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Abstract

Supercapacitors and secondary batteries are indispensable and widely used energy storage components in modern electrical and electronic facilities/devices. However, they both suffer from different technical weaknesses which need to be thoroughly addressed to satisfy the increasing demand for clean energy technologies. For many years efforts to overcome these technical challenges have reached their practical limits, but recent progress on two dimensional (2D) materials, such as thin transition metal dichalcogenides (TMDs), has been considered more encouraging. Owing to their thin and flexible aspects, large electrochemical active surface area (EASA), high surface tunability, rich coordination sites, and both "Faradaic" and "Non-Faradaic" electrochemical behaviours, 2D TMDs play particular roles in improving many aspects of energy storage devices. This concise review summarizes current challenges facing both supercapacitors and secondary batteries, and discusses how 2D TMDs can be utilized to improve their performance. Building on their thin and flexible features, we further discuss how the emerging flexible and thin energy storage devices can benefit from the 2D TMDs, and make suggestions as to how these 2D TMDs can be engineered for future energy storage applications.

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Two-dimensional transition metal dichalcogenides in supercapacitors and secondary batteries

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Two-dimensional transition metal dichalcogenides in supercapacitors and secondary batteries

ABSTRACT: Supercapacitors and secondary batteries are indispensable and widely used energy storage components in modern electrical and electronic facilities/devices. However, they both suffer from different technical weaknesses which need to be thoroughly addressed to satisfy the increasing demand for clean energy technologies. For many years efforts to overcome these technical challenges have reached their practical limits, but recent progress on two dimensional (2D) materials, such as thin transition metal dichalcogenides (TMDs), has been considered more encouraging. Owing to their thin and flexible aspects, large electrochemical active surface area (EASA), high surface tunability, rich coordination sites, and both “Faradaic” and “Non-Faradaic” electrochemical behaviours, 2D TMDs play particular roles in improving many aspects of energy storage devices. This concise review summarizes current challenges facing both supercapacitors and secondary batteries, and discusses how 2D TMDs can be utilized to improve their performance. Building on their thin and flexible features, we further discuss how the emerging flexible and thin energy storage devices can benefit from the 2D TMDs, and make suggestions as to how these 2D TMDs can be engineered for future energy storage applications.

Keywords: 2D TMDs; Supercapacitor; Secondary battery; Fast charge transport; Short ion-diffusion distance

1. Introduction

The supercapacitor and the secondary battery are essential elements of modern energy storage technologies. They could be key contributors to combatting increasing global challenges on energy, environmental and climate change, by storing and delivering clean energies (*e.g.* wind power and solar energy) to supply electronic/electrical devices without greenhouse gases emissions [1,2]. In addition to their booming applications in electrical vehicles [3-8], these energy storage techniques are also commonly used in current portable, implantable and wearable electronic devices (*e.g.* mobile phones) [9-14]. However, modern vehicles and heavy duty power devices are still largely reliant on non-renewable fossil fuels due to the mismatched efficiency of these energy storage devices [1]. For example, the low power density (normally $< 1 \text{ kW kg}^{-1}$) of secondary batteries and the very low energy density ($\sim 1\text{-}10 \text{ Wh kg}^{-1}$) of supercapacitors make them unsuitable for heavy-duty devices and long-term operation, respectively [2, 15, 16]. The energy storage components in small electronic devices also need urgent developments to improve the power performance and to provide additional features such as low weight, thin structure and flexibility [17-19]. How to design and develop electrode materials to realize these anticipated features and efficiently store/deliver energy has become one of the main challenges in this field. Nevertheless, recent developments in materials science suggest that 2D TMDs such as MoS_2 , MoSe_2 , WS_2 , TiS_2 , NbS_2 and VS_2 have great potential to fill the gap between the existing performance and the modern requirements of energy storage devices [20-27]. This particular role is owing to their exceptional superiorities (*e.g.* reactive surfaces and rich coordination sites) over traditional electrode materials and other 2D materials (*e.g.* graphene).

It is well-known that TMDs are a category of materials generally having the chemical composition of TMX_2 (TM: transition metal, X: chalcogen, including similar chalcogenides with more than one TM atom and corresponding X atoms). The majority of them are layered (layers weakly bonded to each other by van der Waals forces (*e.g.* the group 4-7 TMDs) and some are non-layered (*e.g.* from groups 9 and 10) [21]. Bulk-layered TMDs have three polymorphs of 1T, 2H and 3R (the number represents how many TM-X-TM units are in the unit cell). They could be either 1T or 2H (*e.g.* group 5 TMDs), and favour the 1T (*e.g.* groups 4, 7) or 2H structures (*e.g.* group 6), having physical properties varied from each other, *i.e.* 1T TMDs are normally metallic and highly conductive, and their 1H/2H phases are usually semiconductors with poor electrical conductivity [28-30]. Compared with the bulk form, mono- or few-layered 2D TMDs, obtained either through top-down exfoliation of bulk materials or bottom-up syntheses, have dramatically changed properties because of the charge carrier confinement only in two dimensions and relating changes of the electronic structure [31-38]. Charge transport between the electrode and the TMD monolayer is also directly improved by avoiding the inefficient electron hopping between layers [36]. The directly increased edge ratio and surface exposure make 2D TMDs highly tunable (*e.g.* chemical doping, Janus- and hetero-structures), providing physical/chemical versatility with different bandgap energies and carrier types (n- or p-type) [34-40]. The electrochemical reactions of 2D TMDs can be both surface “Faradaic” and “Non-Faradaic” processes, which are considerably quicker than the traditional reactions of conventional anode material (*e.g.* graphite and bulk TMDs). Together with the unique structural anisotropy, all these intrinsic properties endow 2D TMDs with promising mechanical, chemical, and electrical merits in fulfilling the need of emerging electrochemical technologies (*e.g.* thin flexible energy storage devices). Recent progress in this field also indicates that 2D TMDs could be particularly well-positioned if their various features distinguished from the bulk and other 2D materials are suitably explored.

This concise review summarizes the challenges on current supercapacitor and secondary battery technologies and discusses how 2D TMDs can be used to improve their performance. Building on the various merits (*e.g.* thin and flexible) of 2D TMDs, the fabrication and performance of some selected flexible energy storage devices are introduced and highlighted as examples. In this paper, the design and development of next generation 2D TMD based materials for future energy storage applications are also outlined.

2. Supercapacitor

2.1 Challenges

Supercapacitors are electrochemical devices which store charges in electric double layers (also called the “Helmholtz layer”, with a thickness $\sim 3 \text{ \AA}$) formed through physisorption of electrolyte ions onto porous carbon electrodes (Fig. 1a, the “Non-Faradaic” processes: no charge transfer redox reaction involves in this process) [2, 41-43]. They can offer very high charge/discharge rates (not limited by the electrochemical

charge transfer kinetics of batteries) and long lifetimes (e.g. over a million cycles), potentially satisfying the needs of high-power electronic devices and electric vehicles [1, 2, 41]. However, after many years' efforts [44-49], practical applications of supercapacitors are still largely limited by their unsuitably low energy densities which are far lower (~several Wh kg⁻¹, an order of magnitude lower) than those of secondary batteries (Fig. 1c). Many approaches have been proposed to improve their energy densities by activating carbon electrode materials and combining other materials *via* near-surface pseudo-capacitive redox reactions (a Faradaic process involving a charge transfer between the electrode and the active material, but not limited by the slow mass diffusion and bulk phase change process in traditional secondary batteries, Fig. 1b). For example, exotic materials such as transition metal oxide nanoparticles have been frequently used to add pseudo-capacitance [50-55], but their low electrical conductance (e.g. 10⁻⁵-10⁻⁶ S cm⁻¹ of MnO₂ nanoparticles [47]) conversely reduced the power density of the device. Besides, in a common hybrid supercapacitor electrode, the pseudo-capacitive redox reaction only occurs on the top-most surface (using a limited part of the whole nanoparticle, Fig. 1b), meaning that most of the material is wasted, reducing energy capacity and increasing cost. Rapid charge transport between the nanoparticle and carbon material is also critical for fast energy delivery, but this rapid process requires intact contact of the material and is unlikely to be realized by conventional approaches, *i.e.* full packing of the particle by carbon materials without scarifying the ion transport channel.

