBs and SIBs showed relatively low voltages and high electronic conductivities during Li/Na intercalation. Among them, WS_2 and WSe_2 demonstrate the lowest Li/Na ion migration barriers, affording favorable rate performance for advanced secondary batteries [43].

LIBs are one of the most successful examples among various battery technologies [2,4,21]. Currently the commercialized anode materials include natural graphite, artificial graphite, mesocarbon microbeads (MCMBs), $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and silicon/carbon [44]. However, there are still challenges in performance, cost competitiveness, and production technology for these materials (e.g., low capacity, poor conductivity, limited power/energy density, lifetime, safety or all-climate performance issues) to meet the strongly growing market share such as full electrification of the future automotive industry [44,46]. TMDs are a recent addition to the growing list of anode materials for next-generation LIBs (Table S1, S3, and S5 in Supplementary materials)[24,30,47,49]. Moreover, SIBs have also drawn great attention as promising energy storage devices due to the low cost and abundance of sodium [6,50,51]. Although they share the same reaction mechanism with LIBs, however, graphite is not a suitable anode for SIBs since sodium ion could not be inserted into graphite effectively. To solve this problem, apart from the exploration of various oxides and sulfides as anode materials [6,52,54], molybdenum and tungsten dichalcogenides (MoS_2 , WS_2 , MoSe_2 and WSe_2) have been intensively studied and exhibited superior performances associated with the intercalation and conversion during the cycling (Table S2, S4, and S6 in Supplementary materials)[24,30].

Recently, there are some excellent reviews on MoS_2 for energy storage and conversion [38,55,58], however, there is no systematic review on the applications of WS_2 , MoSe_2 and WSe_2 as anode materials for LIBs and SIBs. Considering the importance of these contents, it is extremely necessary to overview the recent studies on WS_2 , MoSe_2 and WSe_2 as anode materials from synthesis to battery performance. In this review, we will systematically overview the research status of WS_2 , MoSe_2 and WSe_2 from the electrode design, synthetic methods and their battery performance. We will also present our insights

on the opportunities and challenges of these TMDs in different energy storage systems in the near future.

2. Lithium-ion batteries

Owing to the similar layered structures features to graphite yet with larger spacing, TMDs composed of group VI metals (Mo and W) and chalcogens (S and Se) with 2D layered crystalline frameworks have shown great potential as alternative advanced anode materials. As a well-studied representative, MoS₂ achieved significant improvements in cycle life and rate performance thanks to numerous efforts devoted to promoting the low intrinsically electrical conductivity as well as creating novel structural and electrode design [5766]. Novel layered WS₂, MoSe₂, and WSe₂ with the same crystal structure but higher intrinsic electronic conductivity, larger interlayer **spacing, and lower** potential plateau should possess more advantages for advanced secondary batteries from commercial aspects [16,17,30,38,6771]. The Li/Na-ion storage mechanism can be briefly expressed by the following equations [30,72,73],

or detailed by the following two-step electrochemical reactions,

2.1. WS₂ for lithium-ion batteries

WS₂ with sandwiched S–W–S layers (interlayer spacing 0.618 nm) stacked together *via* weak van der Waals interaction has received tremendous attention for next-generation rechargeable LIBs due to its higher intrinsic electrical conductivity compared to MoS₂, competitive theoretical capacity of 433 mA h g⁻¹ (based on 4 mol of Li-ion insertion), and a high density of 7.6 g cm⁻³ resulting in a volumetric energy density 4 times higher than that of graphite [69,7478]. However, the electrical conductivity of pristine TMDs and electrode stability need to be further improved for practical application in high power/density energy storage devices.

2.1.1. Structural control of WS₂

Nanostructured electrode materials compared to bulk materials could achieve greatly enhanced electrochemical performance due to their advantages of much higher surface area, reactivity, electric/ionic conductivity as well as reduced dimensions for Li-ion intercalation from shortened transport lengths and separation distances [69,7988]. The control of crystalline preferential orientation such as (001) plane of 2D WS₂ nanosheets further improved the diffusion kinetics and electrochemical performance, as an example, an anode by Zhang and coworkers showed an enhanced reversible capacity of 539 mA h g⁻¹ after 60 cycles at 200 mA g⁻¹ [69]. The WS₂ bundles composed of multiple single sheet crystals can be fabricated from one-dimensional (1D) tungsten oxide nanorods *via* a “shape-transformation” concept, however, the poor Li storage performance need to be further enhanced due to the limited conductivity [87]. Fang et al. exploited a solid-state reaction route to synthesize graphene-like and plate-like WS₂. It is worthy to mention that graphene-like WS₂ exhibited a bent pole structure with 1 μm in diameter and was comprised of stacked sheets in a thickness of 2–8 layers. The assembled few-layer or expanded WS₂ showed a high capacity of ca. 600 mA h g⁻¹ after

100 cycles at 0.05C and **better rate performance** than plate-like WS₂ (1–2 μm in diameter and ~200 nm in thickness) due to the increased surface area and reduced diffusion path [82]. They further explored the Li storage mechanism and claimed that the W does not participate in the reversible electrochemical redox reaction after it was formed in the initial reduction (lithiation) process, i.e., the redox reaction in a WS₂/Li cell was similar to that in a Li–S battery, inconsistent with a completely reversible conversion reaction [69,78,89]. In regard of this, some experts suggested a further sulfuration reprocessing of initial WS₂ for repairing sulfur vacancies to improve the electrochemical performance [90]. In addition to the electrodeposition and various gas-phase deposition techniques (e.g., CVD, metal organic CVD, pulsed laser deposition, sputtering), thin film-like WS₂ can also be prepared by atomic layer deposition (ALD) through the self-saturation growth. When used as thin film anode in LIBs, it showed a stable cycling performance with a high Coulombic efficiency (CE) of over 99% [91].

Similar to the effect of nanosized materials, mesoporous materials with nanoscale crystalline walls, low intrinsic activation energy, and high electrode–electrolyte interface facilitate shortened Li-ion diffusion pathway, offer more active sites for Li-ion storage resulting in higher energy/power density [10,64,79]. For example, Liu et al. synthesized an ordered mesoporous WS₂ with a high surface area (115 m² g⁻¹) and narrowed pore size distribution (3.34 nm) *via* the replication of a 2D hexagonal SBA-15 template. When used as an anode for LIBs, it showed a high Li storage capacity of 805 mA h g⁻¹ after 100 cycles (92.5% capacity retention compared to 2nd cycle) at 0.1 A g⁻¹ and an outstanding high rate capability: 661 mA h g⁻¹ at 1.0 A g⁻¹ (2.25 C) and 504 mA h g⁻¹ at 10 A g⁻¹ (22.5 C). It indicates that mesoporous WS₂ may be a promising material for high power Li-ion batteries [79].

2.1.2. Hybridizing WS₂ with conducting frameworks

To enhance the electrical conductivity as well as the electrode stability for promoting the electrochemical performance of pristine WS₂, the introduction of conducting frameworks such as amorphous carbon [74,76,90,9298], CNTs [78,99101], and graphene [70,102107] is a facile and effective strategy.

Besides the traditional ball milling and calcination method for incorporating amorphous carbon with layered WS₂[89,97], the spray pyrolysis is another facile route to prepare WS₂/C composite, and it could deliver a reversible capacity as high as 555 mA h g⁻¹ after 50 cycles at 100 mA h g⁻¹[94]. An integrated WS₂@CMK-3 nanocomposite with few-layered WS₂ nanosheets embedded in ordered mesoporous carbon CMK-3 matrix was prepared by Pang et al. through a facile hydrothermal method, which delivered a reversible capacity of 720 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹ and a high rate capability of 395 and 307 mA h g⁻¹ at 1.0 and 2.0 A g⁻¹, respectively[96]. A WS₂@NCNFs hybrid structure with WS₂ nanosheets uniformly embedded in N-doped carbon nanofibers (NCNFs) was fabricated by Kim's group *via* an electrospinning method [95]. The interconnected network exhibited an improved capacity of 438 mA h g⁻¹ after 200 cycles at 500 mA g⁻¹, corresponding to a capacity retention rate of 87.2% at the 2nd cycle. The design of hollow structures is an alternative route of tremendous interest for buffering large volume changes and improving charge transfer during the charge/discharge processes, thus benefiting the long-term cycling stability and rate capability [108110]. For example, a hierarchical nanocomposite, hollow N-doped carbon spheres (HNCSs) uniformly decorated with ultrathin (3–5 layers) WS₂ nanosheets (WS₂@HNCSs), demonstrated a high specific capacity of 801 mA h g⁻¹ at 100 mA g⁻¹, excellent rate capacity of 546 mA h g⁻¹ at 2.0 A g⁻¹, and a great cycling stability with a capacity retention rate of 95.8% after 150 cycles at 500 mA g⁻¹[76].

These 2D layers with high surface energy are inclined to restack or re-aggregate during the processes of Li-ion insertion/extraction, thus resulting in a rapid capacity fade and poor rate capability. To overcome these drawbacks, Zou et al. designed a multi-layer-cake WS₂/C nanocomposite *via* an intercalation–transformation method (Fig. 1a), where the few-layered WS₂ were sandwiched between the *in situ* formed amorphous interlayer carbon, forming a unique “regular (phase-pure)” and “alternate (sandwiched)” architecture (Fig. 1b,c). This nanocomposite delivered a high capacity of 829 mA h g⁻¹ after 140 cycles at 300 mA g⁻¹, and demonstrated an excellent rate capacity of 327 mA h g⁻¹ at 8.0 A g⁻¹. The improved performance can be ascribed to the synergistic effect: the intercalated carbon layers helped prevent WS₂ sheets from restacking and increase the conductivity; few-layered WS₂ intrinsically facilitated the transportation of both electrons and Li ions. This intercalation strategy may provide a new facile reference for the design of advanced electrodes of next-generation batteries [74].

Another kind of hybrid sandwiched porous WS₂/CNT electrodes were fabricated *via* homogeneously intercalating SWCNTs into lamellar assembled WS₂ nanosheets through a facile vacuum filtration affording excellent electrochemical performance: a high specific capacity of 862 mA h g⁻¹ after 50 cycles at 100 mA g⁻¹; a rate capability of 440 and 342 mA h g⁻¹ at 1.0 and 2.0 A g⁻¹ [78]. Moreover, the introduction of the third component positively charged CuO nanosheet can integrate with negatively charged WS₂ nanosheets, the formed ternary WS₂/CuO/SWCNT porous laminated hybrid showed an improved performance with an enhanced reversible capacity of 962 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹ and a high rate capacity of 418 mA h g⁻¹ at 2.0 A g⁻¹ [84,99].

