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Graphene and molybdenum disulphide hybrids for energy applications: an update

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ABSTRACT

Graphene and its analog, two-dimensional (2D) layered molybdenum disulphide (MoS_2), have been used for 'clean energy' applications in the last several years because of their remarkable electrochemical, optical, and magnetic properties. Their huge success and application potential in various fields has led to the investigation of new 2D nanomaterials which cross the boundaries of existing graphene-based devices. The combination of chemically inert graphene and redox-active MoS_2 in a single electrode is providing new opportunities to improve the performance of energy devices and circumvent existing limitations. This article updates our previous review on advances in graphene-MoS_2 hybrids for energy-oriented applications. In particular, a summary of recent developments in the synthesis of the graphene-MoS_2 hybrids, with an emphasis on energy storage and hydrogen production, is provided. Future challenges and opportunities associated with the development of 2D hybrid materials, and their applications in energy storage systems, are discussed.

1. Introduction

Among various types of two-dimensional (2D)—layered materials, graphene is considered a potentially disruptive material in a wide range of existing technologies, from energy storage/generation to optical and biological applications [1–5]. Graphene's 2D layered structure, combined with excellent electrical and mechanical properties, makes it a particularly promising material for energy-related applications [6]. The recent success of graphene-based materials in emerging applications has also sparked interest in other 2D materials, which have the potential ability to minimize production costs and boost the efficiency of advanced energy systems.

In particular, 2D transition metal dichalcogenides (TMDCs), which are structurally analogous and have properties that are complementary to graphene, have been demonstrated as attractive electrode materials for future energy conversion and storage applications [7–9]. Molybdenum disulphide (MoS_2), for example, has been shown to be a capable alternative to graphene as an electrode material because of its amazing strength and electrical properties, which include a 2D layered structure and an appropriate band gap. In addition, the facile synthesis and rich abundance of molybdenite makes the compound even more attractive and fascinating [10–12]. There are some differences. In graphene, carbon atoms form a single layer, while MoS_2 consists of a 'sandwich' type structure with three atomic layers, in which the sulfur atoms reside between two planes of molybdenum atoms (Fig. 1). But similar to graphene, in the last few years MoS_2 has been used in various energy-related applications including supercapacitors [13,14], batteries [15,16], and water splitting for hydrogen production [17,18].

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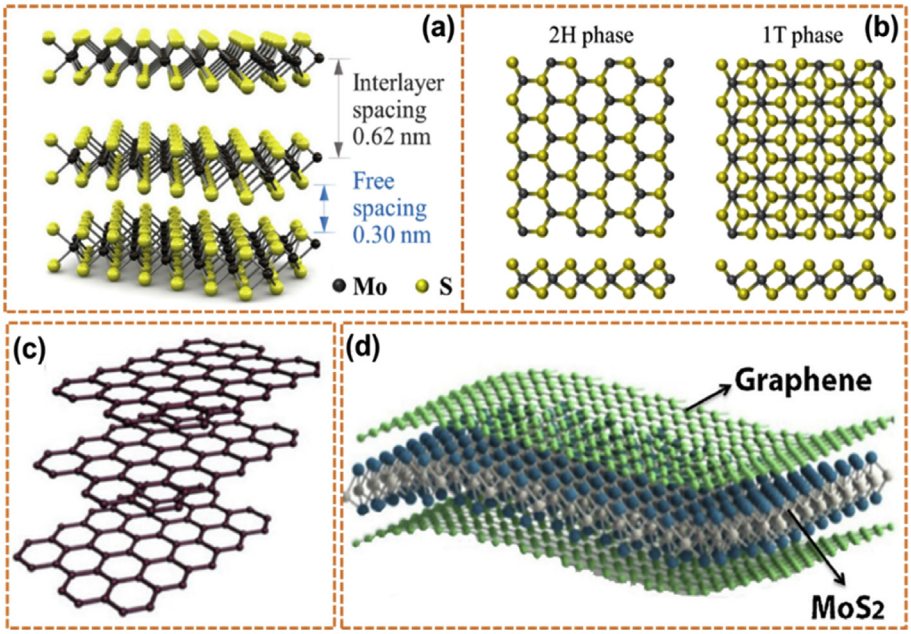

Fig. 1. (a) 3D illustration of MoS_2 structure, adapted with permission from the study by Radisavljevic et al [29]. Atomic positions in (b) the 2H phase with trigonal prismatic coordination and the 1T phase with octahedral coordination. Adopted from the study by Wang and Mi[30] (c) The structure of graphene and (d) Exfoliated few layer MoS_2 and rGO flakes. Adapted from the study by David et al [31].

Because of its distinctive structure and conductivity, MoS_2 is classified as having two separate phases, a semiconducting 2H phase and a metallic 1T phase. The two phases have clear differences in their chemical and physical properties. The metallic 1T phase has higher electrical conductivity than the semiconducting 2H phase [19,20]. As an electrode material, the low electrical conductivity of semiconducting MoS_2 hinders electrochemical processes, and as a result, is mostly unsuited for energy storage applications. However, it has good cycling stability, and its well-developed synthesis procedure makes it popular for other energy-oriented applications [21,22].

To tackle the low conductivity issue of semiconducting MoS_2, it was recently suggested that it be combined as a nanocomposite with another conducting material such as carbon black or graphene. Metallic MoS_2, on the other hand, has high electrical conductivity, which makes it highly desirable for energy storage applications, and removes the need for conductive additives to achieve excellent rate capability [23–25].

Despite recent advances, MoS_2 nanosheets have a tendency to restack. This restacking of the 2D MoS_2 sheets obstructs the charge transfer process, which directly affects the resulting electroactive surface area and electrochemical performance. Because the restacking issue is a limiting factor that hinders performance, simple and effective methods need to be developed to prevent the restacking of the 2D nanomaterial. In some studies, graphene restacking is prevented by inserting a spacer material between the two layers of graphene [26]. A similar strategy can be used with MoS_2-based materials. Another promising way to overcome the restacking issue is to functionalize or hybridize the 2D MoS_2 with another highly conducting material such as graphene. The controlled hybridization of MoS_2 and graphene can modify the physicochemical properties of the individual components and enhance the electrochemical and mechanical properties of the final electrode materials [27,28]. Essentially, the hybridization enhances the electrochemical features of the individual material and its hybrid.

In this review, we introduce recent advances in the synthesis of graphene-MoS_2 hybrids for energy storage and water splitting applications. To begin with, we briefly summarize the diverse synthesis routes used to prepare the graphene-MoS_2 hybrids, and then discuss the effect of hybridized materials in supercapacitors, rechargeable batteries, and water splitting applications. Finally, we present current challenges and future prospects for the development of graphene-MoS_2 hybrids.

2. Synthesis methodologies

Simple, reliable, sustainable, and scalable synthesis methods are always preferred for materials preparation, as well as processes that allow their properties to be tailored for various applications. To develop graphene, MoS_2, and their hybrids, physical (dry process) and chemical approaches (wet process) have typically been explored and used [1,29–31]. More specifically, chemical vapor deposition (CVD), liquid exfoliation methods, microwave synthesis, electrochemical exfoliation, and hydrothermal methods have been successfully used to prepare 2D nanostructures, including graphene and MoS_2 [32]. However, the synthesis of large-area graphene films with low defects is a challenging topic in material science [33]. Various methods similar to those used for graphene have also been used to prepare MoS_2. Among them, CVD is specifically attractive because of its compatibility with electronic device manufacturing technologies. However, many energy-related applications require bulk quantities of the electroactive material, which is not possible to achieve with the CVD method.

The process of dip coating the insulating substrate in a $(NH_4)_2MoS_4$ solution followed by sulfurization at 1000 C in vide supra presence of sulfur vapor has been reported by Liu et al. [34] to form three-layered MoS_2. Similarly, Zhan and co-workers [35] developed MoS_2 thin films by sulfurization of the Mo substrate. Despite these developments, the preparation of large area and uniform 2D MoS_2 thin films by physical methods remains a great challenge.

Using liquid exfoliation methods and other top-down approaches to produce layered materials is a promising alternative to the CVD process and has been widely investigated to prepare large-area 2D nanomaterials, especially for energy applications. Several different methods have been reported so far. For instance, exfoliating parent materials such as graphene or MoS_2 using ultrasonic waves in the presence of a solvent such as dimethylformamide (DMF) or N-methyl-2-pyrrolidone is an efficient and large-scale approach [36]. The sonication method is capable of producing single-and multi-layered MoS_2 material [37].

Another approach, the aqueous solution–based hydrothermal process has also been proposed to prepare MoS_2-based nanosheets, using controlled temperature and pressure operating conditions [38]. In the hydrothermal process, the reaction between the molybdenum source, such as ammonium molybdate, and a sulfur source such as thiourea under controlled pressure and temperature leads to the formation of a MoS_2 nanostructure.

The lithium intercalation and exfoliation method is another effective approach for preparing metallic MoS_2. In organic solvents, the bulk MoS_2 and strong reducing agents (n-butyl lithium or $LiBH_4$) react with each other to form a Li-intercalated MoS_2. Later, the dispersion of Li–MoS_2 in aqueous solvent with subsequent sonication process gives 2D metallic MoS_2 [39].