Fig. 1. (a-b) Schematic of the electric double layer capacitor (a) and the Faradaic supercapacitor (b). In Figure (b), the M and A⁻ are the surface of the electroactive material and electron donating anion, respectively. δe^- is the quantity of the electron which is related to the 'electrosorption valence'. The red circle represents the topmost surface of the particle processing the pseudo-capacitive redox reaction. (c) The Ragone plot shows specific power against specific energy. The time constant shown in the figure is the value of the energy density divided by the power. Figure (c) is reproduced from ref. [41] with permission. Copyright (2008) Springer Nature.

In electrochemical reactions, kinetics of electrode processes (e.g. adsorption/desorption kinetics and mass transfer) dominate the various performance of the energy storage device [47, 56, 57]. A good supercapacitor electrode should feature high electrical conductivity and a large active surface area. Recently developed self-supporting and porous three dimensional graphene (3D-G) has the potential to offer improved electrode kinetics and mass transport with super short electron transport length and ion diffusion distance, which are key to improving the cycle life, energy capacity and power density of the energy storage device [56-58]. Unfortunately, the demonstrated energy capacities of modified and unmodified 3D-G (e.g. 5-40 Wh kg⁻¹) [56, 59-69] are still far lower (1-2 orders) than that of modern Li-batteries [70, 71]. Improvements in the capacitance can be realized by adding exotic nanoparticles, but this addition would severely degenerate the power density and life time due to reasons described above. Improving the energy density and sustaining the various merits of supercapacitors (e.g. rapid charge/discharge rate and long life-time) have become the

major challenges in this regard. Next, we discuss how 2D TMDs can be employed in supercapacitors to produce enhanced performance.

2.2 2D TMDs in the supercapacitor

Fig. 2. (a-b) SEM images of the dispersed monolayered 1T phase MoS₂ nanosheets (a) and the cross-section of the stacked 1T MoS₂ electrode. (c) Schematic shows the interlayer space of restacked 1T MoS₂ nanosheets (set as 6.15 Å) before and after ions intercalation reaction. The K⁺ and Na⁺/Li⁺ are coordinated with two and six water molecules, respectively. The intercalation of organic electrolyte (TEA⁺) gave an additional layer separation of 4.83 Å. (d) Photograph of the 1T MoS₂ sheets on flexible polyimide substrate. (e) Ragone plot of the volumetric power and energy densities of different materials. Figures are reproduced from ref. [37] with permission. Copyright (2015) Springer Nature.

Aside from the significantly improved edge ratio and surface exposure from their bulk phases, 2D TMDs also have graphene-like thin structures (~1 nm thick, in the case of a monolayer) with ideal super short electron transport length and small ion transport distance for fast electrochemical processes. Investigations have suggested that 1H/2H TMDs such as thin MoS₂ sheets have comparable supercapacitor performance to that of carbon nanotube arrays and a theoretical capacity (~1000 F g⁻¹) greater than that of graphite [72, 73]. Nevertheless, the development of 2D TMD-based supercapacitors has not been really successful due to the low electrical conductivity of most stable semiconducting 1H/2H TMDs. By contrast, metallic 1T TMDs are theoretically metastable and have the basal plane with more chemical activity over that of 1H/2H phases [21, 74, 75]. They have very high electrical conductivity (e.g. 10⁻¹⁰⁰ S cm⁻¹ of monolayered 1T MoS₂ sheet at room temperature, 10⁷ times more conductive than 1H MoS₂ monolayers) which is close to that of the best-performing reduced graphene oxide sheets (~100 S cm⁻¹) [37]. Recent progress has suggested that structures of some metallic 1T TMDs are actually stable in certain electrochemical processes [76-78], which promises the great future of 2D TMDs in supercapacitors. This promising application has been demonstrated by Chhowalla *et al.* in 2015, where monolayered 1T MoS₂ sheets (~70% phase ratio, Fig. 2a) were exfoliated from their bulk flakes using organolithium [37]. Owing to their high electrical conductivity, thin flexible supercapacitors can be fabricated purely from these 1T MoS₂ sheets (stacking thickness up to 5 μm, Fig. 2b) without the addition of any binding agents or conductive additives (e.g. the film on polyimide substrate in Fig. 2d) [37]. The packed supercapacitor from this flexible electrode showed volumetric capacitances ranging from 400-700 F cm⁻³ in different aqueous electrolytes (H⁺, Li⁺, Na⁺, K⁺), along with very high, stable (95% capacity

retention after 5000 cycles) energy and power densities in organic electrolytes (the shaded and highlighted region in Fig. 2e). Their cyclic voltammetry (CV) curves in the used potential range (aqueous electrolyte and three electrodes: -1.0 – 0 V vs open circuit potential (OCP); organic electrolyte and two electrodes: 3 V) were all mainly capacitive featured [37], giving very high power and energy densities (Fig. 2e). The energy storage performance in organic electrolyte is significantly higher than those of MXenes (2D transition metal carbides, carbonitrides and nitrides), activated carbon, graphene materials and some thin Li-ion batteries (Fig. 2e). The efficient storage of organic electrolyte ions (e.g. the tetraethylammonium/TEA⁺) and the larger ions beyond the Li⁺ (e.g. Na⁺, K⁺) was mainly owing to the dislocated layers in stacked sheets with both the interlayer space around 6.15 and 11.65–12.15 Å which highly matches the size of these ions (Fig. 2c). Following this principle, other 2D TMDs with high electrical conductivity (e.g. 1T WS₂ and 1T VS₂ sheets) and similar large interlayer spaces are also expected to be highly promising in building high-performing supercapacitors.

Besides these 1T TMDs, recently developed ternary sulfides, the Ni-Co-S [79–82], could be more interesting in supercapacitors owing to their high stability, rich redox reaction sites (over that of the corresponding binary Ni or Co sulphides [79]) and outstanding electrical conductivity, i.e. the NiCo₂S₄ has the electrical conductivity of around 10³–10⁴ S cm⁻¹ at room temperature [80–81], which is 1–2 orders higher than that of 1T MoS₂ monolayers (10–100 S cm⁻¹) [37]. Supercapacitors built from these ternary sulfides with traditional forms (e.g. nanofibers, 3D structures) have been demonstrated by different groups [83–85]. Although the fabrication of ultrathin monolayered ternary sulfides is still challenging, a recent study on CoNi₂S₄ nanosheets (thickness: around 20 nm; 2D size: micrometers) based electrode has provided a high capacitance of 1117 F g⁻¹ (at 2 A g⁻¹, three electrodes technique, 6 M KOH) and good rate performance (e.g. 1002 F g⁻¹ at 10 A g⁻¹) [86]. An asymmetric supercapacitor built from these ternary sulfides gave high power (e.g. 8 kW kg⁻¹ at the energy density of 55.4 Wh kg⁻¹) and excellent cycling performances (> 80% capacity retained after 10000 cycles at 10 A g⁻¹) [86]. Larger capacitance (2906 F g⁻¹) than the above demonstrated value of similar CoNi₂S₄ sheets (thickness: around 45 nm; 2D size: micrometers) based supercapacitor was also achieved at a current density of 5 mA cm⁻² [87]. These performances are already superior to that of their many counterparts with traditional forms [86, 87].