Fig. 1. (a) Schematic illustration of the synthesis process of multi-layer-cake WS₂/C nanocomposite with a unique “regular” and “alternate” architecture DDA, dodecylamine (C₁₂H₂₇N). (b and c) The cross-sectional SEM image and HRTEM image of WS₂/C nanocomposite. Reproduced from Ref. [74] with permission of Wiley-VCH.

Graphene exhibits outstanding advantages in energy conversion and storage due to its high electric conductivity, large surface area, and good geometrical compatibility with layered TMDs for enhanced electrochemical performances [89,104,106,111,112]. For example, Shiva et al. employed a simple hydrothermal process to fabricate uniform graphene-like few-layer WS₂ supported on reduced graphene oxide (rGO) with synergistic interactions between them for superior electrochemical performances. When utilized as anode materials for LIBs, the WS₂-rGO (80:20 and 70:30) composites with a lithiation/delithiation voltage of ~1.0 V and high interface stability showed a much enhanced capacity of 451 mA h g⁻¹ (80:20) after 50 cycles at 100 mA g⁻¹ and a superior rate capability of 236 mA h g⁻¹ (70:30) even at a much higher current density of 4.0 A g⁻¹ compared to bare WS₂ (8 mA h

g⁻¹ at 2.0 A g⁻¹) and rGO [113]. A thin nanoslice-structured WS₂@rGO composite fabricated by Li et al. could deliver an improved capacity of 565 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹ and a high rate capacity of 337 mA h g⁻¹ at 2.0 A g⁻¹ [112]. The first-principles calculations revealed that the electron-rich environment provided by the graphene network increased the binding energy of Li insertion and favored the delithiation process for WS₂; and other advantages such as lowered (diffusion) barrier energy for Li⁺ migration and higher Yong's modulus of the composite in comparison with pristine WS₂ were also indicated [112]. Graphene, as a 2D conducting material with high surface area, can bestow the WS₂ composite with a very low percolation threshold [114,115]. Cho's group prepared a few-layered WS₂-rGO composite by a simple hydrothermal and subsequent freeze-drying method [103]. The composite with a low content of rGO (only ~3 wt%) delivered a good cycling stability of 647 mA g⁻¹ after 80 cycles at 350 mA g⁻¹ and excellent high-rate capacity of 541 and 296 mA h g⁻¹ at a current density of 7 and 14 A g⁻¹, respectively. The N-doping further improved the electron transport properties and electrochemical activity of graphene or rGO [116,117]. Lee's group integrated few-layer WS₂ with N-doped graphene *via* a facile surfactant-assisted hydrothermal synthesis. The *in-situ* nitrogenated graphene/WS₂ delivered a more stable cyclability with a reversible capacity of 830 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹ and better rate performance of ~700 mA h g⁻¹ at a high current of 5.0 A g⁻¹ (80% of the initial capacity at 0.1 A g⁻¹), which may be a promising material for power-oriented applications [70]. For some carbon-based frameworks, they may also help in suppressing the "shuttle effect" of sulfur-containing electrodes *via* adsorbing polysulfide intermediates. The co-doping of carbon component not only increases the electrical conductivity but also enhances the interaction between WS₂ and carbon framework. For example, the WS₂ hybrid with N,S co-doped graphene could show a much higher and stable reversible capacity of 509 mA h g⁻¹ after 500 cycles at 2.0 A g⁻¹, which

was mainly attributed to the pseudocapacitive charge storage [118]. In regard of further improvement of gravimetric energy density, Chen et al. designed a double transition-metal chalcogenide hybrid *via* composition-optimized composition of WS₂, MoS₂, and N-doped graphene the ternary hybrid (W/Mo = 1:1) exhibited a very high and stable reversible capacity of 1032 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹ with a higher initial Coulombic efficiency (ICE) of 90% and an excellent rate performance of ~770 mA h g⁻¹ at 5.0 A g⁻¹, a capacity retention of 75% when the current density increased 50 fold from 0.1 to 5.0 A g⁻¹[119].

2.1.3. Free-standing WS₂ electrodes

Flexible energy storage devices have recently attracted increasing interest as power supplies for wearable smart electronics in modern life [120126]. The design of flexible electrodes with high conductivity, stable structure, superior electrochemical performance and robust mechanical property is of strong demand [106]. The incorporation with carbon fiber cloth is a facile and effective route, which includes carbon cloth, biomaterial-derived carbon paper or electrospun nonwoven conductive matrices [75,77,127]. For example, Hao's group designed a flexible anode for LIBs with metallic 1T@2H WS₂ nanosheet arrays stably anchored on cotton cloth-derived interlinked carbon fiber cloth (CFC). Compared to the semiconducting (2H) phase WS₂ (trigonal prismatic coordination), the metallic (1T) phase WS₂ (octahedral coordination) exhibits higher conductivity *via* the transversal displacement of one of S atomic layer. Through displacement of S atoms in WS₂ induced by incorporation of N atoms and the formation of N–W covalent bonds within the matrix, the metallic 1T phase WS₂ transformed from 2H phase was stably ensured. The as-prepared 1T@2H WS₂@CFC flexible anode showed a smaller initial discharge capacity loss (a higher ICE of 87.4%) and a higher reversible capacity (1130 mA h g⁻¹ after 200 cycles at 0.1 A g⁻¹ and 510 mA h g⁻¹ after 800 cycles at

2.0 A g⁻¹) than that with pure 2H phase, mainly due to the improvement of conductivity and outstanding electrochemical performances *via* capacitance-controlled fast charge storage and long-term cyclability [75]. Zhang et al. developed a flexible hierarchical electrode of few-layer WS₂ nanosheets uniformly grown on graphene-wrapped electrospun carbon fibers (Fig. 2) for remarkably improved electrical conductivity. Benefiting from the synergistic effect of hybrid carbon nanofibers and WS₂ nanosheets, this self-supported membrane possessed a porous and interconnected structure with large surface area, high electrical conductivity and good structural integrity for rapid Li-ions/electrons transfer and overall electrochemical stability. The optimized hybrid binder-free electrode showed a high initial capacity of 1128 mA h g⁻¹ at 100 mA g⁻¹, excellent long-term stability with 95% of the capacity retained after 100 cycles, and an outstanding rate capability of 624 mA h g⁻¹ at 2.0 A g⁻¹[128]. Kong et al. fabricated a similar hybrid electrode of WS₂ nanoplates encapsulated in porous graphitic nanofibers (WS₂@G) *via* electrospinning in combination with chemical vapor deposition (CVD) methods, creating an efficiently conductive and electrolyte-accessible framework (Fig. 3). This integrated highly conductive electrode not only alleviated the volume expansion during the cycling but also enabled a mechanically robust feature. Therefore it demonstrated an excellent cycle life with high capacity of *ca.* 500 mA h g⁻¹ after 300 cycles at 0.5 A g⁻¹, and showed a superior rate capability of 455 mA h g⁻¹ at 1.0 A g⁻¹[129].

Fig. 2. Microstructure of flexible WS₂/GCNF hybrid membrane with WS₂ nanosheets grown on graphene-wrapped electrospun carbon nanofibers: (a and b) SEM, (c) TEM and (d) HRTEM images. Reproduced from Ref. [128] with permission of Royal Society of Chemistry.

Fig. 3. (a) TEM, (b and c) HRTEM images, and (d) dark field TEM image and mapping of the nanocable-like WS₂@G with layered WS₂ nanoplates embedded in electrospun graphitic carbon nanotubes for dual anode material. Reproduced from Ref. [129] with permission of Science China Press and Springer.

The design of flexible free-standing electrode is one of the hottest research topics for higher energy/power density energy-storage devices and the ever-growing market of wearable electronics [120,123]. For example, through embedding WS₂ nanosheets into an interconnected framework of electrospun carbon nanofibers (CNFs) mat, the binder-free WS₂@CNFs exhibited a high reversible capacity of 545 mA h g⁻¹ after 800 cycles at 500 mA g⁻¹ and a high rate capability (62.4% of the

capacity delivered at 0.1 A g^{-1} was retained at 2.0 A g^{-1}). Flexible electrodes can also be fabricated by introducing carbon nanotubes (CNTs) as potential elastic three-dimensional (3D) conductive network, which will not only enhance the electrical conductivity, ion diffusion, but also buffer the volume change, suppress the restacking of WS_2 layers [130]. Ren and coworkers designed a free-standing 3D SWCNTs/ WS_2 -nanosheets foam as LIB anode *via* a simple hydrothermal method coupled with a freeze-drying process, which showed an ultra-long-life performance with a high reversible capacity of 688 mA h g^{-1} after 1000 cycles at 1.0 A g^{-1} as well as a high specific capacity of 1050 mA h g^{-1} at 100 mA g^{-1} [130]. Impressively, it also exhibited a good low-temperature performance with a specific capacity of 840 mA h g^{-1} at 0°C and 689 mA h g^{-1} at -20°C , corresponding to 69% and 57% of the capacity delivered at room-temperature [78]. Besides the chemical methods, Pan et al. exploited a direct sonication assisted liquid-phase exfoliation of commercial WS_2 powder to obtain 2D WS_2 nanosheets with large quantity, low cost, and without pollution. The facile and green route allows large-scale water-borne exfoliation exclusively employing stabilizers for impurity-free few-layered WS_2 rectangular nanosheets of substantial fraction. The WS_2 -based film anode for LIBs *via* vacuum filtration showed an enhanced reversible capacity of 406 mA h g^{-1} at 200 mA g^{-1} after 100 cycles, and when integrated with SWCNTs to increase the conductivity and isolate the 2D WS_2 from restacking, it could achieve a higher capacity of 577 mA h g^{-1} after 100 cycles with 42% increment as well as higher rate capacity of 435 and 363 mA h g^{-1} at 1.0 and 2.0 A g^{-1} , respectively. The route herein opens up new opportunities for easy and clean processing of WS_2 -based film devices with promising potential in energy storage and functional nanocomposites [131].