Similar synthesis routes can be used to prepare graphene-MoS_2 hybrid materials. Typically, graphene or reduced graphene oxide (rGO) is used as a supporting material or substrate to develop the MoS_2-based nanostructures. For example, Zhang et al. [40] prepared the rGO-MoS_2 hybrid using the solvothermal method, in which the graphene oxide was dispersed in DMF with $(NH_4)_2MoS_4$ followed by heating at a reaction temperature of 210 C. It is important to note that the synthesis method and operating conditions strongly affect the quality and physicochemical properties of graphene and MoS_2. Therefore, depending on the application, a suitable method needs to be used to achieve the desired properties of the 2D materials. In the following section, we discuss the different synthesis methods used to prepare graphene, MoS_2, and their hybrid combinations. How the structural and surface properties (such as morphology, surface areas etc.) of the MoS_2-graphene hybrid affect particular applications is discussed.

3. Applications

With their 2D layered structure, excellent electrical conductivity, and well-developed synthesis procedure, graphene-MoS_2 hybrids are promising potential materials for energy storage and water splitting applications. In the past, a range of 2D materials have been investigated for these energy-related applications. Here, we focus on the energy storage (supercapacitors and rechargeable batteries) and water splitting (hydrogen production) applications of graphene-MoS_2 hybrids.

3.1. Supercapacitors

Capacitors are two terminal power components widely used in electronic circuits for various purposes. They have the unique ability to store/release energy at high charging/discharging rates, which makes them especially valuable in power hungry electronic applications [41–43]. Supercapacitors achieve the central position in the Ragone plot because they exhibit higher energy density than traditional capacitors and higher power than rechargeable batteries [44,45]. Supercapacitors can also tolerate more charging/discharging cycles than rechargeable batteries, making them especially suitable for remote or inaccessible applications [46].

Supercapacitors are classified into two subclasses based on the electrode material and their electrochemical signatures: (1) electric double layer capacitors (EDLCs) and (2) surface redox-active material–based pseudocapacitors. In the EDLC, the charges are electrostatically stored at the electrode surfaces. The most promising EDLC electrodes include those prepared with a carbon-based material such as graphene and its derivatives, carbon nanotubes (CNTs), activated carbons, and others [47,48]. Pseudocapacitive materials include transition metal oxides/sulphides and conducting polymers, where the charges are stored through surface redox reactions. The low energy storing capacity of the EDLCs and comparatively low cycling stability and power density of pseudocapacitors limit their practical applications. However, by combining EDLC and pseudocapacitive materials, it is possible to achieve synergic effects which permit the development of high energy and high power systems [49–51].

Fundamentally, the energy storing capacity of the supercapacitor depends upon the physical properties of the electrode materials, such as electrical conductivity and surface area. High electrical conductivity, large surface area, and redox activity are preferred for high-energy supercapacitor applications [52]. Typically, graphene and its derivatives fulfill the first two requirements. The graphene analog–layered MoS_2 is then used as a pseudocapacitive material, thanks to its rapid surface redox activity and good structural stability. However, in supercapacitor electrodes, the material's low electrical conductivity leads to poor rate performance and low cycling stability.

When designing a suitable nanostructure, or making a hybrid with the MoS_2 using another conducting material, such as carbon or a conducting polymer, carbon is the best solution to overcome these limitations. Moreover, it is also beneficial to prepare the MoS_2 on a three-dimensional (3D) conducting substrate, which can enhance the electron transport process. For instance, a graphene-MoS_2 hybrid was reported by Zhang et al. [53] for supercapacitor and lithium-ion battery applications. They prepared highly conducting 3D graphene decorated with a MoS_2 flocculent nanostructure and determined it was promising electrode material, as shown in Fig. 2. The combined effect of the graphene and MoS_2 led to excellent energy storage capacity in both energy storing systems.

In the supercapacitor, the prepared graphene-MoS_2 hybrid electrode worked as a negative electrode and the resultant asymmetric supercapacitor showed the excellent energy density value of 156 Wh/kg at 197 W/kg power density (Fig. 3). Impressively, the asymmetric supercapacitor maintained an energy density of 97 Wh/kg even at a high power density of 8314 W/kg, with a stable cycle life. The electrochemical results clearly showed that the nanocomposite-based asymmetric supercapacitor can simultaneously provide both higher energy and power density, which is very advantageous in advanced electronic applications. Furthermore, the electrochemical performance of the graphene-MoS_2–based asymmetric supercapacitor proved to be superior to traditional activated carbon-based negative electrodes [54].

The energy density values of the supercapacitor depend upon the operating voltage window and the weight of the whole device. Having current collectors that weigh more than the active electrode material affects the energy density values. To overcome this issue, ultralight weight and porous natured graphene aerogels (GAs) were recently proposed as a current collector material and an electroactive material for the supercapacitor application. The highly conducting and 3D porous nature of the GA are suitable for the high-energy supercapacitor application. Most importantly, the GA itself acts as a current collector by removing the need for costly current collectors.

With this motivation, Sha et al. [55] developed a two-step approach to prepare GA-decorated MoS_2/polyaniline (MoS_2/PANI/rGO). The MoS_2/PANI was well dispersed on graphene oxide and

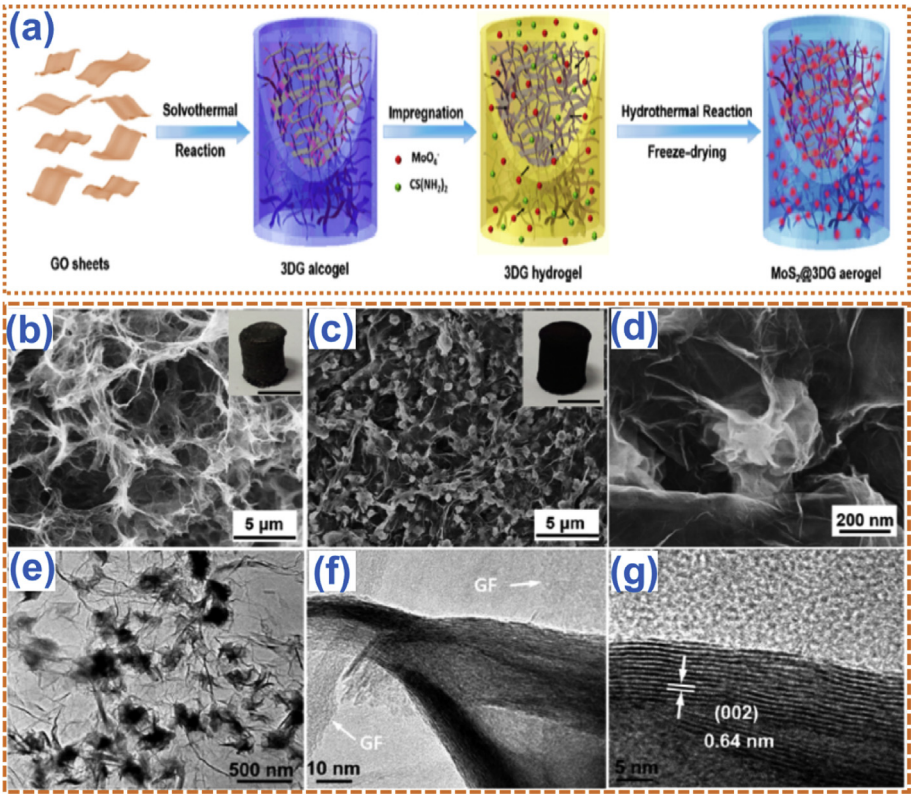

Fig. 2. (a) Schematic of fabrication of the MoS_2-graphene hybrid structure, (b) Scanning electron microscopy (SEM) image of the porous graphene sample, (c) SEM image of the MoS_2-graphene hybrid (inset: optical photograph of MoS2-graphene bulk sample, scale bar: 1 cm). (d) SEM image of MoS_2-graphene hybrid at higher magnification. (e, f) Transmission electron microscopy (TEM) images of the MoS_2-graphene hybrid at different magnifications. (g) High-resolution transmission electron microscopy (HRTEM) image of the MoS_2-graphene composite showing lattice fringes of MoS_2 nanosheets. Adapted from the study by Zhang et al [53].

later reduced using urea in a hydrothermal process, to form a ternary nanocomposite. Electrochemical measurements were carried out for the MoS_2/PANI/rGO ternary nanocomposite electrodes with different rGO ratios, and they displayed a maximum capacitance of 618 F/g at 1.0 A/g with a retention capacity of 96% over 2000 cycles when the MoS_2/PANI to rGO ratio was 1:1. Using a hydrothermal technique, Saraf et al [56] prepared an rGO-MoS_2 hybrid for the supercapacitor application. The prepared rGO-MoS_2 hybrid electrodes showed satisfactory electrochemical performance because of the synergetic effect of both components. The rGO-MoS_2 hybrid exhibited a capacitance value of 387.6 F/g at 1.2 A/g, which was much higher than the pristine rGO and MoS_2 electrode.

In recent studies, it was suggested that heteroatom (such as nitrogen, sulfur, phosphorus etc.) doping of carbon-based materials such as graphene can enhance their capacitive features by enhancing its electrical conductivity and as redox activity. For example, Xie et al. [57] prepared the flower-like MoS_2-nitrogen–doped graphene (MoS_2-NG) hybrid electrode using a one-pot hydrothermal process. The maximum capacitance was found to be 245 F/g at 0.25 A/g, whereas it is decreased to the 146 F/g at 20 A/g. The cycling stability result exhibited around 91.3% capacitance retention after 1000 cycles at 2 A/g. Similar efforts were used in the past to prepare graphene-MoS_2 hybrids for the supercapacitor applications [58–62]. The aforementioned studies demonstrate the enhanced electrochemical performance of graphene-MoS_2 hybrids in supercapacitor applications, where the complementary features of the graphene and MoS_2 lead to excellent electrochemical results. However, the reported electrochemical properties including capacitance, energy density, and the cycling durability have yet to meet commercial standards. Thus, further efforts and strategies are needed to improve the current electrochemical performances of graphene-MoS_2 hybrids for high-energy supercapacitor applications.