Fig. 3. Schematic shows the hybrid structure of 2D TMDs and graphene, where the 2D TMDs intimately contact the graphene's surface with their basal planes.

As for the thin 2D TMD materials with poor electrical conductivity (particularly the semiconducting 1H/2H TMDs), hybrid structures from these TMDs and the graphene (Fig. 3, e.g. through physical stacking or chemical bonding) could be considered to potentially overcome many weaknesses of traditional hybrid supercapacitors, providing improved energy and

power densities, long cycle life and improved safety. Unlike traditional nanoparticles (where only the topmost surface participates in the electrochemical process, Fig. 1b), the whole 2D TMDs (e.g. monolayers) and their highly active edges in this hybrid structure (Fig. 3) could contribute both the Faradaic and Non-Faradaic capacitance, improving material's usage and reducing cost. Comparing it with traditional secondary batteries, the near surface redox reaction is essentially different and associated with much higher energy delivery efficiencies (will be further highlighted in the next section together with an analysis of the secondary battery). In addition, 2D TMDs could intimately contact the graphene wall, which would ensure rapid charge transport between the electrode and the chemically active site (e.g. active sites on 1H semiconducting TMDs) for high power density and improved rate performance. This structure is more promising when more electrically conducting TMDs nanocrystals (e.g. 1T nanocrystals), chemical modifications and 3D-G with large surface areas are introduced. Although hybrid electrodes from strictly monolayered 2D TMDs and graphene still need to be developed, recent reports on similar hybrid structures have confirmed that there is a flourishing future for 2D TMDs in supercapacitors [88–90]. For example, Ajayan and Ye *et al.* have demonstrated the hybrid electrode of CoNi₂S₄-graphene-2D MoSe₂ with graphene and thin MoSe₂ sheets closely attached to each other, and highly conductive CoNi₂S₄ nanoparticles on/between the layers [90]. This electrode exhibited very high capacitance (1141 F g⁻¹, 1 A g⁻¹, three electrodes technique, all in 6M KOH electrolyte), good rate (961 F g⁻¹ at 5 A g⁻¹) and cycling performances (108 % capacitance retention after 2000 cycles, 20 A g⁻¹). The supercapacitor assembled from this electrode also exhibited high power densities (e.g. ~0.89 and 13.3 KW kg⁻¹ at energy densities of 38.6 and 23.7 Wh kg⁻¹). The role of 2D TMDs in supercapacitors is further strengthened, particularly when the materials fabrication on various 2D nanocrystals has been proved to be increasingly successful [31–33, 91–96], which will be further introduced in the later section.

3. Secondary Batteries

3.1 Challenges

Fig. 4. (a) Schematic shows the first Li-ion battery. Reproduced from ref. [98] with permission. Copyright (2015) American Chemical Society.

Unlike supercapacitors, secondary batteries store and deliver energies through reversible chemical reactions (e.g. insertion reactions, alloying-dealloying reactions, phase transition reactions) at both electrodes [97, 98]. The basic working mechanism of the secondary battery is presented in the schematic showing the first Li-ion battery (Fig. 4), which takes energy along with the ions' flow from the cathode to the anode, and

reverses the process to release the energy [98, 99]. This pure Faradaic process endows much higher energy density of the secondary battery over that of the supercapacitor (Fig. 1c). Besides the charge transfer process, the energy storage/delivery of the traditional secondary battery is also limited by the slow ion diffusion and bulk phase change (e.g. the insertion/extraction and conversion reactions at electrodes in Fig. 4), giving much lower power densities than those of supercapacitors (Fig. 1c). Among various developed secondary batteries (e.g. lead acid, NiCd, NiMH and Li-ion batteries), the Li-ion battery is considered to be the most popular energy carrier in current electrical/electronic devices (e.g. mobile phones and laptops) [100-103], owing to advantages such as its relative high energy density, very low toxicity, high coulombic efficiency, larger working temperature range and maintenance-free features [99]. However, it still needs considerable improvement towards higher energy and power densities to meet the increasing demands from fields ranging from small portable electronic devices to long-range electric automobiles. Improvements in the energy density have been achieved by smart cell engineering, but better materials are still needed to further reduce the weight and volume of the device [98]. Unfortunately, improving the energy density *via* the modification (e.g. morphology, size, doping, band gap engineering) of traditional active materials has reached a level of maturity [99]. It has also reached a limit by increasing the operation voltage, due to the decomposition of most organic electrolytes > 5 V.

In recent years, chemistries beyond the “Li-ion” have also been considered in building secondary batteries because of the increasing cost of Li resources [97]. These new energy storage routes include the use of other cheap charge carriers (e.g. Na, K, Mg and Al cations) and the implementation of conversion reactions (e.g. metal-air and Li-S batteries) [104-113]. However, compared with the Li-ion battery, the theoretical energy densities of batteries based on these new metal ions are normally low due to the larger ionic radius and heavier atomic mass than those of the Li^+ . The development of new electrode materials to allow the efficient insertion reaction of these larger ions is also highly sought after [97]. As for the conversion reaction route, batteries such as Li/O_2 , Li/S , $\text{Li}/\text{metal halide}$, and $\text{Li}/\text{metal oxide}$ exhibit many desired features such as lower equivalent weights and considerably higher energy densities (2-10 times greater than for current Li-ions batteries) [110-113]. Nevertheless, achievement of these batteries with a long operation life is still difficult. Significant efforts in both the fundamental research and the manufacture are still needed to improve the performance of secondary batteries in many aspects (e.g. higher energy and power densities, lower cost, higher safety and longer life-time), which may include the development of novel electrode materials and new battery systems.

3.2 2D TMDs in the secondary battery

Although secondary batteries involve such technical challenges, recent developments suggest that their various performances can be potentially improved by combining 2D TMDs. Unlike graphite materials, TMDs have much larger interlayer spaces (e.g. 0.65 nm of MoS_2 vs 0.33 nm of graphite) and related weaker van der Waals interactions between the layers. This interlayer space allows for energy storage with more sustainable larger ions (e.g. Na^+ , K^+ and Mg^{2+}) if the electrical conductivity of the electrode can be well addressed for rapid charge transport. They also have suitable OCP values for the metal ion storage, i.e. many 2D TMDs have optimal OCP values between

0-1 V (vs Na^+/Na) to maximize the energy density and prevent the formation of alkali metal dendrites [114].

Fig. 5. (a) Schematic of the crystalline structure of 1T TiS_2 . (b) Comparison of the *a*- and *c*-axis lattice parameters of different TiS_2 materials against the potential during the intercalation reaction. (c) The CV curve of 2D- TiS_2 in a Li^+ electrolyte shows the composition of both the capacitive and the battery-like responses. (d) Rate capability of 2D- TiS_2 and B- TiS_2 films. Reproduced from ref. [115] with permission. Copyright (2015) American Chemical Society.