The incorporation with graphene for laminar or 3D flexible electrode will be very promising to extend the synergetic advantages of graphene and TMDs [12,75,122,132]. The construction of hybrid

structures with conductive and mechanically strong reduced graphene oxide (rGO) nanosheets is an effective strategy to enhance the conductivity and reduce the restacking effect for both WS₂ and graphene [133]. Liu et al. challenged a like-charged (both negative-charged) WS₂ and GO nanosheets in aqueous dispersion rather than those with opposite charges for easily assembling homogeneous hybrid lamellar films *via* a vacuum filtration process to produce highly efficient flexible anodes for LIBs. The binder-free WS₂/rGO lamellar electrode showed excellent cycling stability, good rate capability and a high reversible capacity of 698 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹, which was much higher than that of pure WS₂ nanosheets (89 mA h g⁻¹) and rGO (60 mA h g⁻¹). This substantially enhanced electrochemical performance can be ascribed to the uniformly alternated lamellar structures, where rGO nanosheets prevented the restacking of WS₂ sheets, enhanced the conductivity, and tolerated the volume variations during Li-ion insertion/extraction [133]. The 3D graphene (3DG) frameworks with interconnected conductive network will further reduce the contact resistance among numerous active nanosheets beyond the advantages such as large surface area, extraordinary physicochemical stability, and good compatibility with other integrated active materials [68,111,134]. A free-standing hierarchical architecture of WS₂ nanotubes/rGO hybrid *via* a simple one-pot hydrothermal reaction was reported by Chen et al. It delivered a high reversible rate capacity of 319 mA h g⁻¹ over 500 cycles at 1.0 A g⁻¹, benefiting from the enhanced conductivity, more reactive sites, large electrolyte/electrode interface for Li-ion diffusion and accommodated volume changes [68]. Yang's group further designed an ice-templated 3D WS₂/CNT-rGO hybrid nanoarchitecture aerogel (Fig. 4a) consisting of WS₂ nanosheets, CNTs, and rGO with ordered microchannels (Fig. 4b–f), which not only provided good electronic transportation routes, but also offered excellent ionic conductive channels. This hybrid aerogel used as free-standing anode materials for LIBs could deliver a high and

quite stable capacity of 572 mA h g^{-1} after 100 cycles at 200 mA g^{-1} (Fig. 4g), and an excellent rate capability of 536, 414, and 337 mA h g^{-1} at 1, 5, and 10 A g^{-1} , respectively [67]. The improved electrochemical performance can be ascribed to the synergistic effect between the rationally arranged CNT-rGO framework and WS_2 nanosheets [68]. However, the low ICE of CNT-rGO component, with irreversible lithium consumption proportional to the active surface area of modified carbons [135], often induces a decreased ICE of the composite electrode. The low ICE, which is inferior for a full cell or batteries, may be further improved by annealing or a pre-lithiation process (i.e., pre-occupying the defects of graphene-based frameworks or additives) [21,136]. It should be noted that although some flexible or free-standing electrodes derived from graphene or CNTs showed potential for wearable energy storage devices, the mechanical properties usually fall short of expectations for practical application, thus the design of robust flexible advanced electrodes is still in high demand [129].

Fig. 4. (a) Photo of the 3D $\text{WS}_2/\text{CNT-rGO}$ aerogel. (b–d) Various SEM images at different magnifications and (e and f) TEM and HRTEM images of ordered $\text{WS}_2/\text{CNT-rGO}$ aerogel. (g) Cycling performance of $\text{WS}_2/\text{CNT-rGO}$ aerogel, WS_2 commercial powder, and CNT-rGO aerogel anodes for LIBs at a current density of 200 mA

g^{-1} , and the corresponding coulombic efficiency of $\text{WS}_2/\text{CNT-rGO}$ aerogel electrode. Reproduced from Ref. [67] with permission of Wiley-VCH.

2.2. *MoSe₂ for lithium-ion batteries*

MoSe_2 is an interesting narrow-band-gap semiconductor with a lamellar crystal structure of Se–Mo–Se sandwich layers, making it a good candidate for LIBs and SIBs by electrochemical intercalation. MoS_2 with a high theoretical capacity and excellent cycling performance has been under focused research, a close analogue MoSe_2 may show more advantages due to the higher electrical conductivity of Se than that of S [41,137,138]. On the basis of crystal structure, MoSe_2 has two phases: semiconductive trigonal 2H- MoSe_2 phase and metallic octahedral 1T- MoSe_2 phase. The 1T- MoSe_2 structure possesses a high intrinsic electronic conductivity and has overcome the sensitivity to air atmosphere (*via* replacing a conventional Li intercalation–exfoliation method with a NH_4^+ intercalation one), thus it is a promising material for practical applications [139,140]. However, the 2H- MoSe_2 electrode usually suffers from low cycling stability and inferior rate capability due to the instability and intrinsic low electronic conductivity (note: the following crystal phases refer to 2H phase unless otherwise specified) [141,143].

2.2.1. *Structural control of MoSe₂*

To further enhance the ionic/electronic conductivity and inhibit the stacking problem as well as the “shuttle effect” of intermediate polyselenides for LIBs, many efforts have been made including nanostructure design [137,144,146], incorporating with carbon-based conductive frameworks (e.g., amorphous carbon, CNTs, graphene) [141,147,154], and fabrication of integrated electrodes [139,140]. For example, Shi et al. synthesized a highly ordered hexagonal mesoporous crystalline MoSe_2 *via* a

nanocasting method using silica SBA-15 as a hard template. The obtained MoSe₂ with a direct bandgap of 1.37 eV demonstrated a high reversible Li storage capacity of 630 mA h g⁻¹ and showed a rate performance better than the analogous mesoporous MoS₂, making it a promising anode for LIBs due to the increased structural stability and conductivity. Through tuning the mesoporous structure, a high reversible Li storage capacity of 744 mA h g⁻¹ at 0.1C and excellent rate capability up to 2C could be achieved [137]. In addition, such nano-replication method for mesoporous TMDs was successfully applied to fabricate other analogues including MoS₂, WS₂, and WSe₂[64]. It exhibited a reversible capacity exceeding the theoretical reversible capacity of MoSe₂ (422 mA h g⁻¹, based on the conversion reaction with Li⁺ followed by forming Mo nanoparticles in the insoluble Li₂Se matrix [150]), which seems to be a common and highly beneficial phenomenon for layer-structured materials due to the additional interfacial Li storage, thus forming a bridge between batteries and capacitors at the mesoscopic scale [88,102,137]. Despite that MoSe₂ with various nanosheet-assembled nanostructures, such as nanocaterpillars, nanosheets, and nanotubes can be synthesized by a general solvothermal method, the incorporation of heteroatoms can be adopted to further endow those layered MoSe₂ with even more exposed active and unsaturated sites as well as enhanced conductivity. The hierarchical S-doped MoSe_{2-x} hybrid nanotubes showed an enhanced reversible capacity as anode material for LIBs [144]. Related electrochemical mechanism need to be further studied for in-depth insight. Surface modification or tuning the band gap *via* formation of heterostructures to enhance the conductivity is another approach for advancing layered MoSe₂ as anode materials. Zhang et al. conceptually designed a strategy to narrow the band gap of MoSe₂ to obtain conductive red MoSe₂nanosheets by constructing the Mo–O bonding on the surface of MoSe₂ nanosheets for enhanced electronic conductivity (Fig. 5a). This material demonstrated a significantly improved Li storage

performance and high-rate capability thereof. The red MoSe_2 nanosheets as anode material for LIBs exhibited a superior reversible capacity of 1126 mA h g^{-1} after 500 cycles at 1.0 A g^{-1} (Fig. 5b), an outstanding high-rate and long-term capacity of 650 mA h g^{-1} at 5.0 A g^{-1} over 4,000 cycles (Fig. 5c) [146]. The design of tunable band gap may extend to other layered TMDs. It is also noteworthy that MoSe_2 may also undergo a phase transition during the initial discharge process, i.e., from 2H- MoSe_2 to O- MoSe_2 , based on a Li-ion vacancy-hopping diffusion mechanism. Nanocrystalline MoSe_2 holds lower charge transfer resistance, better electrochemical performance, and greater potential as anode materials thereof compared with the amorphous one (i.e., calcined at lower temperature), although they may present a same phase transition process after the initial discharge/charge process [155].

Fig. 5. (a) Schematic illustration of the synthesis of conductive red MoSe₂ with a tunable band gap and its application for LIBs. (b) Cycling performance of red MoSe₂, black MoSe₂, and MoO₃ anodes at a current density of 1 A g⁻¹. (c) Cycling performance of red MoSe₂ anode at 5 A g⁻¹. Reproduced from Ref. [146] with permission of American Chemical Society.

2.2.2. Hybridizing MoSe₂ with conductive frameworks

Amorphous carbon is a cost-effective and versatile framework for various composite structures [156159]. Through tuning the glucose-derived carbon ratio in the hydrothermally prepared MoSe₂-C hybrid materials, the optimal one with 15% carbon could deliver a higher reversible capacity of 1165 mA h g⁻¹ after 150 cycles at 200 mA g⁻¹ and 860 mA h g⁻¹ after 150 cycles at 1000 mA g⁻¹, as well as an excellent rate capability of 734 mA h g⁻¹ at 10 A g⁻¹ [150]. This type of hybrid materials with an optimal carbon layer displayed not only increased electric conductivity but also electrode integrity. Wei's group fabricated a MoSe₂/CMK-5 composite with layered MoSe₂ encapsulated in ordered tubular mesoporous carbon CMK-5 *via* a nanocasting route. As a conductive framework with a massive internal surface area, CMK-5 not only increases electric conductivity, shortens ion diffusion pathway but also well accommodates the volume change of MoSe₂ during (de)lithiation process. When this nanocomposite utilized as an anode for LIBs, it delivered an outstanding reversible capacity of 788 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹ with a low self-discharge feature, superior rate performance as well as more stable long-term cycling capability (451 mA h g⁻¹ attained after 1000 cycles at a current density of 2.0 A g⁻¹) [149]. Another kind of hierarchical MoSe₂ microspheres (composed of interconnected nanoflakes) coated with homogeneous thin N-doped carbon (N-C) layer was constructed by Tu and coworkers *via* a facile two-step method of hydrothermal process followed by thermal polymerization of dopamine. The MoSe₂/N-C composite as LIB anode material exhibited

smaller polarization resistance, better reversibility, and enhanced electrochemical reactivity compared to the unmodified MoSe₂. This composite delivered a high reversible capacity of 698 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹, high rate capacity of 471 mA h g⁻¹ at 2.0 A g⁻¹ [148]. It also showed an enhanced long-term cycling stability compared to the glucose-derived carbon coating route [141]. The improved electrochemical properties can be ascribed to incorporation of N-doped carbon coating and the hierarchical microsphere structure with more reactive sites and faster ionic/electronic transfer characteristics. Furthermore, for the incorporation with 1D nanofiber frameworks [152], Yang et al. designed a coaxial-cable MoSe₂/hollow carbon nanofiber (HCF) composite with few-layered ultrasmall MoSe₂ nanosheets decorated HCFs. The MoSe₂/HCFs composite delivered a high and stable specific capacity of 658 and 577 mA h g⁻¹ at 0.5 and 1.0 A g⁻¹ after 100 cycles, with an almost 100% capacity retention rate and a high-rate capacity of 524 mA h g⁻¹ at 3.0 A g⁻¹. The enhanced electrochemical performance can be ascribed to the rational design and the synergistic effect between conductive HCFs and smart MoSe₂ nanoarrays that facilitates electronic/ionic conductivity and electrode structural stability [160]. Wang et al. further fabricated a N-doped carbon/MoSe₂ core/branch nanostructure *via* calcinating a mixture of polyaniline (PANI)-intercalated MoO₃ nanorod hybrid and Se powder in Ar atmosphere. This nanohybrid could deliver a high reversible capacity of 906 mA h g⁻¹ with a capacity retention rate of 97.6% at 100 mA g⁻¹ after 100 cycles and an enhanced rate capability of 560 mA h g⁻¹ at 1.0 A g⁻¹, due to the unique structure of N-doped carbon nanorod cores and the MoSe₂ nanosheet branches [151].