In comparison with the present battery technology, the energy density value of the supercapacitors is negligible. On the other side, supercapacitors have higher power density and cycling stability than the present battery technology. The merging of the battery-type and capacitor-type electrode materials in the single cell can overcome the limitations of the batteries and supercapacitors. Recently, the hybrid capacitors are investigated to merge the features of the supercapacitor and battery in a single cell. Typically, the hybrid capacitor consists of the battery-type negative electrode and capacitor-type positive electrode with non-aqueous electrolytes. The lithium-ion capacitors (LICs) are the best example of the hybrid capacitors, which consist of the carbon-based capacitor-type electrode storing the charges by double layer mechanism. The other electrode is battery-type, such as graphite and $Li_4Ti_5O_{12}$ (LTO), storing the energy *via* intercalation/deintercalation reaction mechanism. Traditionally, the graphite and LTO have been used as anode materials to construct the LICs. However, the poor electrical conductivity and relatively high redox potential (~1.5 V, vs. Li/Li^+) of LTO-based materials limit the resultant electrochemical performance of the LICs, while the poor rate capability of graphite is not suitable for their effective application. Recently, to overcome this issue, Wang et al. [63] developed the LICs using the graphene-MoS_2 as the anode material and the activated carbon as the cathode material. The LICs exhibited an ultrahigh specific energy density of 188 Wh/kg at 200 W/kg and remained 45.3 Wh/kg even at a high specific power density of 40,000 W/kg, as well as long cycle life.

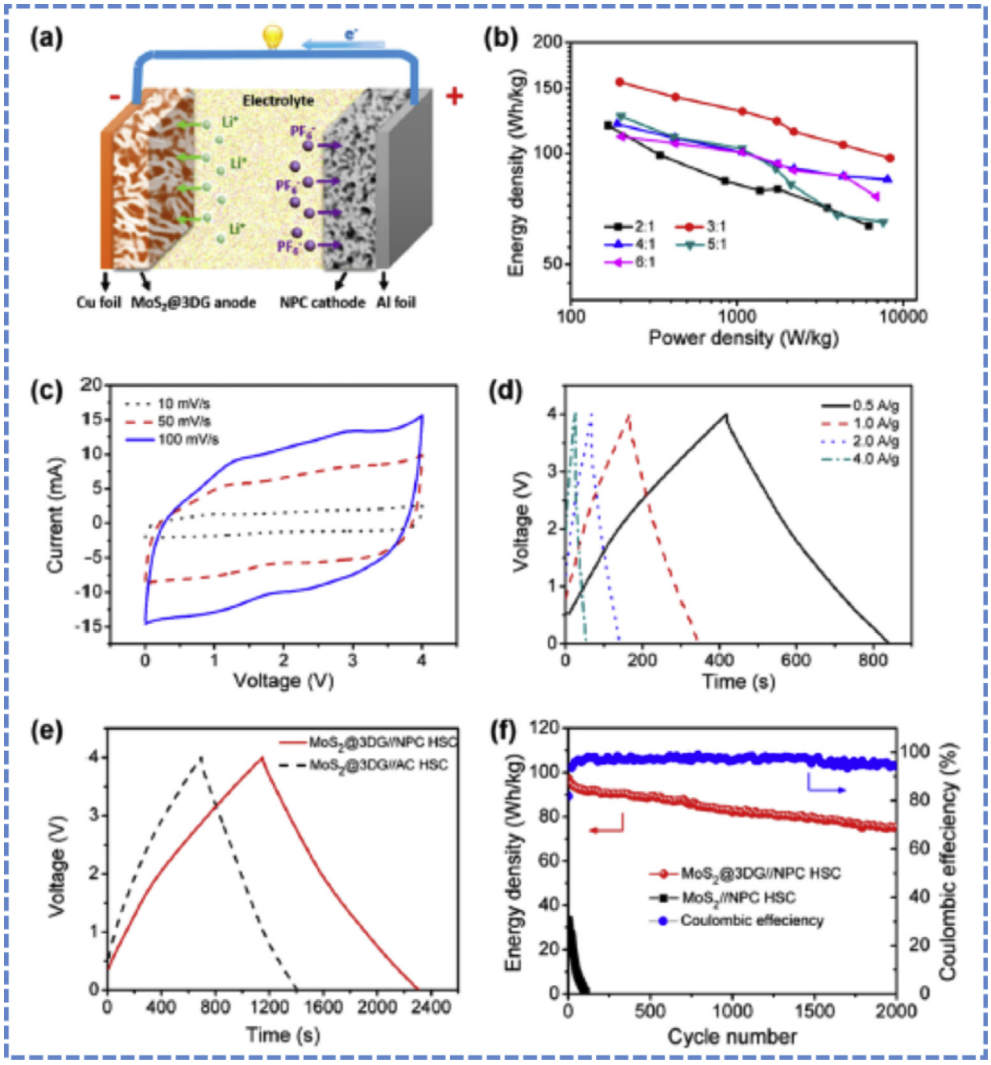

Fig. 3. (a) Schematic illustration of the working mechanism of the MoS_2-graphene nanoporous carbon hybrid supercapacitor (b) The Ragone plot of the hybrid supercapacitor using MoS_2-graphene as a negative electrode and nanoporous carbon as a positive electrode with various mass ratios from 2:1 to 6:1 (positive electrode: negative electrode) over a voltage window of 0.0–4.0 V. (c) CV curves of the MoS_2-graphene nanoporous carbon hybrid supercapacitor over a voltage window of 0.0–4.0 V at different scan rates. (d) Galvanostatic charge/discharge curves of the MoS_2-graphene nanoporous carbon hybrid supercapacitor at different current densities from 0.5 to 4.0 A/g. (e) Galvanostatic charge/discharge curves of the MoS_2-graphene nanoporous carbon hybrid supercapacitor and the MoS_2 nanoporous carbon hybrid supercapacitor as contrast at a current density of 0.2 A/g. (f) Cycling performance of the MoS_2-graphene nanoporous carbon hybrid supercapacitor and MoS_2 nanoporous carbon hybrid supercapacitor at a current density of 1.0 A/g for 2000 cycles. Adapted from the study by Zhang et al [53].

Similar to the LICs, interlayer-expanded MoS_2-rGO has been used as an anode material for the sodium-ion capacitor (NICs) by Zhan et al. [64]. In the MoS_2-rGO hybrid electrode, the graphene frame delivered sufficient enough charges and the highly expanded MoS_2 achieved fast ion diffusion. As a result, the MoS_2-rGO–based NICs reached the energy density of 630 Wh/kg with excellent stability over 10,000 cycles. Ramakrishnan et al. [65] also reported the sodium ion symmetric hybrid supercapacitor with MoS_2 nanoflowers@rGO hybrid system, which was produced *via* a hydrothermal method followed by an ultrasonication process. The developed symmetric hybrid electrode (full cell) delivered a maximum capacitance of 55 F g at 0.03 A/g.

3.2. Rechargeable batteries

3.2.1. Lithium-ion battery

LIBs are the heart of today's advanced electronic gadgets, as nearly all such devices are now powered by LIBs. The high energy density and portability of LIBs make them suitable energy storage devices for a wide range of commercial applications [66]. Constant efforts are being invested by research institutes and industries to further enhance their energy density, cycling stability, and power capability. It is well known that the physical and electrochemical characteristics of the positive and negative electrode materials determine the resulting electrochemical features of the LIBs. In commercial LIBs, graphite is commonly used as an anode because of its low oxidation/reduction potential vs lithium and its abundance and low cost. However, graphite has low energy storage capacity (~370 mA h/g) and inferior cycling performance, which degrades its electrochemical performance [67,68]. Finding superior anode materials for LIBs to overcome the limitations of graphite-based anodes is necessary.

In the literature, different electrochemically active materials such as SnO_2 [69], Fe_2O_3 [70], Fe_3O_4 [71], MoO_3 [72], and Si [73] have been used as anode materials in LIBs, but the practical use of these materials is limited because of the large change in volume

during the charging/discharging process, unstable solid electrolyte interface, and rapid deterioration in capacity after a few electrochemical cycles [74,75]. In recent studies, the graphene-MoS_2 hybrid has been reported to be the best alternative to graphite anodes in LIB applications. The highly conducting nature and 2D layered structure of the graphene, which provides a high surface area, results in a facile path for the charge transport process. On the other hand, graphene is quite suitable for LIB anode applications because it has a higher energy storage capacity (~669 mA h/g), excellent cycling stability, larger interlayer distance (~0.615 nm) with weak van der Waals forces, which allow an easy intercalation/deintercalation process [76]. Accordingly, combining 2D graphene and MoS_2 in a single electrode is a promising strategy to achieve high performance (high capacity and stability) LIBs.

Considering these aspects, Tian et al. [77] combined interconnected graphene nanoribbons and layered MoS_2 *via* a one-pot hydrothermal process for the LIB application. The mesoporous nature and larger surface area of the prepared electrode provided a high contact area between the electrode and electrolyte. As a result, the developed electrode delivered a specific capacity of 1009.4 mA h/g at 200 mA/g. To control the volume expansion of the MoS_2 electrode after long-term cycling, Xue et al. [78] proposed a carbon encapsulation strategy. The core-shell–structured MoS_2@-graphene composite, with MoS_2 spheres as the core and ultrathin graphene sheets as the shell, was synthesized using a novel spray drying method. In the MoS_2@graphene composite, the graphene layer helped to enhance the cycling stability of the MoS_2 during the charge/discharge process. In addition to this, the graphene layer was found to enhance the electrical conductivity of the resultant composite electrode and prevent aggregation during the charge/discharge process. The prepared MoS_2@graphene composite, when used as an anode in the LIBs, showed good reversibility even after 100 charge/discharge cycles, with a coulombic efficiency of over 99%.