In secondary batteries, the advantage of 2D TMDs becomes more significant owing to the highly improved active surface ratios and rapid reactions of both surface adsorption/desorption and insertion/extraction (in multilayers) [115-118]. Generally, the energy density of a secondary battery is determined by the reversible capacity and operating voltage; whilst the power density and rate performance are decided by the electronic/ion mobility in the electrode material. The previously mentioned near surface “Faradaic” capacitance of 2D TMDs can be fully exploited to develop high-performing secondary batteries. Unlike traditional secondary batteries, such surface reactions are much easier and faster by avoiding the slow insertion/extraction diffusion of the ions. Various reports have confirmed that 2D TMDs have significantly decreased ion diffusion barriers and increased adsorption energy from their bulk counterparts, resulting in larger energy and power densities, as well as better cycling performances [114-121]. The ion diffusion barriers of some 2D TMDs are actually already lower than that of the graphite anode (~ 0.2 eV for Li^+) [119], i.e. the Na^+ diffusion barriers on both the 1H and 1T VS_2 monolayers are around 0.085 and 0.088 eV, respectively [122]. Such ion diffusion barriers can be further reduced upon suitable vacancy formation and surface doping, benefitting the energy storage processes in some small and smart self-powered devices, i.e. a solar light or thermal powered cell devices with very small voltages which cannot efficiently mount the energy carriers to the electrode for storage. In addition, many of these surface processes on 2D TMDs are also capable of providing high capacity (e.g. a 1914 mAh g^{-1} of 2D TiS_2 for Ca/Mg storage and 1400 mAh g^{-1} capacity of 2D VS_2 for Li storage [116, 120]) and high operating voltage, giving much larger energy densities than that of graphene (e.g. 600-900 mAh g^{-1} for Li storage) [116-121]. Both the energy and power densities can be further improved if we can fully exploit the multi-layered adsorption of ions and the interaction between the metal ions and the exposed TM atoms on the defected 2D TMDs [116]. Like the interstitial doping of 2D TMDs by Ni atoms (the formation of a metal-metal bond), the metal-metal interactions between the TM site (e.g. at the exposed edge and X-depleted site on the basal plane) and the

smaller ions (Li^+ , Na^+ , K^+ and Mg^{2+}) are also highly possible [75].

In multilayered (e.g. bi- and tri-layered) 2D TMDs, rapid ion intercalation could also be realized, which is completely different from the slow ion insertion reaction in traditional bulk anode materials (the diffusion-controlled mechanism). This difference has been confirmed by demonstrating the rapid Li storage on thin (2-10 layers) TiS_2 sheets with a lateral size of around 50-270 nm [115]. As suggested in Fig. 5a, the 2D TiS_2 nanosheets are 1T metallic materials with an interplanar spacing of ~ 5.7 Å. 1T TiS_2 only appeared in the as-prepared nanocrystals. Compared with the bulk TiS_2 material (B- TiS_2), 2D TiS_2 has a larger unit cell volume and smaller c-axis lattice expansion during the Li^+ insertion/extraction reaction (Fig. 5b). More specifically, c-axis parameters of 2D TiS_2 and B- TiS_2 changed to 5.93 and 6.17 Å respectively during the first cycle insertion reaction. Correspondingly, 2D TiS_2 nanosheets exhibited more stable structures and fewer volume expansions during Li^+ storage, which is more suitable for safer energy storage and longer life-time operation. Unlike conventional anode materials, the charge storage of 2D- TiS_2 also contained significant intercalation pseudo-capacitance (Fig. 5c), giving much higher energy and power densities (Fig. 5d). The formation of such pseudo-capacitance is also very fast with a quasi-2D process mechanism, and similar to the ion diffusion on the surface of monolayered TMDs (capacitive-controlled behaviour). Building on these features of 2D TMDs (even the multilayers), it can be expected that the pure or re-stacked monolayered 2D TMDs would provide high energy and power densities for the secondary battery, that are unlikely to be achieved with traditional structures and materials. The re-stacked 2D TMDs may also be more promising for the storage of ions with larger radius over that of Li^+ owing to the principally larger interlayer spaces. In this regard, however, efficient charge transport of the electrode (e.g. between the TMD layers) should be carefully addressed. The hybrid structure (CoNi_2S_4 -graphene-2D MoSe_2 [90]) we introduced above was just in this position to realize the fast charge transport between the layers. In some 2D TMDs, charge transport between their stacked forms and cross-linked networks is already reported to be efficient for the Faradaic reaction (e.g. 1T MoS_2 and ternary Ni-Co-S sulfide) [37, 123-124]. This has been demonstrated by Zhang *et al.* on the 3D network of 2D NiCo_2S_4 nanosheets (thickness: ~ 10 nm, majority 2D size: 1-2 μm) vertically aligned on carbon cloths. Building on the anode of this 3D network, a high reversible capacity of ~ 1275 mAh g^{-1} (at 1 A g^{-1}), an acceptable good cycling performance (~ 137 mAh g^{-1} was retained after 100 cycles) and rate performance (340 mAh g^{-1} at 5 A g^{-1} and comparable to the theoretical capacity limit of carbon-based electrodes) of the assembled Li-ion battery were demonstrated [124]. Owing to the high electrical conductivity and rich surface chemistries (e.g. the OH^- insertion/extraction reactions), ternary Ni-Co-S sulfide has also been investigated as the cathode for an aqueous rechargeable alkaline battery (anode: TiO_2), although the energy density was not so high [125].

The rich surface chemistry and catalytic activity of 2D TMDs also make them promising for some conversion reactions (e.g. Li-S and metal-air batteries). It is known that the stabilization of the polysulfide shuttle process (the dissolution of intermediate lithium polysulfide) of the Li-S battery is mainly realized by confining the sulfur within the pores of various carbon materials. However, these strategies are still challenged by the low active material loading, poor adsorption of the polysulfides and

the detachment of the lithium polysulfide [126-128]. A recent investigation suggested that the lithium polysulfide can be simply adsorbed by the edge of 2D WS_2 and MoS_2 sheets owing to the unsaturated S atoms (Fig. 6, the middle structure) [128]. These edges also stabilized the polysulfide shuttle process during the conversion reaction of lithium polysulfides (Fig. 6, the middle and right structures) [128], showing many advantages over traditional Li-S batteries, i.e. the metallic edge of 2D TMDs (promises the fast charge-transfer kinetics), the higher electrocatalytic activity over that of carbon electrode, and the absence of physical encapsulation of polysulfides (favor for better rate performance) [128]. Higher loading of the lithium polysulfide is also reasonably expected upon appropriate surface chalcogen depletion which can be realized by various approaches [31, 129]. In past few years, significant efforts have been made in developing the catalysis of 2D TMDs (e.g. the oxygen reduction/ORR and hydrogen evolution reactions/OER [31, 130]). The catalysis at the edge and defected site of modified and unmodified 2D TMDs endows them with interesting futures in metal-air batteries [131-133]. For example, Asadi *et al.* have investigated both the OER and ORR at the edge of 1T MoS_2 nanosheets (thickness: majority 6-16 layers; 2D size: micrometers) in an ionic liquid, giving comparable catalytic activity to that of Au and Pt catalysts [132]. The Li- O_2 battery demonstrated with this system performed capacity of 500 mAh g^{-1} (at 0.1 mA cm^{-2}) and good cycling performances (85% capacity remained after 50 cycles). Nevertheless, significant improvements on the above Li-S and metal- O_2 batteries are still needed in future to approach their theoretical capacity with long life time.

Fig. 6. Schematic of TMDs nanosheets for the Li-S battery, showing the conversions of lithium polysulfides during charge/discharge process in a catholyte solution. Reproduced from ref. [128] with permission. Copyright (2017) American Chemical Society.

4. 2D TMDs in flexible energy storage devices

The roles described above of 2D TMDs in both the supercapacitor and the secondary battery applications have highlighted their promising futures in energy storage, particularly in the thin and flexible energy storage devices which can fully utilize the highly exposed active surface, and the thin and flexible aspects of 2D TMDs to meet diverse power needs of modern gadgets (e.g. health controls and wearable electronic devices) with anticipated features (e.g. low weight, safe, long cycle life, and high-speed operation) [134-138]. The means of integrating 2D TMDs into these flexible and thin energy storage devices will now be discussed with some selected examples.