The design of hollow structure together with introducing conductive carbon frameworks facilitates fast electron/ion transfer and alleviates the stress caused by huge volume changes during charge/discharge process [109,110,142,161,163]. Yang et al. synthesized porous hollow carbon spheres

(PHCS) decorated uniformly and conformally with MoSe₂ nanosheets, which could deliver a reversible Li storage capacity of 681 mA h g⁻¹ after 100 cycles at 1.0 A g⁻¹. The enhanced performance can be explained by that the mechanically robust carbon hollow conductive support accommodated stress from cycling, benefited the conductivity and shortened ion pathway [142]. Pan's group designed similar MoSe₂/C hybrid hollow spheres *via* a colloid template/glucose assisted hydrothermal route followed by annealing treatment. This hollow hybrid demonstrated an excellent reversible capacity of 795 mA h g⁻¹ after 250 cycles at 200 mA g⁻¹, and 744 mA h g⁻¹ after 300 cycles at 1000 mA g⁻¹; and showed a superior rate capacity of 370 mA h g⁻¹ at a very high current density of 10 A g⁻¹ [161]. To further enhance the conductivity of the carbonaceous frameworks, Zhao et al. synthesized a 3D hierarchical hollow MoSe₂/N-doped carbon microsphere (MoSe₂/N-C) composite *via* dopamine-assisted chemical precipitation followed by an annealing treatment. The hollow spherical MoSe₂/N-C composite exhibited a superior capacity of 1313 mA h g⁻¹ at 1.0 A g⁻¹ after 100 cycles, and an excellent rate capacity of 597 mA h g⁻¹ at a current density at 10 A g⁻¹ [162].

The optimized synergistic effect of layered MoSe₂ and the most promising matrix graphene will enhance the electronic/ionic conductivity and integrity of the electrode [143,164]. For example, few-layered MoSe₂/rGO hybrid with ultrathin MoSe₂ well dispersed and anchored on the flexible graphene nanosheets could be synthesized by a facile ionic liquid-assisted hydrothermal route, which exhibited a high reversibility of ~1100 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹ and greatly improved cycling stability [143]. The similar hierarchical MoSe₂/rGO composite obtained *via* a hydrothermal/solvothermal route also showed enhanced electrochemical performance: Zhang et al.'s work on MoSe₂/rGO hybrid exhibited an excellent rate performance and cycling capacity of 917 mA h g⁻¹ at 0.5 A g⁻¹ (750 mA h g⁻¹ at 1.0 A g⁻¹) after 100 cycles [164]; Yao et al. reported a 3D

MoSe₂/rGO foam composed of nanolayered MoSe₂ affording a long-term cycling stability with a 89.1% capacity retention rate ($> 470 \text{ mA h g}^{-1}$) after 600 cycles at 0.5C [153]; a kind of 2D hybrid nanosheets with high-density few-layered MoSe₂ arrays vertically and uniformly grown on both sides of rGO sheets (*ca.* 90% loading content) exhibited an excellent cycling stability up to 1000 cycles with an attainable capacity of 637 mA h g^{-1} at 1.0 A g^{-1} [154]. The incorporation of graphene effectively enhances the structural integrity of MoSe₂ and improves its electrochemical performance, and thus holds great potential as advanced anode material for LIBs.

2.2.3. MoSe₂-based heterostructures and alloys

Heterostructures of TMDs, combining merits of different TMDs, have been regarded as a promising strategy tuning the electronic properties thereof with great potential in energy conversion and storage, catalysis and electronics [13,43,165169]. For example, Zhao et al. designed a carbon-free hybrid nanostructure of lamellar MoSe₂ nanosheets embedded with MoO₂ nanoparticles (MoO₂@MoSe₂) via a simple hydrothermal method followed by freeze-drying in vacuum, where the MoSe₂ nanosheets provide a flexible substrate and the MoO₂ nanoparticles act as spacers to inhibit restacking and provide higher active surface area for electrolyte. In addition, the heterojunctions at the interface (*i.e.*, heterointerfaces) between MoSe₂ and MoO₂ introduce a self-built electric field for promoted lithiation/delithiation process. As a result, this lamellar hybrid could deliver a long-term cycling capacity of 520 mA h g^{-1} at a high current density of 2.0 A g^{-1} over 400 cycles (with CE approaching 100%) and an excellent rate performance [170]. Yang et al. designed a facile, low-cost, and high-yield solution-phase strategy for creating MoS₂–MoSe₂ p–n heterostructures with vertically grown MoSe₂ (p-type) nanosheet array on layered MoS₂ (n-type) followed by a coating process with amorphous carbon. This heterostructure delivered a superior electrochemical activity and excellent Li-ion storage

properties with a high reversible capacity of 676 mA h g⁻¹ after 200 cycles at 200 mA g⁻¹. The unique compositional and structural features include porous architecture for shortened Li-ion diffusion channels and optimized interfaces between electrode and electrolyte, edge-to-edge configuration with more exposed active sites, and high-quality heterointerface within the heterostructures for fast interfacial charge transfer; all these contribute to the enhanced electrochemical activity and efficiency [165]. And the advantages were also verified by the first-principles calculations where the MoS₂/MoSe₂ heterointerface could effectively reduce the band gap, diversify Li adsorption sites and enhance the electrochemical properties in heterostructure [167]. The incorporation of TiO₂ with a relatively high (de)lithiation voltage can efficiently avoid the formation of solid electrolyte interface (SEI) layers and thus enhance the safety performance of the batteries. Taking the decoration of few-layered MoSe₂ nanosheets on C/TiO₂ nanobelts as an example *via* a glucose-assisted hydrothermal process, the MoSe₂@C/TiO₂ heterostructure as LIB anode material showed an enhanced reversible capacity of 987 mA h g⁻¹ after 100 cycles at 500 mA g⁻¹ and an outstanding rate capacity of 860 mA h g⁻¹ at a current rate of 3.0 A g⁻¹, much better than its individual components [171].

Theoretical and experimental studies have revealed that the introduction of Se into molybdenum sulfides by forming MoS_{2(1-x)}Se_{2x} alloys may not only widen the interlayer spacing for more effective diffusion of ions/electrons during charge/discharge process, but also decrease the energy barriers to pass through the layers due to the slight distortion and polarized electric field in the basal planes caused by the incorporation of Se with bigger radius [172,174]. As an example, the optimized 2D layered mesoporous MoS_{2(1-x)}Se_{2x}/rGO electrode prepared by Wang et al. could deliver a high capacity of 830 mA h g⁻¹ at 100 mA g⁻¹ after 150 cycles, and an enhanced capacity of 415 mA h g⁻¹ at 1000 mA g⁻¹ [172]. MoSe₂ can also be used to enhance the cycling and rate performances of other transition-

metal chalcogenides (TMCs). For example, the material $\text{Cu}_{2-x}\text{Se}@\text{C}$ nanosheets coated with MoSe_2 nanoparticles showed an improved reversible capacity of 432 mA h g^{-1} after 100 cycles at 100 mA g^{-1} as well as enhanced rate capacity, much higher than that of $\text{Cu}_{2-x}\text{Se}@\text{C}$ or pure phase Cu_{2-x}Se nanosheets (166 and 82 mA h g^{-1} , respectively). The sandwich-like structure not only enhances the electrical conductivity but also buffers the volume change and increases the structural stability during cycling [175]. In addition, MoSe_2 may be also utilized to enhance the electrochemical stability of elemental Se as anode for LIBs by buffering volume changes and inhibiting aggregation during cycling, thus the combination of MoSe_2 and Se is expected to provide a higher reversible capacity and excellent rate capability. As an example, the $\text{CNTs}@\text{C}@\text{MoSe}_2@\text{Se}$ hybrid could deliver a specific capacity of 1010 mA h g^{-1} after 100 cycles at 100 mA g^{-1} and a high-rate capacity of 508 mA h g^{-1} at 5.0 A g^{-1} after 500 cycles [176].

2.2.4. Flexible MoSe_2 electrodes

Recent progressive techniques in flexible portable electronic apparatuses triggered the intensive interests for flexible electrodes and soft batteries as energy sources with features of light weight and high specific capacity [120,121,139]. For flexible MoSe_2 anode in advanced LIBs, Zhu et al. constructed a N-doped 1D carbon backbones supported MoSe_2 nanosheets ($\text{MoSe}_2/\text{N-CNFs}$) for superior flexible electrodes (Fig. 6) via combining the techniques of electrospinning, hydrothermal treatment, and calcination. It delivered an initial discharge capacity of 863 mA h g^{-1} at 100 mA g^{-1} with an ICE of 76.3%, a reversible capacity of 611 mA h g^{-1} after 100 cycles, corresponding to a CE higher than 98%. This flexible hybrid electrode also demonstrated a good rate performance with reversible specific capacities of 532 , 452 , and 302 mA h g^{-1} at 0.5 , 1.0 , and 2.0 A g^{-1} , respectively [140]. Xiang et al. fabricated a 2D stable metallic 1T- MoSe_2 with an expanded interlayer spacing of

10.0 Å that was *in situ* vertically grown on CVD-derived SWCNTs (1T-MoSe₂/SWCNTs) film (Fig. 7a–c) via a solvothermal route for hybridized flexible anode of LIBs (Fig. 7d inset). This binder-free electrode delivered an outstanding capacity of 971 mA h g⁻¹ after 100 cycles at 300 mA h g⁻¹ and an excellent rate capability of 630 at 3.0 A g⁻¹ (Fig. 7d–f). It is confirmed by an X-ray absorption near-edge characterization that a strong electrical and chemical coupling (i.e., C–O–Mo bonding) was formed between SWCNT and 1T-MoSe₂ nanosheets, which remarkably enhanced the electron/ion transport (Fig. 7g) and structural stability for high Li storage performance thereof. The flexible full cell assembled with a LiFePO₄ cathode showed excellent cycling reversibility and mechanical flexibility, i.e., a good overlapping in CV curves and galvanostatic charge/discharge process and a negligible decrease after 50 bendings compared to the original flat battery [139]. The synthetic strategy shown here may provide inspiration for fabricating other flexible energy storage devices.