It is well documented that bulk MoS_2 has limited Li-ion storage capacity because of its structural disorder and low electrical conductivity. To overcome this issue, Li et al. [79] recently proposed a surface modification–triggered self-assembling strategy to boost the Li-ion storage capacity of bulk microsized MoS_2. Commercially available micron-sized MoS_2 was used as a raw material during *in-situ* polymerization. A subsequent hydrothermal process and sintering treatment were carried out to prepare the composite electrode for the LIBs, as shown in Fig. 4(a). Initially, the edge activation of the bulky micron-sized MoS_2 was performed by etching process in 6 wt% H_2O_2. Then, the MoS_2 was coated with polydopamine and graphene oxide. Hydrothermal and sintering processes were carried out to produce the final MoS_2@C/RGO aerogels. In this composite, the carbon and rGO components helped not only to immobilize the active Mo atoms and polysulfide ions during extended cycles but also to release volumetric strain and accelerate electron transport. As a result, the prepared composite electrode exhibited a discharge capacity of 1189 mA h/g at 200 mA/g after 100 cycles. More importantly, the full cell LIB showed good energy density, implying this was an effective strategy for enhancing the Li-ion storage capacity of the MoS_2.

Combining the MoS_2 and graphene as a single hybrid electrode can effectively improve the overall electrochemical performance of the system. However, typically, powder samples are used to prepare the electrode with a slurry coating method, in which some polymeric binders and conductive additives are added to the host material. These additives can affect the rate capability of the electrode by reducing electrical conductivity. In addition, the polymeric binder and metallic conductor reduce gravimetric capacity, which will limit practical applicability. Preparing free-standing electrodes is considered to be a promising solution. Lee et al. [80] developed a free-standing, additive-free MoS_2-graphene aerogel paper. A self-assembling process was used to prepare the free-standing composite electrode. Graphene aerogel paper first served as the conductive medium for the MoS_2 sheets and later as a free-standing support for the current collector. Fig. 5(a) shows a schematic diagram of the preparation of the MoS_2-graphene aerogel paper composite. The electrochemical results showed improved energy storing capacity, with a cycling performance of over 700 cycles at 101.1% capacity retention. This might be attributable to the highly conducting and porous nanostructure of the MoS_2-graphene, as seen in Fig. 5. A MoS_2/graphene composite has been also used for the quasi-symmetrical MoS_2 battery, in which an electrochemical activity modulation strategy was used to activate redox in the electronegative and electropositive parts [81]. Several similar approaches to enhance the Li-ion storage capacity of MoS_2-graphene–based hybrid electrodes have been discussed in the literature. Combining both electroactive materials in a single electrode is an effective strategy to enhance the cycling stability and resultant energy storing capacity of the LIBs.

3.2.2. Sodium-ion battery

Given the high cost and limited availability of Li in the earth's crust, researchers have been actively attempting to find its alternative. Recently, sodium-ion batteries (NIBs) have attracted extensive attention because of their wide availability and accessibility. Over the past few years, tremendous efforts have been devoted to developing the NIBs with excellent electrochemical features and they can overcome the limitations of the LIBs. Similar to the LIBs, the different electrode materials, such as metals/alloys, phosphorus/phosphides, and metal oxides/sulfides/selenide, have been tested for the NIB applications. The larger ionic radius (1.02 Å) of Na than Li ion (0.76 Å) results in the lower electrochemical performance in terms of the power capability, rate capability, and cycling stability. The most common graphitic carbon anode materials are inactive for the NIBs because of their high ionic radius [82]. Thus, developing electrode materials with enough channels and/or interstitial sites for Na-ion intercalation/deintercalation process is principally required.

Layered MoS_2 is the suitable candidate for the NIBs because of its large interlayer spacing of approximately 6.2 Å, which is nearly twice of graphite (3.2 Å). Moreover, MoS_2 layers are connected each other by the weak van der Waals forces, and therefore the larger metal ions, such as Na^+ and Mg^+, can be accommodated during the electrochemical process. Moreover, merging MoS_2 with highly conducting graphene simultaneously enhances the energy storing capacity, power capability, and cycling stability. Recently, Li et al. [83] reported a NIB using a MoS_2@liquid-phase exfoliated graphene (LEGr) composite as an anode electrode. The microwave-assisted solvothermal method was used to prepare the MoS_2@LEGr composite electrode, in which the LEGr was used as a support for the MoS_2. The prepared composite electrode exhibited initial discharge and charge capacities of 615.6 and 400.5 mA h/g, with 70.1% capacity retention over 100 cycles. Brown et al. [84] developed a 3D freeze-printing method to prepare MoS_2-graphene aerogels for NIB application. The prepared hybrid MoS_2-rGO aerogel was tested as an anode electrode and exhibited a high initial specific capacity of over 429 mA h/g at C/3.3 rate in the potential range of 2.5–0.10 V (vs Na^+/Na). The single-sheet tulip-like MoS_2 was anchored over the N-doped graphene substrate (tulip-MoS_2/NG) using an *in-situ* synthesis technique with the help of N-methyl-2-pyrrolidinone as the 'sacrificial agent' [85]. As an NIB anode, the tulip MoS_2-NG electrodes exhibited good capacity retention and long cycling stability, with over 1000 charge/

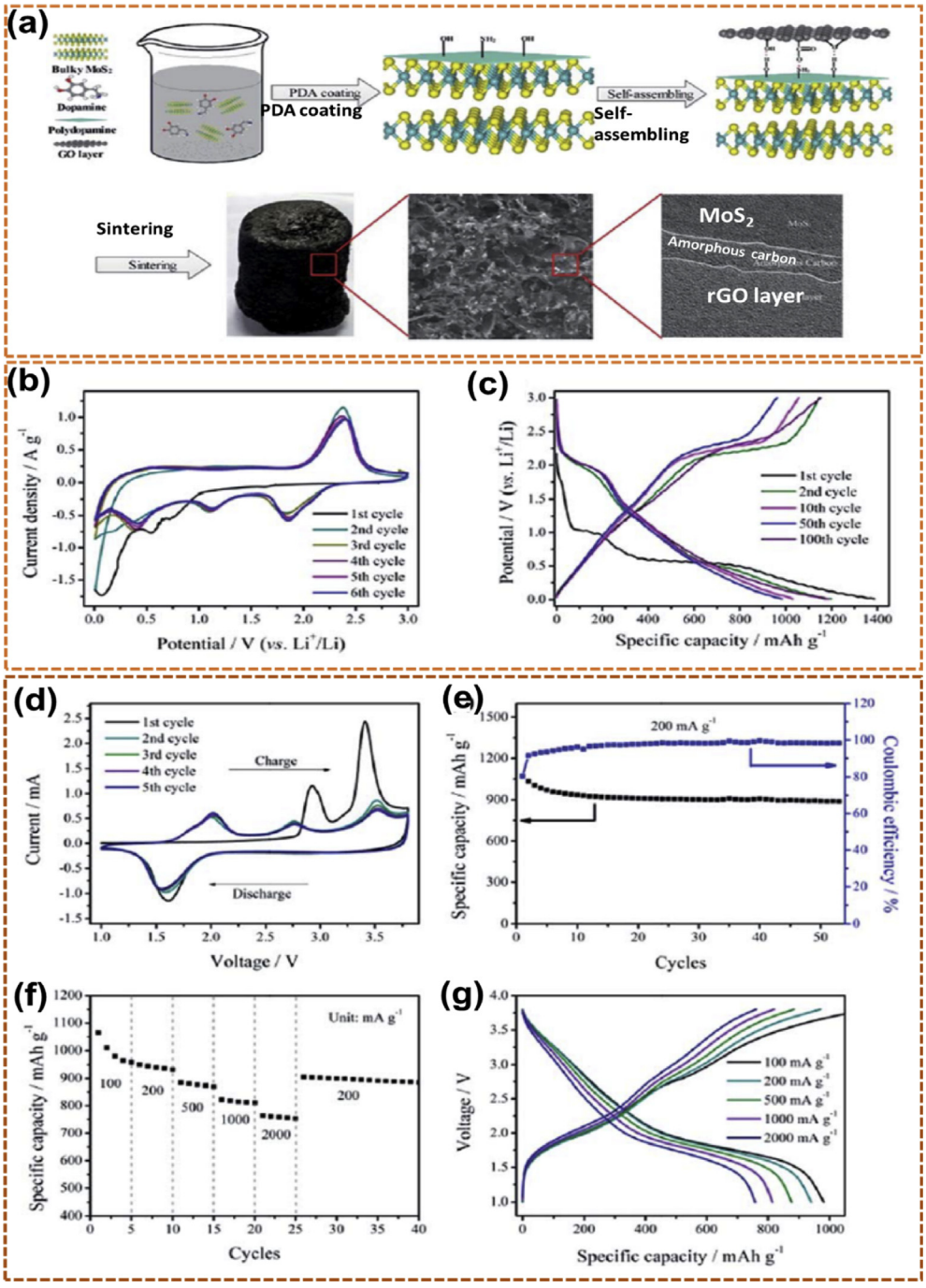

Fig. 4. (a) Schematic of the synthesis strategy and electrochemical performance of the MoS@C/RGO composite, electrochemical performance of the MoS_2@C/RGO composite. (b) CV curves from 0.01 to 3.00 V at 0.2 mV/s, (c) typical charge-discharge profiles for different cycles and electrochemical properties of the MoS_2@C/RGO//$LiCoO_2$ full cells. (d) CV curves between 1.0 and 3.8 V at 0.2 mV/s, (e) cycling performance at 200 mA/g, (f) rate performance, and (g) corresponding charge-discharge profiles from 1.0 to 3.8 V. The full cells were assembled based on the reversible capacities of MoS_2@C/RGO (approximately 1200 mA h/g) and commercial $LiCoO_2$ (150 mA h/g) with 5% cathode excess to achieve full utilization of MoS_2@C/RGO. Adapted from the study by Li et al [79].

discharge cycles, opening a new frontier in the design of low-cost electrodes. Li et al. [86] prepared NIB anode material consisting of few layered MoS_2-decorated sulfur-doped graphene nanosheets (MoS_2-SG). The MoS_2-SG anode retained the capacities of 619.2 and 265 mA h/g after 100 and 1000 cycles, respectively, at 200 and 1000 mA/g with excellent cycling stability over 1000 cycles at current density of 1.0 A/g. The enhanced cycling stability is contributed to the synergistic coupling effect between MoS_2 and S-doped graphene.