In the Chhowalla's work mentioned above (Fig. 2), the flexible, thin supercapacitor fabricated from 1T MoS_2 sheets (400-700 F cm^{-3} in aqueous electrolytes) showed very high stability and high energy and power densities (Fig. 2e) [37]. These performances were mainly determined by the reversible surface

chemistry (e.g. ion adsorption and desorption), the high electrical conductivity and the large interlayer space of the restacked sheets, although they were also affected by the electrode fabrication techniques in most cases. Compared with their metallic phases, semiconducting TMDs such as 1H/2H MoS₂ are typically not as good at fabricating high-performing energy storage devices, mainly due to their low electrical conductivity. For example, Liu *et al.* have prepared 2H MoS₂ nano-flakes (2D size: 200 to 500 nm, multilayered) *via* probe sonicating (note: the ratio of the thin sheets from this method is typically low, although many reports have claimed a high ratio of monolayers) [139]. They fabricated highly flexible electrodes by mixing these MoS₂ nano-flakes with carbon nanotubes (CNTs) to improve the electrical conductivity and the mechanical strength [139]. **Fig. 7a** shows an image of such an electrode, which has the highest energy and power density of around 0.92 mWh cm⁻³ and 2.1 W cm⁻³ (in polyvinyl alcohol/PVA-H₂SO₄ electrolyte, areal capacity of 37 mF cm⁻² at the scan rate of 20 mV s⁻¹), respectively. These performances are significantly lower than those on pure 1T MoS₂ thin sheets (**Fig. 2e**) [37] due to likely the lower electrical conductivity [36,37], the thick sheet morphology (see their XRD pattern with an intense 002 diffraction peak of MoS₂, although the average thickness of the flakes was claimed to be 2.5 nm) [139], and the relatively lower chemical activity on the basal plane of the 1H/2H sheet than that of their 1T counterpart [21,74,75].

Fig. 7. (a) MoS₂/CNTs coated paper shows excellent flexibility of the electrode. Reproduced from ref. [139] with permission. Copyright (2017) Elsevier. (b) Schematic of the hybrid core-shell structure of WO₃-WS₂ electrode. Reproduced from ref. [140] with permission. Copyright (2016) American Chemical Society. (c-d). The flexible electrode fabricated from the vertically aligned MoS₂ sheets on the Mo foil (c) and the TEM image of the edge aligned sheets (d). Reproduced from ref. [146] with permission. Copyright (2014) John Wiley & Sons.

For the most stable 1H/2H 2D TMDs, high energy and power densities can actually be realized if the poor charge transport issue is adequately addressed. For example, Jung *et al.* proposed improving the charge transport between the electrode and the chemically active surface by forming a core-shell structure as shown as that in **Fig. 7b** [140]. In this hybrid structure, the WO₃ core and 2H WS₂ shell (~8–9 layers) were intimately in contact with each other (WO₃ and WS₂ were grown on the flexible W substrate with a general crystal growth model) to offer good mechanical robustness, which were also used for carrier transport and ionic absorption, respectively (**Fig. 7b**). The flexible supercapacitor assembled from this electrode

showed the highest energy and power densities of around 0.06 Wh cm⁻³ and 30 W cm⁻³ (areal capacity of 33 mF cm⁻² at the scan rate of 10 mV s⁻¹), respectively in 0.1 M Na₂SO₄ electrolyte [140]. The above performance was close to those found on pure 1T MoS₂ sheets in an organic electrolyte [37] and greater than many MXenes and graphene based energy storage devices [140]. The power performances of the flexible device were highly stable even after being folded 100 times at 90° and after 30,000 charge/discharge cycles. Like the pseudo-capacitance formed in metallic TiS₂ sheets (the highlighted rectangular region in **Fig. 5c**), the achievement of this desirable power performance was also mainly because of the rapid ion adsorption/desorption on the surface and rapid intercalation in the interlayers of 2D WS₂ (the CV curve in the measured potential range was also capacitive featured) [140].

To improve the charge transport, the formation of vertically aligned semiconducting 2D TMDs on conducting and flexible substrates has also been considered. Like the vertically aligned 2D TMDs on electrically conducting substrates for improved electrocatalysis [141–145], these structures can offer more exposed active sites and sustain good electron transport between the electrode and the TMD's layer. The growth of such aligned 2D TMDs, in principle, is simple owing to the anisotropic feature of the crystal and the lowest surface energy at the basal plane. In the research by Tour *et al.* (in 2014), vertically aligned MoS₂ sheets (around 5 layers, 2D edge size around 10 nm, **Fig. 7c–d**) were grown on the flexible Mo substrate with a general chemical vapor deposition (CVD) approach [146]. The flexible electrode (**Fig. 7c**) was further packed as a supercapacitor and a high areal capacity was demonstrated around 12.5 mF cm⁻² at the scan rate of 50 mV s⁻¹ (in PVA and 1M LiOH electrolyte) [146]. This capacity was further increased even after 10000 cycles, possibly owing to the formation of more activated sites [146]. Comparison of the areal capacity with other devices is difficult since it is highly dependent on the mass of the active materials in the electrode, the electrolyte and the scan rate. Nevertheless, these studies have demonstrated the mechanical robustness, the versatile surface and edge chemistry of 2D TMDs for promising flexible supercapacitors.

Besides the thin and flexible supercapacitor, 2D TMDs can also be engineered to build thin/flexible batteries which are more suited for storing larger ions beyond Li⁺ (e.g. Na⁺ and K⁺) owing to the large interlayer space. For example, considering the volume change of traditional materials during Na insertion (up to 500% in some cases), Singh *et al.* (in 2014) proposed a Na ion battery building on a hybrid composite of the thermally reduced graphene oxide (rGO) and MoS₂ flakes [147], which has two predicted charge steps (intercalation and conversion reactions) as shown in the schematic (**Fig. 8a**). To prepare such composite paper, they mixed the pre-prepared GO and exfoliated MoS₂ sheets, followed by a filtration treatment. Electrode materials were prepared *via* annealing the filtered paper at different temperatures in an argon atmosphere. As suggested by **Fig. 8b–d**, the annealed paper contained many sheets which were identified as the MoS₂ and rGO sheets. Having made these preparations, Singh *et al.* demonstrated a charge capacity of 338 mAh g⁻¹ (at current density of 25 mA g⁻¹) at the first cycle with 83% capacity retention (approximately 98% average efficiency) during the 20 cycles test. Although these performances were not good enough and need significant improvements, the fabricated electrodes can be highly flexible depending on the addition ratio of MoS₂ (**Fig. 8e**). Increasing the loading ratio of MoS₂ improved the cell capacity but re-

duced the flexibility. The demonstrated 60MoS₂ (60% mass ratio of MoS₂) electrode had high fracture strength at ~2.1 MPa and modulus at ~120 MPa and a strain to failure at around 2%. The energy storage and the mechanical performances can be further improved by modified fabrication approaches, as agreed by the authors. Nevertheless, this work has already demonstrated that 2D TMDs such as MoS₂ can be successfully used in a flexible secondary battery beyond Li⁺.

Fig. 8. (a) Schematic of the predicted Na⁺ storage process of the MoS₂/rGO composite. (b-c) SEM images of the 60MoS₂ composite paper. Insets in image (b) are the corresponding energy dispersive X-ray spectroscopy (EDS) spectra. (d) TEM image of the 60MoS₂ composite paper showing the hybrid structure of MoS₂ and rGO. Inset is the SAED pattern of the hybrid flakes, giving different patterns from both the MoS₂ and rGO and their dislocated structures in the composite. (e) Photo of a fabricated hybrid electrode. (f) The stress-strain plot for rGO, 40MoS₂, and 60MoS₂ free-standing papers. Figures are reproduced from ref. [147] with permission. Copyright (2014) American Chemical Society.