Fig. 6. (a) SEM, (b and c) TEM and (d) HRTEM images of flexible $\text{MoSe}_2/\text{HPCFs}$ with MoSe_2 nanosheets anchored on N-doped 1D carbonaceous backbones as binder-free electrodes. Reproduced from Ref. [140] with permission of Elsevier.

Fig. 7. (a) SEM, (b) TEM, and (c) HRTEM images of the 1T-MoSe₂/SWCNTs hybridized flexible binder-free electrode with MoSe₂ nanosheets (characterized by an enlarged interlayer distance of 10.0 Å) intimately anchored on the surface of SWCNT bundles. Electrochemical performance evaluations of 1T-MoSe₂/SWCNTs hybrids: (d) charge and discharge curves (inset: film electrode), (e) cycling performance at 300 mA g⁻¹, (f) rate performance, and (g) the Nyquist plots. Reproduced from Ref. [139] with permission of American Chemical Society.

2.3. WSe₂ for lithium-ion batteries

WSe₂ is a vital member of TMDs and has raised intensively interests owing to its unique properties with a small band gap of 1.6 eV and a large adjacent layer spacing of 0.648 nm (two times larger than that of graphite), which can effectively facilitate reversible ion intercalation and extraction [177]. Thanks to its very high density of 9.32 g cm⁻³, WSe₂ has a high volumetric capacity [178]. To overcome the common defects of TMDs for enhanced electrical conductivity and suppressed volume changes during the electrochemical reaction processes, effective methods have been attempted including structural design and hybridizing with other conductive components [177,180]. For instance, Wei and coworkers fabricated an orderly mesoporous WSe₂/CMK-5 nanocomposite through a nanocasting route by introducing the unique mesoporous carbon CMK-5 as a nanoreactor. Benefiting from the synergetic effect of few-layered WSe₂ and mesoporous carbon for improved redox kinetics and structural stability, this hybrid showed an enhanced rate capability of 400 and 320 mA h g⁻¹ at 1.0 and 2.0 A g⁻¹, respectively; an outstanding long-term cycling stability with a specific capacity of 490 mA h g⁻¹ after 600 cycles at 500 mA h g⁻¹ and a CE of above 99% [177]. It should be noted that the introduction of carbon conductive framework enhanced the electrochemical properties such as reversibility, cycling stability and rate capability, however, it usually reduced the ICE [178]. For example, CMK-5 exhibited an initial discharge–charge capacities of 1559 and 496 mA h g⁻¹ with a CE of merely 31.8% due to the formation of SEI film [177]. Thus a pre-lithiation treatment of the anode materials will be very beneficial for a practical application in the full cells or batteries.

3. Sodium-ion batteries

Sodium-ion batteries (SIBs) have attracted great attention and have been considered as a promising alternative for LIBs in cost-effective electrochemical energy storage, however, it is still challenging

but greatly desired to design and develop novel electrode materials with high reversible capacity, long cycling life, and good rate capability toward high-performance SIBs [57,50]. Sodiation/desodiation with Na ions in layered TMDs is based on an intercalation followed by conversion reaction, which not only is able to deliver higher capacity than the intercalation reaction, but also provide capacitive storage. The structural design of electrodes and introduction of conductive matrices for TMDs/C composites can substantially improve Na storage behavior by accommodating large volume changes and facilitating fast ion diffusion [6,29,50,56].

3.1. WS_2 for sodium-ion batteries

2D semiconductive WS_2 has a large interlayer spacing ($d = 6.2 \text{ \AA}$ for (002) facial) with weak van der Waals interaction in-between layers [181]. Theoretically, it affords easier and rapid Na-ion transport during the sodiation/desodiation processes compared with metal oxides. However, pristine or pure WS_2 usually suffers from relatively low electroconductive response, not affordable for rapid charging/discharging processes of SIBs [84,182]. Recent studies have shown the benefits from the morphology control or nanostructuring [67,183], the incorporation with conductive substrates such as carbon (including CNTs, graphene) [96,97,134]. Greatly improved electrochemical performance can be achieved due to the enhanced Na-ion/electron conductivities, shortened diffusion/transfer pathway, and the improved electrode structural stability [96,97,184].

3.1.1. Structural control of WS_2

Firstly, nanostructures play a significant role in improving the electrochemical performance of WS_2 . As an example, Zhou et al. exploited a scalable synthesis route for high-quality WS_2 nanosheets via a NaCl template-assisted *in situ* CVD process [80]. The as-prepared WS_2 nanosheets with a single-crystalline structure showed higher structural stability and conductivity. When utilized as SIB anode,

it delivered a high reversible capacity of 461 mA h g⁻¹ at 100 mA g⁻¹ after 60 cycles and exhibited a greatly enhanced rate capacity of 389, 371, and 351 mA h g⁻¹ at 1, 2, and 5 A g⁻¹, respectively. It is claimed that the excellent rate performance was attributed to the enhanced Na-ion reaction kinetics that were mainly controlled by the capacitive process. This synthesis method is applicable to produce other TMDs, such as MoS₂, MoSe₂, and WSe₂ nanosheets. Secondly, in addition to the influence of different sulfur sources or nanostructures just discussed above [185], Wang et al. further revealed that the (002)-oriented WS₂ nanosheets with large interlayer spacing by controlled sulfuration time can deliver a better cycling stability and higher rate performance than other (100)-oriented WS₂[183]. However, due to the relatively sluggish electrode kinetics of SIBs, the Na storage capacity of the same electrode is usually smaller than that of LIBs [96]. Thirdly, expanding adjacent layers of bare WS₂ is a promising approach to improve the Na storage. Liu et al. synthesized thin WS₂ nanowires (diameter ~25nm) with expanded interlayer spacing of 0.83 nm *via* a facile solvothermal route followed by a heat treatment, which not only provided more active sites and open channels for the intercalation of Na⁺ ions but also facilitated the electron and ion diffusion. When evaluated as a SIB anode it showed a higher reversible capacity of 483 mA h g⁻¹ after 50 cycles at 100 mA g⁻¹ and a good rate capability of 430, 368, and 236 mA h g⁻¹ at 1, 2, 5 A g⁻¹, respectively, over the potential window of 0.5–3.0 V; and this potential range was chosen to suppress the irreversible conversion reaction and maintain the reversible intercalation-type mechanism. It also exhibited an ultra-long cycle life of 1400 cycles with a capacity of ~330 at 1.0 A g⁻¹ and a high CE of > 99%. Through the HRTEM observation of the intermediate it was revealed that the WS₂ layers were further expanded during cycling, e.g., with an interlayer spacing of 1.28 nm after 10 cycles and almost separated into single layers after 100 cycles. When paired up with a NaVPO₄F/C cathode (theoretical capacity of 128 mA h g⁻¹), the Na-ion full

cell delivered an initial capacity of $\sim 330 \text{ mA h g}^{-1}$ and relatively good stability with a 76% retention rate after 20 cycles (based on the mass of WS_2 anode) when tested between 3.01.0 V at 100 mA g^{-1} [186].

3.1.2. Hybridizing WS_2 with conducting frameworks

As for LIBs, similar efforts have been made to improve the electrochemical performance of WS_2 for SIBs by incorporating with electrical conducting matrices [101]. For example, N-doped conductive carbon was involved into WS_2 nanosheets for a higher conductivity, the as-prepared WS_2 -NC nanocomposite showed an enhanced reversible capacity of $\sim 360 \text{ mA h g}^{-1}$ at 100 mA g^{-1} and 200 mA h g^{-1} at 1.0 A g^{-1} [187]. The WS_2 @CMK-3 hybrid fabricated by Pang et al. based on ordered mesoporous carbon matrix showed an enhanced capacity of 333 mA h g^{-1} at 100 mA g^{-1} without any fading over 70 cycles, and a rate capability of 230 mA h g^{-1} at 2.0 A g^{-1} [96,129]. For the carbon-incorporated 2D-TMDs materials, MOF-derived well-defined morphology and nanostructures is an alternative choice of great advantages as a highly conductive matrix [188]. Prussian blue (PB), a subset material of MOF families, can be directly pyrolyzed to produce nanoporous carbon framework with well-defined nanocubic morphology as well as high surface area and interconnected pores useful for improved electrochemical performance of active materials. By incorporation with an outer shell of few-layered WS_2 nanosheets, Yang and coworkers designed a unique cubic-shaped WS_2 @NC hybrid nanostructure with WS_2 nanopetals on PB-derived N-doped carbon framework (Fig. 8). This material possesses several advantages such as improved electronic conductivity, buffered volumetric change, reduced ion diffusion length, and a larger surface area for sodiation/desodiation. The incorporating of PB-derived N-doped carbon framework greatly improved the rate capability of WS_2 , and this hybrid exhibited a stable cycling performance with a specific capacity of 320 mA h g^{-1} after 200 cycles at a

current density of 200 mA g^{-1} and with one of the highest ICE reported of 79.8% [184]. Developing a facile and up-scalable strategy to construct desirable TMDs/C hybrids with open and unstacked active nano-building blocks and strong interconnection with the conductive matrix would be very promising for practical application. Yu and coworkers designed a one-step *in situ* solid-state hybridization strategy to construct WS_2 nanowall arrays anchored on N-doped carbon layers (NCLs) as shown in Fig. 9a[73]. The exposed active edge sites will be maximized and the exchange current density of 2D TMDs will be enhanced compared to the structure parallel to the substrates [189,190]. This lamellar hybrid architecture demonstrated largely improved Na storage performance as SIB anode materials. The WS_2/C in such structure delivered a stable reversible capacity of 180 mA h g^{-1} over the potential range of 0.4–3.0 V vs. Na^+/Na after 1200 cycles at 1.0 A g^{-1} with a mean capacity loss as low as $0.015 \text{ mA h g}^{-1}$ per cycle (Fig. 9b left). It implies that the unique 2D@2D hybrid structure accounts for the excellent Na-ion storage properties, as illustrated in Fig. 9b (right). This structure allows the direct and full contact of open nanowalls of expanded interlayers with electrolyte without “dead volume” for increased ion diffusion kinetics, more active sites, reduced internal resistance and structural strain during the electrochemical reactions as well as intimate coupling with the NCLs substrates [73].