3.3. Water splitting for hydrogen production

Presently, fossil fuel energy resources fulfill the majority of the world's energy demand. However, the excessive use of these fossil fuels contributes to rising global temperature and air pollution. Finding carbon-free alternative energy resources is necessary to mitigate these issues [87–89]. Hydrogen energy is the best alternative solution to fossil fuels because the combustion of hydrogen only produces water as a by-product. This is compared with the

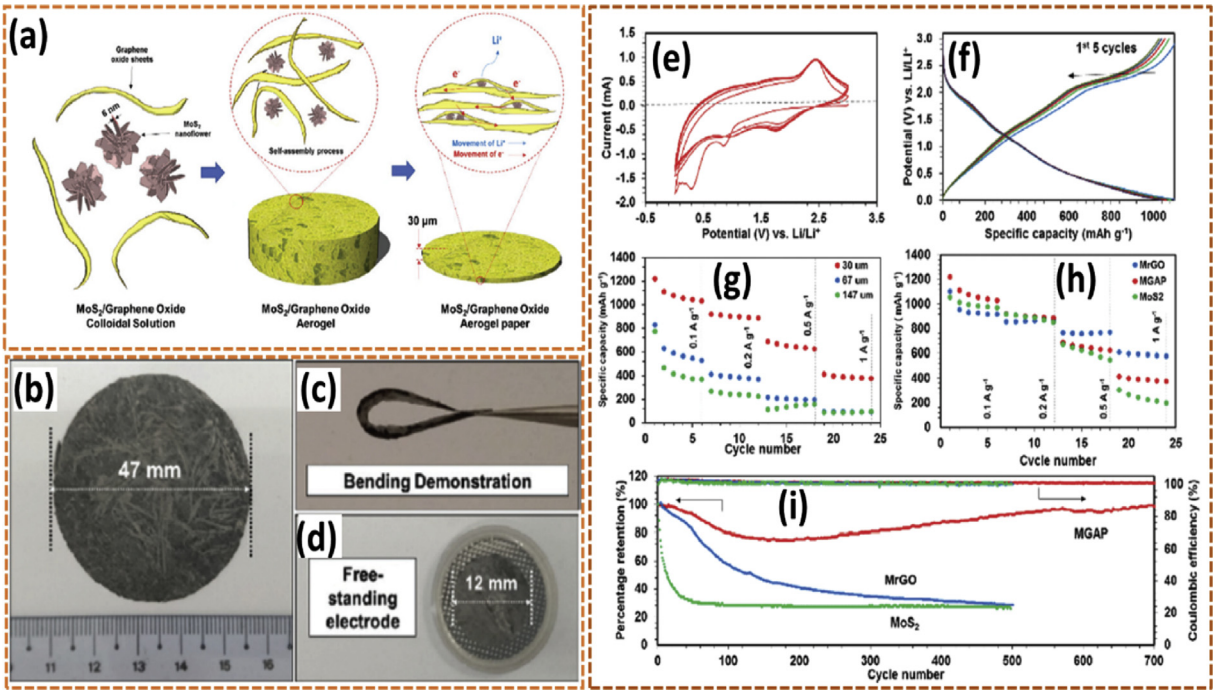

Fig. 5. (a) Schematic diagram to prepare the free-standing MoS_2-graphene aerogel paper electrode, (b) fabricated free-standing MoS_2-graphene aerogel paper electrode, (c) flexibility test for the MoS_2-graphene aerogel paper electrode, (d) 12 mm diameter free-standing electrode used directly for LIB testing. The electrochemical performance for the MoS_2-graphene aerogel paper electrode as an anode for the LIBs. (e) First 5 CV curves of MoS_2-graphene aerogel paper electrode; (f) first 5 galvanostatic charge/discharge profiles of MoS_2-graphene aerogel paper electrode at 0.1 A g−1; (g) specific capacity of MoS_2-graphene aerogel paper electrode (MGAP) with various thicknesses at various current densities; (h) specific capacities of MGAP, MoS_2-graphene oxide powder (MrGO), and pristine MoS_2 at various current densities; and (i) cyclic performance and coulombic efficiency of MGAP, MrGO, and pristine MoS_2 cycled at 0.5 A/g. Adapted from the study by Lee et al [80]. LIBs, lithium-ion batteries.

combustion of fossil fuels, which produce greenhouse gases, and are not suitable for a healthy atmosphere [90,91].

Today, natural gas is used to produce hydrogen *via* steam methane reformation, which emits CO_2. To tackle this issue, hydrogen production *via* water splitting is considered to be one of the most efficient and sustainable approaches. In 1972, for the first time, Honda and Fujishima proposed hydrogen production *via* photoelectrochemical water splitting using a Pt−TiO_2 electrode [92]. Pt and its alloys are still promising catalysts for the hydrogen evolution reaction (HER) because of its excellent electrical conductivity, catalytic activity, and low overpotential [93,94]. Nevertheless, the large-scale application of Pt-based electrodes for HER is hampered by the limited natural availability of Pt and its high cost. This has stimulated a wide number of investigations to find an alternative to Pt electrodes for the water splitting application.

Among these, 2D MoS_2 has been intensively studied for the water splitting application because of its low cost, good chemical stability, and high HER activity [95–97]. However, issues with restacking, low electrical conductivity, and small surface area remain as obstacles. Several efforts to address these deficiencies have been reported in the literature, including heteroatom doping, surface modification, and the preparation of a carbon-based nanocomposite [98–101]. Making a MoS_2-carbon composite has lots of advantages, including a high surface-to-volume ratio, good stability, and fast electron transfer, which boosts HER activity [102,103]. Li et al. [104] prepared MoS_2 quantum dots (MoS_2 QDs)–decorated rGO *via* a facile sonication method, as highly effective electrocatalysts for the HER. Electrochemical measurements showed good HER activity in terms of lower overpotential (64 mV at 10 mA/cm^2) and a Tafel slope as small as 63 mV per decade. The catalytic activity resulted from the zero-dimensional MoS_2 QDs, which have a defect-rich structure, endowing the quantum dots with a multitude of active sites, which can further enhance catalytic activity *via* a synergistic effect with rGO. Electron flow from the current collector to the edges of the MoS_2 occurred because of the high electrical conductivity of the MoS_2 edges.

Deng et al. [105] prepared ultrathin nanosheets composed of MoS_2 perpendicular to rGO (MoS_2-rGO) for the HER application

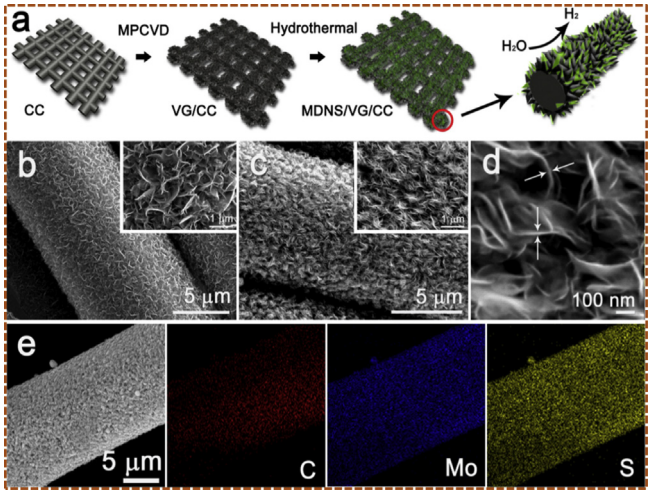

Fig. 6. (a) Schematic illustration of the fabrication of MDNS/VG/CC for the HER application, the low and high-magnified (insets) for the (b) VG/CC, (c, d) few-layers molybdenum disulfide nanosheets supported by vertical graphene on conductive carbon cloth (MDNS/VG/CC), (e) Energy-dispersive X-ray spectroscopy (EDS) mapping for the MDNS/VG/CC composite. Adopted from the study by Zhang et al [106].

using a simple hydrothermal process. The perpendicular morphology of the MoS_2 on rGO enhanced the electron transport through each MoS_2 nanosheets, resulting in an overpotential of 172 mV at 10 mA/cm^2 current density.