In 2016, Li and Coleman *et al.* reported an improved method for building the flexible electrode and demonstrated better performances for Na storage [148]. This thin and flexible electrode (Fig. 9a) was manufactured from the liquid phase exfoliated MoS₂ nanosheets and single wall CNTs. The flexibility and the stretchability of the electrode were made possible by the CNTs and 2D MoS₂ sheets and their networks (Fig. 9b-c). This film has a thickness of around 15-90 μm and electrical conductivity of up to 10² S cm⁻¹, although the CNT content was only 20 wt%. Building on this fabrication, Li *et al.* demonstrated a specific capacity of >400 mAh g⁻¹, a volumetric capacity of ~650 mAh cm⁻³, an areal capacity of up to > 6.0 mAh cm⁻² with good cycling performance (tested for 100 cycles and a retention rate of up to 90%, depending on the electrode thickness). Such energy storage performances are better than those of many other materials such as the commercial Li ion battery electrodes, the Si-based materials and the modified MXenes [149-151]. Similar thin and flexible paper-like electrodes based on other 2D TMDs have also been reported. Fig. 9c shows a flexible electrode fabricated from the 2D SnS₂ and graphene nanoribbons. Like the case in the network of CNTs and 2D MoS₂ (Fig. 9b-c), the microstructure of this paper was also crossed with networks, giving flexibility of the electrode. The battery fabricated from this electrode had a high volumetric capacity

of 508-244 mAh cm⁻³ (current density from 0.1-10 A g⁻¹) and good capacity retention with 1500 cycles for Na⁺ storage [152]. All these applications have demonstrated the highly effective roles of 2D TMDs in thin and flexible secondary batteries. Nevertheless, if these devices are to have more of the features anticipated in the future (e.g. high safety, implantable, smaller), additional research will be needed beyond the 2D materials, which may include cell fabrication techniques (e.g. the micro-fabrication technique), new electrolytes (e.g. solid-state or gel-type electrolytes) and rational electrode design (e.g. the use of planar configuration and 3D electrodes).

Fig. 9. (a-c) Photograph (a) and SEM microstructures of the flexible electrode (b-c) built by 2D MoS₂ and CNTs. Figures are reproduced from ref. [148] with permission. Copyright (2016) American Chemical Society. (d-f) Photograph (d) and SEM microstructures of the flexible electrode (e-f) built by 2D SnS₂ and graphene nanoribbons. Figures are reproduced from ref. [152] with permission. Copyright (2017) American Chemical Society.

5. Fabrication of 2D TMDs

Now, we summarize the main fabrication techniques (by categories) developed so far of the 2D TMDs associated with their applications in energy storage devices. Early studies of TMDs on catalysis, electronic and energy storage devices were mainly impeded by the lack of suitable fabrication approaches. The discovery of graphene in 2004 has triggered research interests in 2D TMDs materials, including their fabrication, properties and applications [153]. 2D TMDs can be achieved from their bulk flakes by using mechanical exfoliation (peel off the sheets layer by layer, a top-down approach) [38] like that of graphene [153], which is definitely unsuitable for large-scale implementations. Alternatively CVD (as well as the epitaxial growth) is one of the most frequently used techniques to achieving 2D TMDs with high quality (e.g. from monolayer to 2-5 layers) [154, 155]. It has been explored to grow vertically aligned TMDs sheets [140, 144-146], Janus [156], van der Waals heterostructures [157-159] and other complex vertically aligned heterostructures (with tuned charge transport and catalytic activity) [160] for both catalysis and energy storage applications. Nevertheless, these fabrications are still difficult for large scale preparation of materials using in energy storage devices. Comparing with the CVD technique, the solvothermal synthesis (and other similar bottom-up approaches in solution) is relatively cheaper. Directly bonding of 2D TMDs to the graphene can be realized via similar approach (in-situ growth in solvent) [161]. It is also suited for the growth of vertically aligned TMDs nanosheets with different sizes, enlarged interlayers and dopants [142,143], but more works on reducing the thickness and size (the TMDs are still large and not thin enough) and building complex heterostructures for various purposes are need to be involved in future.

Table 1. Electrochemical performances of various TMDs in the supercapacitor and the secondary battery. SCE: saturated calomel electrode; EMIMBF₄: 1-ethyl-3-methylimidazolium tetrafluoroborate; MeCN: methyl cyanide; TFSI: bis(trifluoromethylsulfonyl)imide; DOL: 1,3-dioxalane; DME: dimethyl ether; DEC: diethyl carbonate; EC: ethylene carbonate; EMC: ethyl methyl carbonate; DMC: dimethyl carbonate; SWCNT: single walled carbon nanotube; PVC: polyvinyl chloride.