Fig. 8. (a) Schematic illustration of the WS₂@NC synthesis process derived from Prussian blue (PB) nanocubes. SEM images of (b) PB nanocubes, (c) derived porous N-doped carbon nanocubes (NC) and (d) WS₂@NC samples. Insets show SEM images at lower magnification. Reproduced from Ref.[\[184\]](#) with permission of Royal Society of Chemistry.

Fig. 9. (a) Schematic illustration of the procedure to fabricate the lamellar hybrid structure (*lower left*: SEM image) of MS₂/C (M = Mo, W) with MS₂ nanowall arrays anchored on a carbon layer by an *in-situ* hybridization strategy and the Na⁺ intercalation in the obtained MS₂/C hybrid electrode. (b) Cycling performance of the obtained WS₂/C hybrid at 1 A g⁻¹ (*left*), and schematic diagram of fast Na⁺/electron transport in the hybrid electrode with expanded WS₂ interlayers (*right*). Reproduced from Ref. [73] with permission of Wiley-VCH.

Recently, graphene-based TMDs have been developed with significantly improved Na-ion storage properties, since the 2D graphene nanosheets with excellent physical and chemical features

can effectively enhance the electrochemical conductivity and buffer the volumetric expansion as well [12,22]. Dou and coworkers fabricated a WS₂@graphene nanocomposite by a hydrothermal route, which showed a long-cycle reversible capacity of 329 mA h g⁻¹ over 500 cycles at 20 mA g⁻¹, much higher than that of bare WS₂ (32 mA h g⁻¹) [191]. Furthermore, those 3D graphene structures fabricated from 2D sheets can not only exhibit the merits of graphene including fast electronic transport and preventing aggregation of active materials, but also demonstrate excellent mechanical strength for potential flexible energy storage and conversion devices. Choi and Kang prepared a hybrid structure of layered WS₂ nanosheet-decorated 3D rGO microspheres (WS₂-3D rGO) using a facile two-step ultrasonic spray pyrolysis combined with a sulfidation process (Fig. 10a). The as-prepared WS₂-3D rGO microsphere material showed superior Na-ion storage properties to the metal oxide analogue (i.e., WO₃-3D rGO microspheres), although the theoretical capacity of WO₃ is higher than that of WS₂. When evaluated by galvanostatic measurements, the WS₂-3D rGO material showed an enhanced rate capability and a discharge capacity of 334 mA h g⁻¹ after 200 cycles at a current density of 200 mA g⁻¹ with the CE high than 99.9%, in sharp contrast to that merely 118 mA h g⁻¹ for WO₃-3D rGO under the same conditions (Fig. 10b). It is noteworthy that although the as-prepared WS₂-3D rGO microspheres material delivered a much superior capacity and long-term cycling performance compared to pure WS₂, it suffered from a low ICE since the rGO incorporated has a relative low ICE of 23.2% related with the large irreversible capacity. Thus the ICE of the hybrid electrode needs be further improved for practical application [192].

Fig. 10. (a) Schematic diagram for the formation mechanism of 3D WS₂-rGO microspheres. (b) The cycling performances of as-prepared microspheres and counterparts for Na-ion storage at a current density of 200 mA g⁻¹. Reproduced from Ref. [192] with permission of Royal Society of Chemistry.

3.1.3. WS₂-based heterostructures

Although TMDs have been recently considered as a class of high-capacity alternative anode materials to metal oxides due to the large interlayer space, reversible conversion reaction and higher conductivity of Na₂S products, they may also encounter with the “shuttle effect” that occurs in the Li-S battery system, namely, the sulfur dissolution problem originating from soluble polysulfide intermediates during the Na₂S formation/decomposition process resulting in loss of active sulfur

components and a fading capacity. In this regard, the introduction of a protective layer such as carbon or metal oxide on the surface is preferably adopted, Taylor's group exploited a more facile and advanced coating process to precisely control the surface layer on the metal sulfide nanomaterial [72]. The as-designed heterogeneous WS_x/WO_3 core-shell hybrid with thorn-bush nanofiber (NF) structures *via* electrospinning and post-thermal treatment with metal oxide coating on the WS_x NF ($2 < x < 3$) showed an enhanced Na-ion storage performance (Fig. 11a). Compared to pristine WS_x NF electrode (44% capacity retention), WS_x/WO_3 NFs retained 74% of the capacity obtained at the 2nd discharge capacity after 100 cycles at 100 mA g^{-1} (Fig. 11b), and comparable rate capability at high current densities. Using the *ex situ* XRD characterization of the disassembled Na electrode, it was confirmed that the modification of metal sulfide electrode with oxide passivation surface layer effectively alleviated sulfur dissolution for achieving both high capacity and improved cycle performance [72].

Fig. 11. (a) Schematic illustration of the synthetic strategy for heterogeneous WS_x/WO_3 thorn-bush (core-shell) nanofibers and the corresponding Na-ion storage reaction mechanism during cell operation. (b) Cycle performance of WS_x nanofibers and the post-calcined WS_x nanofibers (WS_x/WO_3 or WO_3) over a voltage window of 3.0–0.01 V at a current density of 100 mA g⁻¹. Reproduced from Ref. [72] with permission of American Chemical Society.

3.1.4. Flexible WS_2 electrodes

Flexible WS_2 electrodes for SIBs have also been demonstrated [193,194]. Yu and coworkers prepared a 3D porous interconnected WS_2/C nanocomposite on a Ti foil *via* a facile electrostatic spray deposition (EDS) technique, which is comprised of 0D WS_2 (~10 nm), 1D CNTs and 2D rGO. This

annealed WS₂/C nanocomposite electrode showed an excellent rate performance (with capacities of 393, 270, 199, and 81 mA h g⁻¹ at 100, 500, 1000, and 5000 mA g⁻¹, respectively) and long cycling stability (267 and 219 mA h g⁻¹ at 500 mA g⁻¹ after 200 and 300 cycles, respectively). The EDS technique for porous interconnected nanocomposite structures offers an alternative solution for high rate and long cycling SIB anodes, and may be expanded to produce materials for thin film batteries [195]. In addition, as a free-standing dual anode for SIBs besides LIBs, a hybrid film of WS₂ nanoplates embedded in graphitic carbon nanotubes (WS₂@G) abovementioned could deliver a stable reversible Na-ion storage capacity of more than 340 mA h g⁻¹ over 600 cycles at 500 mA g⁻¹ and a high rate capacity of 289 mA h g⁻¹ at 3.0 A g⁻¹ [129]. The WS₂/CNT-rGO hybrid aerogel abovementioned delivered a Na-ion storage capacity of 253 mA h g⁻¹ after 100 cycles at 200 mA g⁻¹, higher than those of commercial WS₂ powder (23 mA h g⁻¹) and pure CNT-rGO aerogel (61 mA h g⁻¹) [67]. Wang et al. designed a 3D carbon foam supported WS₂ nanosheets with decorated N-doped graphene quantum dots (NGQDs-WS₂/3DCF) for cable-shaped flexible SIBs. Benefiting from the 3D robust porous interpenetrating scaffold and the NGQDs modification, the free-standing electrode of hybrid nanoarchitecture could deliver a high capacity of 392 mA h g⁻¹ at 200 mA g⁻¹ after 1000 cycles with an extraordinary capacity retention of 97.1% *versus* that of the first cycle, and an enhanced rate capability of 268 mA h g⁻¹ at 2.0 A g⁻¹. When developed as a cable-shaped flexible full SIB, it also exhibited high capacity and fine flexibility [194].

3.2. MoSe₂ for sodium-ion batteries

3.2.1. Structural control of MoSe₂

Compared with MoS₂, the analogue MoSe₂ exhibits some advantages for SIBs due to its larger interlayer spacing (0.646 nm) and higher electric conductivity originating from the small band gap,

which both enable fast charge transfer and enhanced reversible electrochemical charge/discharge processes [196,197]. The design of (porous) nanostructured anode materials, in consideration of larger radius and slower reaction kinetics for Na ions compared to Li ions, will benefit high reversible capacity and prolonged cycle life [198,202]. The porous/hollow structures with high surface area will show an improved performance than solid analogues since the activation barrier for Na-ion transportation on the surface (0.344 V) is much lower than that of interlayers (1.28 V) of MoSe₂, i.e., a larger Na-ion diffusion coefficient on the surface [202]. For example, a hierarchical yolk-shell-structured MoSe₂ microspheres synthesized by a facile selenization of MoO₃ precursor could deliver an initial capacity of 527 mA h g⁻¹ and a better cycling capacity of 433 mA h g⁻¹ after 50 cycles at 200 mA g⁻¹ as well as a high rate capability of 364 and 345 mA h g⁻¹ at 1.0 and 1.5 A g⁻¹ [203]. Furthermore, the accurate control of various hollow structures and their evolution process is of great interest and challenge. Cao's group developed a new strategy on Hansen solubility parameter (HSP)-guided solvent selection to initiate Ostwald ripening for accurate synthesis of interior space-tunable MoSe₂ spherical structures (i.e., solid, core-shell, yolk-shell and hollow spheres; see Fig. 12a,b) with outer shells composed of few-layer nanosheets (Fig. 12c-e), which showed architecture-dependent electrochemical performances. The as-obtained hollow spheres showed a superior initial discharge capacity of 710 mA h g⁻¹ at 100 mA g⁻¹ with an impressively high ICE of 91.3% as well as outstanding stable cycling performance (694 mA h g⁻¹ after 100 cycles with CE over 98%) and rate capability, much higher than those of yolk-shell and solid spheres (Fig. 12f,g). The enhanced performance is attributed to the synergistic effects including enhanced electrical conductivity by increasing crystallinity, more electrochemical active sites due to higher specific surface area, and fast mass transfer kinetics with enlargement of interior space [204]. Similarly, Zhang et al. prepared a rod-like