Similarly, Zhang et al. [106] reported a MoS_2-graphene composite for the water splitting application. The vertically aligned graphene was prepared on a carbon cloth (CC) substrate *via* microwave plasma enhanced chemical vapor deposition. Then, MoS_2 nanosheets were decorated on the graphene using a hydrothermal process as presented in Fig. 6(a). The composite electrode showed significant HER electrocatalytic activity, including an onset potential of 50 mV, an overpotential of 78 mV at 10 mA/cm^2 (η10), and a Tafel slop of 53 m/dec (Fig. 7). The low overpotential was attributed to the abundant active edges provided by the vertical MoS_2 nanosheets and the effective electron transport route provided by the graphene arrays. In other work, a microwave-assisted synthesis process was used by Cao et al. [107] to prepare MoS_2 nanosheets/rGO with a small Tafel slope of 57 mV/dec and an overpotential of 130 mV at 10 mA/cm^2 current density.

Zhou et al. [108] studied the effect of MoS_2 mass loading on the catalytic performance of a MoS_2-rGO electrode. The mass loading of the redox-active material played an essential role in the catalysis process. The prepared MoS_2-rGO composite electrode contained 94 wt% MoS_2 and 6 wt% rGO. Compared with the baer MoS_2 electrode, the MoS_2-rGO composite had ten-fold higher catalytic activity.

Doping can also change the catalytic activity of the MoS_2 hybrid electrode. Recently, Guo et al. [109] studied the effect of vanadium and nitrogen codoped MoS_2 on rGO for HER application. Doping can expand interlayer spacing, with enhanced defect sites at the edges of the MoS_2 to boost the catalytic activity. As a result, the prepared vanadium and nitrogen codoped MoS_2 on an rGO electrode showed the extremely low overpotential of 68 mV at 10 mA/cm^2 and a Tafel slope of 41 mV/dec.

Li et al. [110] studied the effect of a Cu-doped MoS_2-rGO hybrid for the HER application with a Tafel slope as low as 90 mV/dec. Similarly, Wu et al. [111] reported a manganese (Mn)-doped MoS_2-rGO composite for the HER application. They found that the Mn-doped MoS_2-rGO composite had higher catalytic activity than the MoS_2-rGO and MoS_2 electrodes.

Similar to other applications described in the previous section, nitrogen (N)-doped graphene also plays an essential role in water splitting. Nitrogen doping the graphene can essentially enhance the catalytic activity toward the HER. Recently, Xu et al. [112] demonstrated the HER activity of N-doped rGO (N-rGO)—decorated Ni_3S_4/MoS_2 (Ni_3S_4/MoS_2@N-rGO). The resulting electrode showed a low overpotential of 94 mV and a small Tafel slope of 56 mV/dec in acidic electrolyte. Similarly, Dong et al. [113] prepared a MoS_2-N-rGO composite for the HER application and reported a low overpotential of 112 mV and a small Tafel slope of 44 mV/dec.

4. Summary and outlook

Graphene and its 2D analogs, the inorganic layered metal dichalcogenides, have been widely investigated for various applications in the last few years, owing to their high electrical conductivity, low dimensionality, and high surface area. Among the different 2D materials, graphene, MoS_2 and their hybrids have been particularly emphasized in recent studies on energy-related applications. To date, such studies have demonstrated enormous progress in the preparation of graphene-MoS_2—based hybrids, using various synthesis methods. In the energy storage and

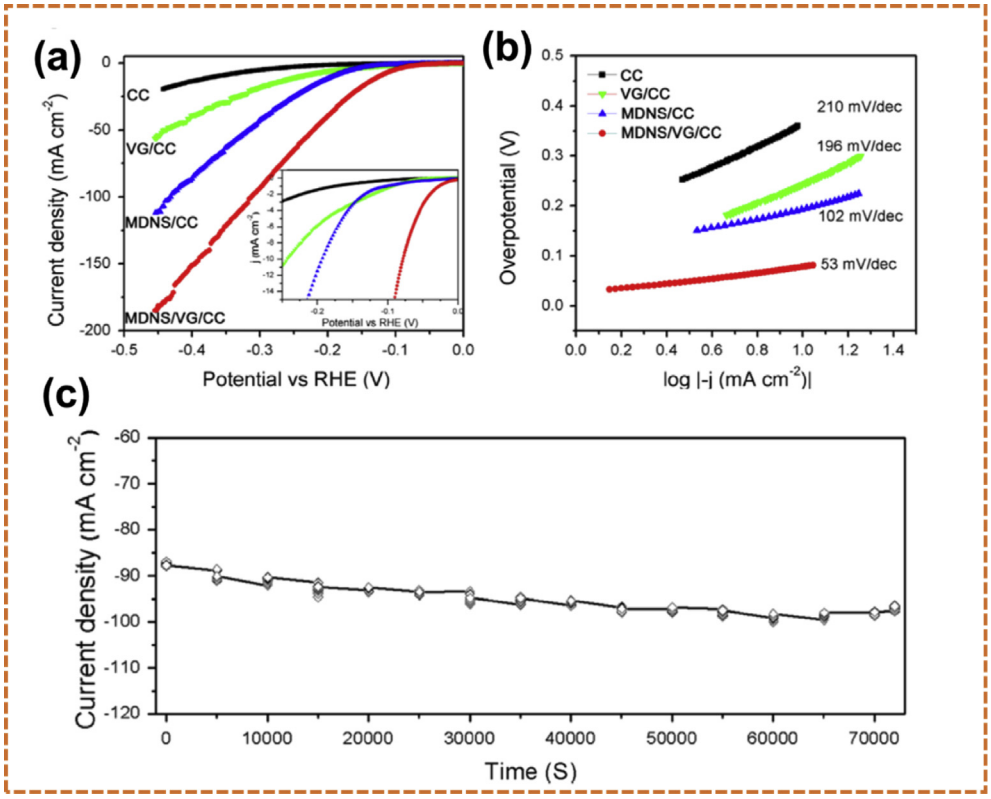

Fig. 7. (a) The polarization curves corresponding (b) Tafel plots for the carbon cloth (CC), vertical graphene/carbon cloth (VG/CC), few-layers molybdenum disulfide nanosheets supported by vertical graphene on conductive carbon cloth (MDNS/VG/CC), MDNS/CC electrodes, (c) the stability for the MDNS/VG/CC at an overpotential of 0.25 V. Adopted from the study by Zhang et al [106].

generation field, graphene-MoS_2 hybrids have shown tremendous potential because of their higher electrical conductivity, layered structure merged with larger interlayer spacing, which allows facial electrolyte penetration. Moreover, the combination of different electrode materials in a single system has been demonstrated to be beneficial as an approach to avoid the individual issues of graphene and MoS_2. Many encouraging concepts and results have recently been reported for energy storage applications using graphene-MoS_2 hybrids. However, issues remain which must be solved.

A large number of synthesis processes, such as CVDs, wet chemical methods, liquid exfoliations, ion intercalation and exfoliations, hydrothermal treatments, and liquid exfoliation, have been used to prepare the graphene-MoS_2 hybrids for various applications. Regardless of the synthesis routes, the controlled synthesis of the 2D materials is quite essential to maintain their physical and chemical features. For example, the conductivity of the 2D materials is prominently depending upon the number of stacked layers. In addition to this, the mass production of the 2D materials with controlled number of their layers is crucial for their real-life applications. Therefore, it is essential to have appropriate fabrication technology to tune and control the number of layers. In addition to this, developing the green, easy, and ecofriendly synthesis approach is required to prevent pollution.

The surface energy, redox activity, and conductivity of the electrode materials are the very essential parameters for their energy-related application. The lower surface energy and the redox activity of the 2D graphene-based materials can be enhanced by doping some heteroatoms or by reacting with other materials to form heterostructures. For example, nitrogen-doped graphene has been used in nearly every energy-related field, providing considerable improvements in energy storage devices. In addition to this, synthesizing new form of the graphene, such as edge-free graphene, holey graphene, 3D graphene, graphene aerogel and so on, is beneficial to improve the electrochemical performance of electrochemical cells. In the energy storage and water splitting fields, overall electrochemical performance depends on the physical and electrochemical properties of the electrode materials. This makes it essential to understand the energy storing mechanism of the graphene and MoS_2-based hybrids *via* advanced *in-situ* microscopic and spectroscopic techniques. Moreover, standardized methods should be developed to report the electrochemical parameters to avoid any kind of confusion. Furthermore, most of the time the electrochemical parameters for the energy storage devices are reported in the literatures with low active mass loading (~1 mg/cm^2). However, it is misleading to take advantage of the high capacity by low active material mass loading to compare with the commercial devices, which generally have a high mass loading on the order of ~10 mg/cm^2. Reporting the electrochemical parameters for high mass-loaded electrodes are essentially required for their practical applications. The lower electrochemical cycling stability is another obstacle for the graphene/MoS_2—based electrodes that needs to be overcomed.