Supercapacitor				
Materials and references	3 electrode technique		2 electrode technique	
	Test conditions	Performance	Test conditions	Performance
iT MoS ₂ : 100% mono-layer, 70% iT phase [37]	0.5 M KBr; -0.15 – 0.85 V vs NHE	650 F cm ⁻² at 20 mV s ⁻¹ , 5000 cycles (93% capacitance, 2A g ⁻¹)	1 M EMIM BF ₄ /MeCN, 3.0 V	250 F cm ⁻² , 1.1 W cm ⁻² , 5000 cycles (90% capacitance)
MoS ₂ : 40% iT phase, 95% monolayer [165]	6M KOH; -0.1 to 0.5 V vs SCE	366.9 F g ⁻¹ , 1000 cycles (92.2%, 0.5 A g ⁻¹)		
2H WS ₂ /rGO [166]: 1-5 nm, 2D size: 1-3 μm			1 M Na ₂ SO ₄ , -0.1 – 0.9 V; stainless steel current collector	350 F g ⁻¹ at 0.5 A g ⁻¹ , stable with 1000 cycles at 3 A/g, the highest energy density: 49 Wh kg ⁻¹
iT WS ₂ [167]: 20-200 nm width, 3-5 nm thickness	1 M H ₂ SO ₄ , -0.8 to -0.2 V, on carbon electrode	2813 mF cm ⁻² , 200 cycles (~60% capacitance, unstable)		
MoS ₂ /WS ₂ /graphene [168]	3 M KOH	365 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	0-1.6 V, 373 W kg ⁻¹ at 15Wh kg ⁻¹ , 3000 cycles (70% capacitance)
MoSe ₂ [169]: cross-linked by sheets (several layers, ~10 nm size)			stainless steel current collector, 0.5 M H ₂ SO ₄ , 0-0.8 V	49.7 F g ⁻¹ at 2 mV s ⁻¹ , 10000 cycles (75% capacitance at 5 A g ⁻¹), single electrode capacitance of 198.9 F g ⁻¹
NiSe@MoSe ₂ hetero-structures [170]	2 M KOH	223 F/g at 1 A/g.	1.65 V	415 W kg ⁻¹ at 32.6 Wh kg ⁻¹ , 5000 cycles (91.4% capacitance)
iT TiS ₂ [115]: 2-10 layers, 50-100 nm size			1 M LiClO ₄ in propylene carbonate	220-460 F g ⁻¹ at 5-100 mV s ⁻¹
iT VS ₂ [171]: 8-14 layers, micrometer size	0.5 M H ₂ SO ₄ , -0.3 to 0.6 V vs NHE	860 F g ⁻¹ at 5 mV s ⁻¹ , 1000 cycles (85% capacitance)		
NiSe ₂ [172]: down to monolayer with pores	1 M KOH, 0-0.7 V vs Hg/HgO	466 F g ⁻¹ at 3A g ⁻¹ , 1000 cycles (76.2% capacitance)		
TaS ₂ [173]: monolayer, with sub-nanopores			0-0.9 V, PVA/LiCl	508 F cm ⁻² at 10 mV s ⁻¹ , 1316 W L ⁻¹ at 58.5 Wh L ⁻¹ , 4000 cycles (92% capacitance)
CoNi ₂ S ₄ -G-MoSe ₂ [90]	6M KOH, 0-0.4 V vs Ag/AgCl	1141 F g ⁻¹ at 1 A g ⁻¹ , 2000 cycles (108% capacitance at 20 A g ⁻¹)	6 M KOH, on Ni foam	13.3 KW kg ⁻¹ at 23.7 Wh kg ⁻¹
Secondary Battery				
Materials and references	Battery type	Conditions (e.g. size, electrolyte, voltage)	Performance	
iT MoS ₂ [174]: monolayered sheets on rGO	Li-ion	75 wt% of MoS ₂ (monolayered sheets, iT ratio unknown), layer-by-layered stacked with rGO	800 mAh g ⁻¹ at 100 mA g ⁻¹ , 500 cycles at 400 mA g ⁻¹ (stable capacitance)	
MoS ₂ [175] vertically aligned on rGO	Na-ion	Thickness < 10 layers, Al foil, NaClO ₄ (1 M)/ethylene carbonate /diethylene carbonate /ethyl-methyl carbonate (equal volume)	255 mAh g ⁻¹ at 0.2 A g ⁻¹ , 1300 cycles (95.65% capacitance retained, at 1 A g ⁻¹)	
MoS ₂ nanoflakes [176]	Li-S	Thin to under 10 layers, Al foil, 1 M LiTFSI and 0.2 M Li ₂ S ₆ in a 1 : 1 (v/v) DOL/DME mixture	826.5 mAh g ⁻¹ at 8C, 600 cycles (>99% capacitance retained at 0.5 C)	
MoS ₂ nanoflakes [132]	Li-O ₂	Size:110-150 nm, aluminum mesh, 2-4.2 V vs Li/Li ⁺ , MIM-BF ₄ with 0.1 M LiTFSI	500 mAh g ⁻¹ at 0.1 mA cm ⁻² , 50 cycles (85% capacity)	
WS ₂ nanosheets on-SWCNT [177]	Li-ion	Cu foil, 1 M LiPF ₆ /EC: DEC (1:1 by volume), 0.01-3 V	1050 mAh g ⁻¹ at 0.1 A g ⁻¹ , 1000 cycles (113% capacity at 1 A g ⁻¹)	
WS ₂ nanosheets [178]	Na-ion	micrometers size, thickness around 10 nm,	453 mAh g ⁻¹ at 0.1 A g ⁻¹ , 80 cycles (stable)	
WSe ₂ nanosheets on carbon fiber [179]	Li-S	LiTFSI in DOL/DME (1:1 by volume) with 1 wt% LiNO ₃ , 1.7-2.7 V	1180 mAh g ⁻¹ at 0.5 C, 1500 cycles (2C, 90% capacity)	
VS ₂ sheets [180]	Na-ion	~ 500 nm 2D size, sheets stacked; 1 M NaSO ₃ CF ₃ dissolved in diglyme. 0.4-2.2 V vs Na ⁺ /Na	250 mAh g ⁻¹ at 0.2 A g ⁻¹ . 600 cycles (no capacity fading at 5 A g ⁻¹)	
VS ₂ nanosheets on rGO [181]:	Li-S	Sheet thickness 3.46 nm thickness (AFM), Al foil, lithium anode, 0.8 mol L ⁻¹ of Li-TFSI	950 mAh g ⁻¹ at 1 C, 300 cycles (532 mAh g ⁻¹ at 5 C, ~99% capacity)	
MoSe ₂ nanosheets on rGO [182]	Li-ion	Thickness < 10 nm, 2D size < 100 nm; 0.01 V – 3 V (vs Li/Li ⁺) 1M LiPF ₆ in EC/DMC (1:1 v/v)	715 mAh g ⁻¹ at 0.1 A g ⁻¹ , 1000 cycles (519 mAh g ⁻¹ at 0.1 A g ⁻¹)	
SnSe ₂ nannplate on graphene [183]	Li-ion	~20 nm thickness, 100-400 nm 2D size; Cu foil, 1 M LiPF ₆ in EC/DEC (1:1 v/v), 1 mV – 3V	420 mAh g ⁻¹ at 0.04 A g ⁻¹ , 30 cycles (capacity of 260 mAh g ⁻¹).	
SnS ₂ nanosheets [184]	Na-ion	3-4 nm thickness, μm scale; Cu foil, 1 M NaClO ₄ in propylene carbonate with 5% fluoroethylene carbonate	733 mAh g ⁻¹ at 0.1 A g ⁻¹ , 435 mAh g ⁻¹ at 2 A g ⁻¹ . 50 cycles (capacity of 647 mA hg ⁻¹ at 0.1 A g ⁻¹)	
NiCo ₂ S ₄ nanosheets vertically aligned on carbon cloth [124]	Li-ion	thickness: ~10 nm, majority 2D size: 1-2 μm) vertically aligned on carbon cloths. 0.01-3 V (vs Li/Li ⁺), LiPF ₆ (1 M) in EC/DEC (1:1 vol%)	~1275 mAh g ⁻¹ at 1 A g ⁻¹ , 340 mAh g ⁻¹ at 5 A g ⁻¹ , 100 cycles (capacity of ~1137 mAh g ⁻¹ at 1 A g ⁻¹)	
TiS ₂ nanoplate [125]	Na-ion	1 M NaClO ₄ in EC/DEC (1:1 v/v), 1-3V (vs Na/Na ⁺)	186 mAh g ⁻¹ at 0.2 C, 100 mAh g ⁻¹ at 10 C, 100 cycles (170 mAh g ⁻¹ at 0.2 C)	
CoSe ₂ /NbSe ₂ nanosheets [185]	Li-ion	10 nm thickness of NbSe ₂ (2D size: ~500 nm), part of the nanosheets were replaced by CoSe ₂ ; 0.005 to 3.0 V (vs Li/Li ⁺),	607 mAh g ⁻¹ at 0.1 A g ⁻¹ , 345 mAh g ⁻¹ at 5 A g ⁻¹ , 1500 cycles (capacity of 364.7 mAh g ⁻¹ at 5 A g ⁻¹)	

Besides the above bottom-up approaches, several top-down techniques have also been developed for 2D TMDs. We have witnessed that several energy storage devices were fabricated from the 2D TMDs based on liquid phase exfoliation (a surface energy related technique) and their modified approaches (e.g. acid-assisted approach) [139, 147, 162]. This technique can produce some monolayered TMDs [162], but is still unsuitable for large production due to the low yield of the ultrathin (e.g. 1-2 layers) TMDs sheets. This weakness also resulted in unsatisfied performances of the fabricated energy storage devices [139, 147]. By contrast, chemical exfoliation is considered more promising in generating monolayered TMDs with high yield [163-164]. It has also been developed for monolayered 1T TMDs nanocrystals and rich edge structures [91]. The only limitation of this approach is the use of unsafe chemicals (e.g. butyl lithium). More convenient techniques for monolayered TMDs nanocrystals could be the tandem intercalation [94] and potassium intercalation and disintegrating routes [31, 33]. The former requires a small size and high crystallinity of the raw material, and the latter is limited by the violent reaction (need additional safe controls) between the potassium and solvent (EtOH/H₂O). Besides, nanocrystals from these approaches were mainly 1H phase, which is unfavorable for direct uses in high-performing energy storage devices, i.e. a fast energy storage device requires high electrical conductivity of the active material. In energy storage applications, the 2D TMDs may need to be combined with other materials, doped and defected further for better performances (e.g. higher capacity, stability and electrical conductivity). Therefore, various techniques beyond just the fabrication of the pure 2D TMDs are sought after for future development in this field, which will be further introduced in the next section.