hollow structure composed of interlayer-expanded MoSe₂ nanosheets with a 54.8% expansion of (002) planes up to 10.0 Å. The hierarchically nanotubular architecture was a result of oriented attachment/assembly and Ostwald ripening effects during the one-pot solvothermal route. When utilized as a SIB anode in a controlled cut-off voltage range of 0.5–3.0 V within an intercalation mechanism, it exhibited a highly durable and stable cycling performance with a discharge capacity of 228 mA h g⁻¹ after 1500 cycles at 1.0 A g⁻¹. It is also noteworthy that for the controlled potential range of 0.5–3.0 V, although showing herein a lower capacity than those obtained in the potential range of 0.01–3.0 V, it did exhibit a much better cycling performance due to the integrity of the layered structure of the electrode based on a limited intercalation-type reaction [201]. Shi et al. synthesized an *in-situ* carbon-doped Mo(Se_{0.85}S_{0.15})₂ hierarchical nanotubes (diameter of 300 nm, wall thickness of 50 nm) composed of 2D layered nanosheets *via* a solvothermal method followed by selenizing the precursor of MoS₂:C nanotubes at 900 °C. The Mo(Se_{0.85}S_{0.15})₂:C hierarchical hybrid performed as a robust host material for Na-ion storage. It could deliver an enhanced capacity of 421 mA h g⁻¹ (close to the theoretical capacity of MoSe₂) at 200 mA g⁻¹ after 100 cycles with a high ICE of 82.3%. Moreover, it showed a remarkable and stable capacity of 360 mA h g⁻¹ at a high current density of 2.0 A g⁻¹ over 100 cycles and a superior rate capability (e.g., with a capacity retention of 81.8% compared to that at 50 mA g⁻¹). The combined structural features are beneficial for the fast Na⁺ ion and electron kinetics and excellent performances thereof [199]. On the other hand, some S-doped 2H-MoSe₂ porous nanospheres assembled from few-layered nanosheets also showed enhanced electrical conductivity, expanded layer spacing, and improved Na-ion storage performance thereof [176,200,204].

Fig. 12. (a) The evolution process of MoSe₂ solid spheres to hollow spheres (HSs) and (b) corresponding schematic graphs with different reaction times in DMF (2–48 h). (c–e) TEM and HRTEM images of MoSe₂ HSs. (f) Cycling performances of different MoSe₂ electrodes for SIBs over the voltage window of 0.01–3.0 V and the coulombic efficiency of MoSe₂ HSs at 100 mA g⁻¹. (g) Rate capability of different MoSe₂ electrodes for SIBs. Reproduced from Ref. [204] with permission of Wiley-VCH.

3.2.2. Hybridizing MoSe₂ with conductive frameworks

For the improved electrochemical performance of MoSe₂, coupling with electrically conductive matrices such as carbon is a popular and effective strategy [142,162,164,205,206]. For example, Qiu's group synthesized one type of carbon-stabilized interlayer-expanded few-layer MoSe₂ nanosheets *via* a combined process of oleic acid/dopamine-assisted solvothermal, self-polymerization and calcination. The incorporation of N-doped carbon (N-C) expands the interlayer spacing of MoSe₂ from 6.4 to 7.0 Å, facilitates the permeation of electrolyte into the interlayers and enhances electronic/ionic conductivity as well as buffers volume changes during charge/discharge processes. When used as a SIB anode, the MoSe₂@N-C can delivered a high reversible capacity of 445 mA h g⁻¹ at 1.0 A g⁻¹ after 100 cycles and a significantly improved rate capability of 367 mA h g⁻¹ at 5.0 A g⁻¹. When assembled into full SIBs with Na₃V₂(PO₄)₃ cathode, the hybrid anode exhibited an impressively high capacity of 421 mA h g⁻¹ at 200 mA g⁻¹ after 100 cycles [205]. Using an alternative carbon resource such as cassava starch, the interlayer spacing could be further expanded up to 10 Å for the expanded (002) planes of few-layered MoSe₂ in the flower-like MoSe₂/C composite, which could deliver a long-term reversible capacity of *ca.* 360 mA h g⁻¹ after 350 cycles at 500 mA h g⁻¹ and a high rate capacity of 266 mA h g⁻¹ even at 4.0 A g⁻¹ [205,207]. Well-defined nanostructures such as hollow structures have attached great interest due to their unique advantages especially for the enhanced tolerance for volume expansion or structural strain [108,109,208]. The introduction of core in this encapsulation-type structure will further increase the volumetric energy density of SIBs [108-110]. Liu et al. designed such a type of MoSe₂@hollow carbon nanosphere (HCNS) with confined few-layer MoSe₂ nanosheets of exposed (002) planes, the layer spacing of which was expanded to 1.02 nm compared to the intrinsic value of 0.646 nm for pristine MoSe₂ (Fig. 13a-e) [196]. This hybrid MoSe₂@HCNS as anode

materials for SIBs showed excellent rate capabilities, ultralong cycling life with high Coulombic efficiency: it maintained a capacity of 501 and 471 mA h g⁻¹ after 1000 cycles at 1.0 and 3.0 A g⁻¹ (Fig. 13f), respectively, with a rate capacity retention of 382 mA h g⁻¹ at 10 A g⁻¹. Such high performance can be attributed to the 2D few-layer nanosheets with expanded (002) planes and the unique conductive hybrid shell structure for improving electrons/ions transfer, buffering volume changes and promoting the reversible desodiation–sodiation processes. The aforementioned MoSe₂@PHCS hollow structures as dual anodes also exhibited an enhanced reversible Na storage capacity of 580 mA h g⁻¹ after 100 cycles at 200 mA g⁻¹ due to the optimized synergic effects of the carbon hollow structure and thin MoSe₂ nanosheets [142]. A debatable issue about the capacity degradation mechanism is the shuttle effect of polyselenides, similar to that of polysulfides in Li–S batteries, leading to the loss of active materials and fast capacity fading [197]. The fabrication of conductive core/shell structures can alleviate volume changes of active materials (e.g. MoSe₂) and prevent them from “shuttle effect” and enhance the electrical conductivity. However, in some cases, only the conductivity of surficial active materials adhered to the conductive shell is improved, the conductivity of the core part is still low if the hybrid structure has relatively large dimensions. Fan and coworkers proposed a unique urchin-like MoSe₂@N-C composite structure with few-layer MoSe₂ nanosheets uniformly distributed on highly conductive N-doped carbon (N-C) matrix to meet these considerations for SIBs. The as-prepared MoSe₂/N-C composite spheres showed much improved rate capability and cycling stability compared with pure MoSe₂ sample. The high capacity retention up to 500 cycles (89.8% from the 2nd cycle at 500 mA g⁻¹) was mainly based on the alloying reaction, which benefits from the enhanced conductivity and accommodation of large volume expansion [197].

Fig. 13. (a) SEM, (b and c) TEM, and (d) HRTEM images of encapsulation-type MoSe₂@HCNS with expanded (002) planes confined in hollow carbon nanospheres (HCNS), and SAED (inset in (c)). (e) EDX mapping images (elements C, Se, Mo) of the fabricated few-layer MoSe₂@HCNS samples. (f) Cycling capability of MoSe₂@HCNS with prolonged cycle life (1000 cycles) for ultrahigh-performance SIBs at 1 and 3 A g⁻¹. Reproduced from Ref. [196] with permission of Wiley-VCH.

Beyond traditional amorphous carbon, nanostructured carbon materials such as carbon nanotubes (CNTs) [160,209,210] and graphene [154,164] have been extensively used to improve the performance of MoSe₂ as anode materials for SIBs by minimizing the restacking of MoSe₂ layers, providing abundant active sites and enhancing the electrical conductivity. For example, a composite ultrathin MoSe₂ nanosheets firmly anchored on the surface of MWCNTs was synthesized *via* a one-step hydrothermal route, and could deliver an enhanced reversible specific capacity of 459 mA h g⁻¹ at 200 mA g⁻¹ after 90 cycles, and a rate capacity of 385 mA g⁻¹ at 2.0 A g⁻¹, much better than those of MoSe₂ nanosheets [210]. As a dual anode material, the coaxial-cable MoSe₂/HCFs composite also showed an enhanced and stable specific capacity of 423 and 395 mA h g⁻¹ at 0.5 and 1.0 A g⁻¹ after 100 cycles, and a high rate capacity of 337 at 3.0 A g⁻¹ [160]. Choi and Kang synthesized 3D porous CNT-microspheres embedded with ultrafine MoSe₂ nanocrystals *via* a spray pyrolysis followed by a selenization process, which showed excellent Na-ion storage properties with a long-term cycling capacity of 296 mA h g⁻¹ after 250 cycles at a high current density of 1.0 A g⁻¹, and delivered high rate capabilities of 280 and 255 mA h g⁻¹ at 3.0 and 5.0 A g⁻¹, respectively [211].

Graphene, as the most promising conductive matrix, can effectively buffer the volume expansion/contraction of active materials, enhance the electrical conductivity, and shorten the ionic pathway due to the large contact area between electrode and electrolyte [12,164,212,214]. For example, a hierarchical MoSe₂/rGO dual anode composite could deliver an enhanced cycling capacity of 430 mA h g⁻¹ at 0.5 A g⁻¹ (380 mA h g⁻¹ at 1.0 A g⁻¹) after 200 cycles with a CE of 99% [164]. To control the dispersity of MoSe₂ on graphene, Du's group constructed a high quality MoSe₂/rGO hybrid nanostructure with monodispersed flower-like MoSe₂ anchored rGO framework. This hybrid showed an improved electrochemical performance as anode materials for SIBs both in half cell and full cell

systems [215]. To further enhance the conductivity and the interaction with active species, Niu et al. designed a hybrid few-layered MoSe₂ on N,P-codoped rGO nanosheets (MoSe₂/N,P-rGO) *via* a solvothermal reaction followed by calcination. This hybrid showed a greatly improved electrochemical performance including outstanding long-term cycling stability with a specific capacity of 378 mA h g⁻¹ after 1000 cycles at 500 mA g⁻¹ (87% capacity retention compared to that at the 2nd cycle), excellent rate capabilities even at a very high current density up to 15 A g⁻¹ due to the enhanced capacitive contribution. The superior cycling stability of the electrode could be attributed to the strong interaction of dual-doped carbon with (poly)selenides, as supported by a theoretical simulation. The insight into the conversion mechanism was revealed by *ex situ* Raman spectra and HRTEM analyses, i.e., the element Se rather than MoSe₂ was formed after the charging process. When paired with Na₃V₂(PO₄)₃/C cathode, it demonstrated an excellent performance in the full cell with highly stable cycling behavior and competitive energy density of 57.6 Wh kg⁻¹ at 1.68 kW kg⁻¹ (voltage window of 3.4–1.0 V), showing a promising potential for advanced SIBs [216].