Finally, great progress in the development of graphene-MoS_2 hybrids has been evident in recent years in energy fields, making them some of the most attractive electrode materials. However, 'the job' is still not yet complete: there is still plenty of room to further enhance their electrochemical performance. Such results are anticipated in the near future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] N.A. Kumar, M.A. Dar, R. Gul, Jong-Beom Baek, Graphene and molybdenum disulphide hybrids: synthesis and applications, Mater. Today 18 (2015) 1369–7021, https://doi.org/10.1016/j.mattod.2015.01.016.
[2] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, Carbon 45 (2007) 1558–1565, https://doi.org/10.1016/j.carbon.2007.02.034.
[3] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, Graphene and graphene oxide: synthesis, properties, and applications, Adv. Mater. 22 (2010) 3906–3924, https://doi.org/10.1002/adma.201001068.
[4] M.D. Stoller, S. Park, Y. Zhu, J. An, R.S. Ruoff, Graphene-based ultracapacitors, Nano Lett. 8 (2008) 3498–3502, https://doi.org/10.1021/nl802558y.
[5] Si-Hwa Lee, V. Sridhar, Jung-Hwan Jung, K. Karthikeyan, Yun-Sung Lee, R. Mukherjee, N. Koratkar, Il-Kwon Oh, Graphene-Nanotube-iron hierarchical nanostructure as lithium ion battery anode, ACS Nano 7 (5) (2013) 4242–4251, https://doi.org/10.1021/nn4007253.
[6] X. Li, L. Zhi, Graphene hybridization for energy storage applications, Chem. Soc. Rev. 47 (2018) 3189–3216, https://doi.org/10.1039/C7CS00871F.
[7] Y. Jung, J. Shen, Y. Sun, J.J. Cha, Chemically synthesized heterostructures of two-dimensional molybdenum/tungsten-based dichalcogenides with vertically aligned layers, ACS Nano 8 (9) (2014) 9550–9557, https://doi.org/10.1021/nn503853a.
[8] J.R. Brent, N. Savjani, P. O'Brien, Synthetic approaches to two-dimensional transition metal dichalcogenide nanosheets, Prog. Mater. Sci. 89 (2017) 411–478, https://doi.org/10.1016/j.pmatsci.2017.06.002.
[9] R. Kumar, S. Sahoo, E. Joanni, R.K. Singh, R.M. Yadav, R.K. Verma, D.P. Singh, W.K. Tan, A. Pérez del Pino, S.A. Moshkalev, A. Matsuda, A review on synthesis of graphene, h-BN and MoS_2 for energy storage applications: recent progress and perspectives, Nano Res. 12 (2019) 35–37, https://doi.org/10.1007/s12274-019-2467-8.
[10] D. Sarkar, D. Das, S. Das, A. Kumar, S. Patil, K. Nanda, D.D. Sarma, A. Shukla, Expanding interlayer spacing in MoS_2 for realizing an advanced supercapacitor, ACS Energy Lett. 4 (7) (2019) 1602–1609, https://doi.org/10.1021/acsenergylett.9b00983.
[11] Y. Huang, J. Guo, Y. Kang, Y. Ai, C.M. Li, Two dimensional atomically thin MoS_2 nanosheets and their sensing applications, Nanoscale 7 (2015) 19358–19376, https://doi.org/10.1039/C5NR06144J.
[12] G. Li, D. Zhang, Q. Qiao, Y. Yu, D. Peterson, A. Zafar, R. Kumar, S. Curtarolo, F. Hunte, S. Shannon, Y. Zhu, W. Yang, L. Cao, All the catalytic active sites of MoS_2 for hydrogen evolution, J. Am. Chem. Soc. 138 (2016) 16632–16638, https://doi.org/10.1021/jacs.6b05940.
[13] A. Paravannoor, A. Babu, MoS_2/Graphene nanocomposites for efficient electrochemical energy storage - a novel strategy based on electrolyte formulation, Surfaces and Interfaces 14 (2019) 256–261, https://doi.org/10.1016/j.surfin.2018.11.006.
[14] D. Sarmah, A. Kumar, Layer-by-layer self-assembly of ternary MoS_2 -rGO@ PPyNTs nanocomposites for high performance supercapacitor electrode, Synth. Met. 243 (2018) 75–89, https://doi.org/10.1016/j.synthmet.2018.06.001.
[15] J. Xiao, D. Choi, L. Cosimbescu, P. Koech, J. Liu, J.P. Lemmon, Exfoliated MoS_2 nanocomposite as an anode material for lithium ion batteries, Chem. Mater. 22 (2010) 4522–4524, https://doi.org/10.1021/cm101254j.
[16] Y. Jiao, A. Mukhopadhyay, Y. Ma, L. Yang, A.M. Hafez, H. Zhu, Ion transport nanotube Assembled with vertically aligned metallic MoS 2 for high rate lithium-ion batteries, Adv. Energy Mater. 8 (2018) 1702779, https://doi.org/10.1002/aenm.201702779.
[17] P.D. Tran, M. Nguyen, S.S. Pramana, A. Bhattacharjee, S.Y. Chiam, J. Fize, M.J. Field, V. Artero, L.H. Wong, J. Loo, J. Barber, Copper molybdenum sulfide: a new efficient electrocatalyst for hydrogen production from water, Energy Environ. Sci. 5 (2012) 8912, https://doi.org/10.1039/c2ee22611a.
[18] D. Merki, X. Hu, Recent developments of molybdenum and tungsten sulfides as hydrogen evolution catalysts, Energy Environ. Sci. 4 (2011) 3878, https://doi.org/10.1039/c1ee01970h.
[19] X. Geng, Y. Zhang, Y. Han, J. Li, L. Yang, M. Benamara, L. Chen, H. Zhu, Two-dimensional water-coupled metallic MoS 2 with nanochannels for ultrafast