6 Summary and Prospect

To satisfy the increasing demands for higher energy and power densities, along with the demand for other key features (e.g. long life-time, high safety and low cost), the energy storage techniques of both the supercapacitor and the secondary battery need to be improved. For such purposes, techniques such as the modification of traditional electrode materials and the energy storage pathways (e.g. energy storage beyond the "Li-ion") have been tested, which are not considered really successful. By contrast, recently developed 2D thin TMDs are considered to be more promising in improving many aspects of both supercapacitors and secondary batteries, owing at least to the following reasons:

- They have a thin structure similar to graphene, and could offer ideal super short electron transport length and small ion transport distance for the fast charge/discharge; Full 2D TMDs could participate in energy storage processes, increasing energy density and reducing manufacturing costs;
- Compared with traditional electrode materials (e.g. bulk TMDs, graphite and even graphene), the electrochemical behaviours of the surface of 2D TMDs can be both "Faradaic" and "Non-Faradaic" with higher adsorption energy and lower ion diffusion barriers, improving energy, power and cycling performances;
- In multilayered 2D TMDs, the intercalation between the interlayers is still a very fast quasi-2D process, ensuring a fast charge/discharge process. Energy storage with larger metal ions beyond Li⁺ is also appropriate in these 2D TMDs owing to their larger interlayer space;

- They have interesting catalytically active edges which can be appropriately developed for energy storage, i.e. by introducing conversion reactions;
- The flexibility, the large EASA, the high surface tunability and rich coordination sites of 2D TMDs can be fully utilized to improve the areal and volumetric capacities of small and thin flexible devices which are expected to be some of the key features of future energy storage devices.

However, the energy storage research on the 2D TMDs is still at its very early stage. Relating device demonstrations based on purely monolayered or thin layered TMDs (< 5 layers) are rather limited. **Table 1** summarizes the electrochemical performance of some recently developed 2D-like (most are not thin enough) TMDs in energy storage. Most of these performances are still far below than the future demand or their theoretical ones, which is mainly due to the reasons:

- Many TMDs (particularly the 1H/2H phases) in energy storage devices are not thin enough. How to fabricate the strictly monolayered TMDs with high yield at large scale is still a challenge;
- Most 2D 1T-TMDs are thermally unstable. Techniques for the stabilization of these 1T TMDs with high electrical conductivity have not been well developed;
- Electrical conductivity of the most stable 1H/2H TMDs is too poor to afford the application in high-performing energy storage devices.

There are several suggestions that may be followed for future improvements. As we know, the most 1T TMDs are metallic with high electrical conductivity [21], which in principle can be successfully used in building energy storage devices with high power performances. However, techniques are still required to improve both the phase yield (e.g. lower than 70% of the chemical exfoliation method [37, 91]) and the stability of 1T TMDs. Improvement on the phase yield can be realized by the stabilization of the 1T TMDs which is also imperative for durable and reversible energy storage operations. Several investigations suggest that 1T TMDs can be stabilized by suitable chemical doping [187-189]. Nevertheless, how these chemical modifications affect the electrochemical performances (e.g. binding energy with the ions, the ion diffusion barrier, the electrical conductivity and the surface wettability) of 1T TMDs is still unclear, which should be established correspondingly. Beyond the 1T TMDs, some stable 2D ternary sulfides (e.g. the NiCo₂S₄ and CoNi₂S₄) are also highly conducting [80-82]. Nevertheless, the fabrication of ultrathin 2D ternary sulfides (e.g. down to the thickness of 1-2 nm) is still challenging, which should be appropriately improved to reduce the thickness for more interesting applications in energy storage devices.

For the most stable 1H/2H mono- and few-layered TMDs, the building of some hybrid structures to secure the rapid charge transfer process is highly recommended, i.e. building the vertically aligned (on graphene or other conducting materials) heterostructure of semiconducting TMDs thin layers and their oxide counterparts (e.g. MoS₂ on MoO₃) with higher electrical conductivity. Like the vertically aligned electrode (**Fig. 7b**), this structure can fully apply the conducting transition metal oxides to inject the charge from the substrate to the TMD layers. The key factor here would be the controlling growth/fabrication of the heterostructure interstitially stacked by different ultra-thin nanosheets. More convenient approach-

es could be including graphene and 2D TMDs materials (e.g. monolayered nanocrystals) into a hybrid structure with intimate contact (e.g. via strong physical and chemical interactions). In this case, 3D-G can be used as a support of 2D TMD nanocrystals (loaded on the channel of 3D-G) to ensure the efficient charge transfer between the electrode and the surface of the 2D TMDs, and also to provide a porous channel for efficient mass transfer. Alternatively, a flat layer-by-layer stacked hybrid structure of graphene and 2D TMDs (e.g. monolayered sheets or nanocrystals) could also be considered to avoid the inefficient electron hopping between the layers of TMDs. A technique issue here is to secure the strong bond between the TMD materials (e.g. monolayered nanocrystals) and the graphene. This structure would also be capable of providing larger interlayers for energy storage of large metal ions beyond the Li^+ (e.g. Na^+ and K^+). To realize such conceptual devices with high performances, the size and the stacking limit of the 2D TMDs on the graphene sheet would need to be optimized. As for a higher loading of the active TMDs on graphene (for higher energy densities), heterostructures of 2D TMDs and electrochemical conducting thin materials may be more promising to be considered for the rapid charge transfer. This structure, in principle, can be formed by the sulfuration of thin MoO_3 and MoO_3 nanocrystals.

Except the above works, other factors, such as the mechanical strength of the hybrid structure (especially the 3D hybrid structure) should also be considered to afford robust energy storage performance (e.g. in flexible devices). For such a purpose, the functionalization of the 3D graphene channels with a thin electrical conducting polymer layer is suggested, which is feasible by adapting the similar approach established previously [190]. Besides the above discussions, future works in this field can also involve other strategies to improve the energy storage performance, which may include the chemical doping/modification of both the surface and the edge (to tune the charge mobility and catalytic activity) [75, 187-189], the building of van der Waals heterostructures [40, 157-159] and the creation of Janus 2D TMDs [38, 39, 156]. It also includes the development of the catalytically active site (for metal-air batteries) and the demonstration of the Li-S battery by using the monolayered TMDs (e.g. MoS_2) nanocrystals with rich edge and activated surface sites (e.g. by surface S depletion [31]). Nevertheless, before these can be success, both the theoretical and experimental understanding of the modified 2D TMDs in energy storage should be well developed. Understanding of the energy storage mechanism of the 2D TMDs can be realized by investigating difference of the redox peak potentials, establishing the relationship between the response current and the sweep rate, and quantifying the relative contribution of the capacitive and diffusion-limited process of the energy storage devices, which have been well established previously [191]. Besides, recent development suggests that the electrochemical tests building on the micro-fabrication and micro-cell could be adapted to reveal the pure mechanism by avoiding influences from other factors, although it has not been well used in this field [171, 192].

In summary, this mini review summarized challenges facing current supercapacitor and secondary battery technologies. How and why the 2D TMDs can perform perfectly in these devices are discussed. From all these discussions, it can be reasonably expected that 2D TMDs would be highly promising in improving both the supercapacitor and secondary battery. Nevertheless, several technical weaknesses are still need to be

improved, including the fabrication and modification techniques of the materials, the design and building of hybrid structures we have outlined. This review provides deep insight into developing future high-performance energy storage devices by exploring the various merits of 2D TMDs.

ASSOCIATED CONTENT

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Notes

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