Dual carbon frameworks may further improve the conductivity, electrode stability and long-term cycling performance thereof. Tu and coworkers designed a facile one-step hydrothermal strategy to fabricate a 3D C-coated MoSe₂/rGO composite with both high porosity and large surface area by introducing rGO as a conductive skeleton and glucose-derived carbon as a protective layer. This composite could deliver an ultrastable reversible capacity of 445 mA h g⁻¹ after 350 cycles at 200 mA g⁻¹ and a high rate capability of 228 mA h g⁻¹ at 4.0 A g⁻¹, much better than those of C-MoSe₂ nanosheets. By further *ex-situ* XPS and TEM analyses, it was claimed that the reaction mechanism between MoSe₂ and Na⁺ did not follow the typical route but similar to that of a Se/C anode: after the charging process, a mixture electrode of Se (or polyselenide) and Mo were formed rather than

MoSe₂[217]. Cui et al. synthesized MoSe₂@C@graphene hybrid nanofibers *via* electrospinning followed by calcination to further optimize the electrochemical performance of MoSe₂@C hybrid nanofibers by introducing low-content 2D graphene for boosting the Na-ion storage performance. The 1D nanofiber showed enhanced structural stability due to the sufficient tolerance to stress, and the additional graphene improved the surface properties for higher conductivity as well as enhanced electrode reaction kinetics and rate performance thereof. It can deliver a high reversible capacity of 367 mA h g⁻¹ after 200 cycles at 200 mA g⁻¹ and a stable rate capability of 353 and 320 mA h g⁻¹ at 1.0 and 2.0 A g⁻¹, respectively [218]. Kang's group further exploited an efficient procedure for large-scale production of highly porous MoSe₂ hybrid powder (MoSe₂-rGO-CNT) containing ultrafine MoSe₂ nanocrystals embedded in synergistic rGO and CNTs matrix (Fig. 14a) *via* a spray pyrolysis and annealing route. The as-prepared ternary hybrid exhibited an excellent cycling discharge capacity of 393 mA h g⁻¹ after 200 cycles and 335 mA h g⁻¹ after 400 cycles at 1.0 A g⁻¹, and a competitive rate capability of 275, 225, and 173 mA h g⁻¹ at 5, 15, and 30 A g⁻¹, respectively, which are superior to the analogue binary hybrids or pristine MoSe₂ (Fig. 14b–d) [209].

Fig. 14. (a) Schematic illustration of the highly porous MoSe₂-rGO-CNT composite by spray pyrolysis for superior Na-ion storage. Electrochemical properties of MoSe₂-rGO-CNT, MoSe₂-rGO, MoSe₂-CNT, and bare MoSe₂ powders: (b) cycling performances, (c) rate performances, and (d) long-term cycling performance and Coulombic efficiency of MoSe₂-rGO-CNT. Reproduced from Ref. [209] with permission of American Chemical Society.

3.2.3. Free-standing MoSe₂ electrodes

For the attractive next-generation flexible electrode design [120,193], carbon cloth and graphene with porous 3D structure is a highly desirable flexible and robust substrate [219,220]. For example, a flexible MoSe₂/N-CNFs dual anode material utilized for Na-ion storage can deliver a reversible capacity of 347 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹ without the detectable decay, and showed a robust long-term cycling performance with a maintained capacity of 234 mA h g⁻¹ (a retention rate of 88.9% compared to that of 2nd cycle) after 1500 cycles at 1.0 A g⁻¹ [140]. A robust and flexible MoSe₂/CF composite electrode was fabricated by Du's group *via* solvothermal synthesis of thin MoSe₂ nanosheets (thickness of 20 nm) uniformly grown on carbon fiber (CF) cloth [219]. This binder-free SIB anode demonstrated a stable specific capacity of 453 mA h g⁻¹ and kept a 85.5% retention after 100 cycles at 200 mA g⁻¹ and high rate capability, which makes it a promising flexible electrode for advanced SIBs. Tu and coworkers further developed a self-supported sandwiched vertical graphene (VG)/MoSe₂/N-doped carbon (N-C) composite arrays (Fig. 15a–d) *via* a combined hydrothermal and polymerization method [221]. The flexible ternary core/shell electrode with high electrical conductivity, robust mechanical stability, and large porosity exhibited a high reversible Na-ion storage capacity of 534 mA h g⁻¹ at 200 mA g⁻¹ over 400 cycles, and enhanced high-rate capability with long-term cycling stability, i.e., 398 and 298 mA h g⁻¹ after 1000 cycles at 1.0 and 2.0 A g⁻¹ (Fig. 15e), respectively. Overall, the smart hybridization of active materials into tailored flexible electrode with dual conductive carbon networks provides a general method for high-performance electrochemical energy storage devices.

Fig. 15. (a–d) Schematic illustration of the synthesis of self-supported (vertical graphene and N-doped carbon) sandwiched VG/MoSe₂/N-C ternary core/shell arrays. (e) Cycling stability of VG/MoSe₂/N-C electrodes for SIBs at 1 and 2 A g⁻¹, respectively. Reproduced from Ref. [221] with permission of Wiley-VCH.

3.3. WSe₂ for sodium-ion batteries

Amongst TMDs, WSe₂ has received increasing attention due to its specific features such as highly hydrophobic surface, ultralow thermal conductivity, and efficient p-type field-effect properties. However, little attention was paid to their energy storage applications, partially because of the difficulties in the synthesis and the intuitive expectation that TMDs containing heavier elements may

not show advantages for high specific capacities [179,222,223]. After some highlights on the similarities and differences between the conversion reactions for MoS₂, WS₂, and WSe₂, the low overpotential and better volumetric capacity of WSe₂ manifest itself as a candidate material for next-generation SIB anode materials [179,222,223]. For example, Yang et al. synthesized a 2D WSe₂ hexagonal nanoplate material. When used as SIB anodes, it showed an excellent cycling performance of 384 mA h g⁻¹ after 50 cycles at 400 mA g⁻¹ and a high rate capacity of 317 mA h g⁻¹ at 2.0 A g⁻¹ after 40 cycles [179]. Taking the gravimetric density of WSe₂ (9.32 g cm⁻³) into consideration, it may afford a quite high volumetric energy density, a more important characteristic than gravimetric energy density for practical applications due to the limited battery packing space. The further *ex situ* XRD and Raman spectroscopy characterizations revealed that WSe₂ reacted with Na⁺ more easily and thoroughly than Li⁺, and it showed difference from the traditional conversion mechanism for LIBs. The Na₂Se in the sodiated state is oxidized to amorphous Se during the subsequent charge process rather than reverting to WSe₂ as in the Li storage mechanism. Zhang et al. synthesized a WSe₂/C nanocomposite with crystal WSe₂ nanoparticles uniformly distributed in a carbon matrix using a simple solid-state reaction of W, Se, and Super P carbon black powder. This hybrid nanomaterial demonstrated a high initial discharge capacity of 467 mA h g⁻¹ and an enhanced cycling stability with a reversible capacity of 270 mA h g⁻¹ after 50 cycles at 200 mA g⁻¹ without any notable loss. While pure WSe₂ nanoplate anode underwent an apparent capacity decline during the initial 20 cycles and decreased to 81 mA h g⁻¹. The improved cycling and rate performances should be ascribed to the buffering effect from carbon matrix for accommodating volume changes and high electric conductivity for fast charge transfer [222].

4. Conclusions and future perspectives

In this review, we summarize the recent advances in the development of graphene-like layered metal dichalcogenides WS_2 , $MoSe_2$, WSe_2 and their composites beyond MoS_2 as the electrode materials in Li-ion and Na-ion batteries. The abovementioned hybrid materials have seen remarkable achievements made to date, however, there still are many challenges need to be addressed in the future.

The performance of TMDs at high current drain is constrained by their limited electronic conductivity limiting the affordable power density. Compared to the most studied TMD MoS_2 , the layered WS_2 , $MoSe_2$, and WSe_2 possess a well-defined layered structure and higher intrinsic electronic conductivity. They have been recently studied as an attractive class of anode material for Li-ion and Na-ion batteries especially for high rate applications despite their lower theoretical capacity. However, the research on WS_2 , $MoSe_2$, and WSe_2 -based carbon and other advanced hybrids still in their infancy. Researchers should pay attention to solve the problem of poor cycling stability due to large volume changes during ions insertion and extraction processes. Further study should focus on the electrochemical operating mechanism, optimizing the electrode preparation process, improving the phase and structural stability of electrode materials, enhancing the electrochemical cycle stability. And some vital technological applications of the aforementioned TMDs are also of great concern.

i) The mechanism for the intercalation and conversion processes should be further studied to clarify the debatable transformation behaviors of these transition metals, and the reversible process thereof.

ii) The capacity fading mechanism for TMDs and the impact of shuttle effect need to be further investigated.

iii) The incorporation of TMDs with carbon matrix with more active sites especially for graphene improves the energy and power densities, but also reduces the initial Coulombic efficiency (ICE). An annealing/calcination post-treatment of these hybrid materials will greatly enhance the ICE and benefit the application in full cells or batteries, which is among several useful strategies to minimize the irreversible capacity including pre-lithium/sodium intercalation and electrolyte improvement.

iv) Doping or intercalation by heteroatoms including S, Se, C is favorable for enhancing the conductivity and expanding interlayer spacing, thus improves the electrochemical performances.

v) Heterostructures combining merits of different layered TMDs will be good candidates for rational design of advanced electrodes based on 2D materials for superior and tunable electrochemical performances.

vi) For flexible electrodes, the mechanical properties of electrospun or freeze-dried composite electrodes for example need to be further improved for practical application.

vii) The relatively high potential of TMDs is a double-edged sword, but generally speaking, TMDs could be safely utilized as anode materials especially for power batteries because of the excellent rate capability and superior cycling stability which would make up the shortcomings although it simultaneously avoids the danger for safety derived from dendrites.

Although there are still some significant challenges for the practical utilization of advanced energy storage devices based on the abovementioned TMDs, great stride has been achieved during the past decade. It would be reasonable to believe that further fundamental understanding and exploration in this field will lead to more exciting achievements for novel high-performance rechargeable batteries.

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Supplementary materials

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