supercapacitors, Nano Lett. 17 (2017) 1825–1832, https://doi.org/10.1021/acs.nanolett.6b05134.
[20] K. Lee, H.-Y. Kim, M. Lotya, J.N. Coleman, G.-T. Kim, G.S. Duesberg, Electrical characteristics of molybdenum disulfide flakes produced by liquid exfoliation, Adv. Mater. 23 (2011) 4178–4182, https://doi.org/10.1002/adma.201101013.
[21] X.-Y. Yu, H. Hu, Y. Wang, H. Chen, X.W.D. Lou, Ultrathin MoS 2 nanosheets supported on N-doped carbon nanoboxes with enhanced lithium storage and electrocatalytic properties, Angew. Chem. Int. Ed. 54 (2015) 7395–7398, https://doi.org/10.1002/anie.201502117.
[22] X.-Y. Yu, Y. Feng, Y. Jeon, B. Guan, X.W.D. Lou, U. Paik, formation of Ni-Co-MoS 2 nanoboxes with enhanced electrocatalytic activity for hydrogen evolution, Adv. Mater. 28 (2016) 9006–9011, https://doi.org/10.1002/adma.201601188.
[23] X. Geng, Y. Jiao, Y. Han, A. Mukhopadhyay, L. Yang, H. Zhu, Freestanding metallic 1T MoS 2 with dual ion diffusion paths as high rate anode for sodium-ion batteries, Adv. Funct. Mater. 27 (2017) 1702998, https://doi.org/10.1002/adfm.201702998.
[24] Y. Wang, J. Zeng, J. Li, X. Cui, A.M. Al-Enizi, L. Zhang, G. Zheng, One-dimensional nanostructures for flexible supercapacitors, J. Mater. Chem. 3 (2015) 16382–16392, https://doi.org/10.1039/C5TA03467A.
[25] S. Yang, K. Zhang, C. Wang, Y. Zhang, S. Chen, C. Wu, A. Vasileff, S.-Z. Qiao, L. Song, Hierarchical 1T-MoS 2 nanotubular structures for enhanced supercapacitive performance, J. Mater. Chem. 5 (2017) 23704–23711, https://doi.org/10.1039/C7TA08115D.
[26] Y. Wang, Y. Wu, Y. Huang, F. Zhang, X. Yang, Y. Ma, Y. Chen, Preventing graphene sheets from restacking for high-capacitance performance, J. Phys. Chem. C 115 (2011) 23192–23197, https://doi.org/10.1021/jp206444e.
[27] D.P. Dubal, O. Ayyad, V. Ruiz, P. Gómez-Romero, Hybrid energy storage: the merging of battery and supercapacitor chemistries, Chem. Soc. Rev. 44 (2015) 1777–1790, https://doi.org/10.1039/C4CS00266K.
[28] Y. Deng, L. Ding, Q. Liu, L. Zhan, Y. Wang, S. Yang, Two-dimensional MoS_2-graphene hybrid nanosheets for high gravimetric and volumetric lithium storage, Appl. Surf. Sci. 437 (2018) 384–389, https://doi.org/10.1016/j.apsusc.2017.12.020.
[29] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, Single-layer MoS_2 transistors, Nat. Nanotechnol. 6 (2011) 147–150, https://doi.org/10.1038/nnano.2010.279.
[30] Z. Wang, B. Mi, Environmental applications of 2D molybdenum disulfide (MoS 2) nanosheets, Environ. Sci. Technol. 51 (2017) 8229–8244, https://doi.org/10.1021/acs.est.7b01466.
[31] L. David, R. Bhandavat, G. Singh, MoS 2/graphene composite paper for sodium-ion battery electrodes, ACS Nano 8 (2014) 1759–1770, https://doi.org/10.1021/nn406156b.
[32] M. Velický, P.S. Toth, From two-dimensional materials to their heterostructures: an electrochemist's perspective, Appl. Mater. Today 8 (2017) 68–103, https://doi.org/10.1016/j.apmt.2017.05.003.
[33] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S.K. Banerjee, L. Colombo, R.S. Ruoff, Large-area synthesis of high-quality and uniform graphene films on copper foils, Science 324 (2009) 1312–1314, https://doi.org/10.1126/science.1171245.
[34] K.-K. Liu, W. Zhang, Y.-H. Lee, Y.-C. Lin, M.-T. Chang, C.-Y. Su, C.-S. Chang, H. Li, Y. Shi, H. Zhang, C.-S. Lai, L.-J. Li, Growth of large-area and highly crystalline MoS 2 thin layers on insulating substrates, Nano Lett. 12 (2012) 1538–1544, https://doi.org/10.1021/nl2043612.
[35] Y. Zhan, Z. Liu, S. Najmaei, P.M. Ajayan, J. Lou, Large-area vapor-phase growth and characterization of MoS 2 atomic layers on a SiO 2 substrate, Small 8 (2012) 966–971, https://doi.org/10.1002/smll.201102654.
[36] C. Zhi, Y. Bando, C. Tang, H. Kuwahara, D. Golberg, Large-scale fabrication of boron nitride nanosheets and their utilization in polymeric composites with improved thermal and mechanical properties, Adv. Mater. 21 (2009) 2889–2893, https://doi.org/10.1002/adma.200900323.
[37] J.N. Coleman, M. Lotya, A. O'Neill, S.D. Bergin, P.J. King, U. Khan, K. Young, A. Gaucher, S. De, R.J. Smith, I.V. Shvets, S.K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G.T. Kim, G.S. Duesberg, T. Hallam, J.J. Boland, J.J. Wang, J.F. Donegan, J.C. Grunlan, G. Moriarty, A. Shmeliov, R.J. Nicholls, J.M. Perkins, E.M. Grieveson, K. Theuwissen, D.W. McComb, P.D. Nellist, V. Nicolosi, Two-dimensional nanosheets produced by liquid exfoliation of layered materials, Science 331 (2011) 568–571, https://doi.org/10.1126/science.1194975.
[38] H.S.S. Ramakrishna Matte, A. Gomathi, A.K. Manna, D.J. Late, R. Datta, S.K. Pati, C.N.R. Rao, MoS_2 and WS2 analogues of graphene, Angew. Chem. Int. Ed. 49 (2010) 4059–4062, https://doi.org/10.1002/anie.201000009.
[39] Q. Hu, J. Liao, X. He, S. Wang, L. Xiao, X. Ding, C.-H. Chen, In situ catalytic formation of graphene-like graphitic layer decoration on Na 3 V 2−x Ga x (PO 4) 3 ($0 \leq x \leq 0.6$) for ultrafast and high energy sodium storage, J. Mater. Chem. (2019) 20–23, https://doi.org/10.1039/C8TA11890F.
[40] X. Zhang, M. Zhang, Y. Tian, J. You, C. Yang, J. Su, Y. Li, Y. Gao, H. Gu, In situ synthesis of MoS 2/graphene nanosheets as free-standing and flexible electrode paper for high-efficiency hydrogen evolution reaction, RSC Adv. 8 (2018) 10698–10705, https://doi.org/10.1039/C8RA01226A.
[41] D.P. Dubal, N.R. Chodankar, D.-H. Kim, P. Gomez-Romero, Towards flexible solid-state supercapacitors for smart and wearable electronics, Chem. Soc. Rev. 47 (2018) 2065–2129, https://doi.org/10.1039/C7CS00505A.
[42] N.R. Chodankar, I.V. Bagal, Sang-Wan Ryu, Do-Heyoung Kim, Hybrid material passivation approach to stabilize the silicon nanowires in aqueous electrolyte for high-energy efficient supercapacitor, Chem. Eng. J. 362 (2019) 609.
[43] D.P. Dubal, S. Abdel-Azeim, N.R. Chodankar, Y.-K. Han, Molybdenum nitride nanocrystals anchored on phosphorus-incorporated carbon fabric as a negative electrode for high-performance asymmetric pseudocapacitor, IScience 16 (2019) 50–62, https://doi.org/10.1016/j.isci.2019.05.018.
[44] S. Shyamal, P. Hajra, H. Mandal, A. Bera, D. Sariket, A.K. Satpati, M.V. Malashchonak, A.V. Mazanik, O.V. Korolik, A.I. Kulak, E.V. Skorb, A. Maity, E.A. Streltsov, C. Bhattacharya, Eu modified Cu2O thin films: significant enhancement in efficiency of photoelectrochemical processes through suppression of charge carrier recombination, Chem. Eng. J. 335 (2018) 676–684, https://doi.org/10.1016/j.cej.2017.11.004.
[45] K. Jayaramulu, D.P. Dubal, B. Nagar, V. Ranc, O. Tomanec, M. Petr, K.K.R. Datta, R. Zboril, P. Gómez-Romero, R.A. Fischer, Ultrathin hierarchical porous carbon nanosheets for high-performance supercapacitors and redox electrolyte energy storage, Adv. Mater. 30 (2018) 1705789, https://doi.org/10.1002/adma.201705789.
[46] M. Sevilla, R. Mokaya, Energy storage applications of activated carbons: supercapacitors and hydrogen storage, Energy Environ. Sci. 7 (2014) 1250–1280, https://doi.org/10.1039/C3EE43525C.
[47] T. Liu, F. Zhang, Y. Song, Y. Li, Revitalizing carbon supercapacitor electrodes with hierarchical porous structures, J. Mater. Chem. 5 (2017) 17705–17733, https://doi.org/10.1039/C7TA05646J.
[48] D.P. Dubal, N.R. Chodankar, Z. Caban-Huertas, F. Wolfart, M. Vidotti, R. Holze, C.D. Lokhande, P. Gomez-Romero, Synthetic approach from polypyrrole nanotubes to nitrogen doped pyrolyzed carbon nanotubes for asymmetric supercapacitors, J. Power Sources 308 (2016) 158–165, https://doi.org/10.1016/j.jpowsour.2016.01.074.
[49] D.P. Dubal, G.S. Gund, C.D. Lokhande, R. Holze, Decoration of spongelike Ni(OH) 2 nanoparticles onto MWCNTs using an easily manipulated chemical protocol for supercapacitors, ACS Appl. Mater. Interfaces 5 (2013) 2446–2454, https://doi.org/10.1021/am3026486.
[50] G. Yu, L. Hu, N. Liu, H. Wang, M. Vosgueritchian, Y. Yang, Y. Cui, Z. Bao, Enhancing the supercapacitor performance of graphene/MnO 2 nanostructured electrodes by conductive wrapping, Nano Lett. 11 (2011) 4438–4442, https://doi.org/10.1021/nl2026635.
[51] L. Li, Z.A. Hu, N. An, Y.Y. Yang, Z.M. Li, H.Y. Wu, Facile synthesis of MnO 2/CNTs composite for supercapacitor electrodes with long cycle stability, J. Phys. Chem. C 118 (2014) 22865–22872, https://doi.org/10.1021/jp505744p.
[52] C.D. Lokhande, D.P. Dubal, O.-S. Joo, Metal oxide thin film based supercapacitors, Curr. Appl. Phys. 11 (2011) 255–270, https://doi.org/10.1016/j.cap.2010.12.001.
[53] F. Zhang, Y. Tang, H. Liu, H. Ji, C. Jiang, J. Zhang, X. Zhang, C.-S. Lee, Uniform incorporation of flocculent molybdenum disulfide nanostructure into three-dimensional porous graphene as an anode for high-performance lithium ion batteries and hybrid supercapacitors, ACS Appl. Mater. Interfaces 8 (2016) 4691–4699, https://doi.org/10.1021/acsami.5b11705.
[54] N.R. Chodankar, D.P. Dubal, S.J. Patil, G.S. Rama Raju, S.V. Karekar, Y.S. Huh, Y.-K. Han, Ni2P2O7 micro-sheets supported ultra-thin MnO2 nanoflakes: a promising positive electrode for stable solid-state hybrid supercapacitor, Electrochim. Acta 319 (2019) 435–443, https://doi.org/10.1016/j.electacta.2019.06.166.
[55] C. Sha, B. Lu, H. Mao, J. Cheng, X. Pan, J. Lu, Z. Ye, 3D ternary nanocomposites of molybdenum disulfide/polyaniline/reduced graphene oxide aerogel for high performance supercapacitors, Carbon 99 (2016) 26–34, https://doi.org/10.1016/j.carbon.2015.11.066.
[56] M. Saraf, K. Natarajan, S.M. Mobin, Emerging robust heterostructure of MoS 2 −rGO for high-performance supercapacitors, ACS Appl. Mater. Interfaces 10 (2018) 16588–16595, https://doi.org/10.1021/acsami.8b04540.
[57] B. Xie, Y. Chen, M. Yu, T. Sun, L. Lu, T. Xie, Y. Zhang, Y. Wu, Hydrothermal synthesis of layered molybdenum sulfide/N-doped graphene hybrid with enhanced supercapacitor performance, Carbon 99 (2016) 35–42, https://doi.org/10.1016/j.carbon.2015.11.077.
[58] R. Thangappan, S. Kalaiselvam, A. Elayaperumal, R. Jayavel, M. Arivanandhan, R. Karthikeyan, Y. Hayakawa, Graphene decorated with MoS 2 nanosheets: a synergetic energy storage composite electrode for supercapacitor applications, Dalton Trans. 45 (2016) 2637–2646, https://doi.org/10.1039/C5DT04832J.
[59] S.P. Jose, C.S. Tiwary, S. Kosolwattana, P. Raghavan, L.D. Machado, C. Gautam, T. Prasankumar, J. Joyner, S. Ozden, D.S. Galvao, P.M. Ajayan, Enhanced supercapacitor performance of a 3D architecture tailored using atomically thin rGO–MoS 2 2D sheets, RSC Adv. 6 (2016) 93384–93393, https://doi.org/10.1039/C6RA20960B.
[60] W. Xiao, W. Zhou, T. Feng, Y. Zhang, H. Liu, L. Tian, Simple synthesis of molybdenum disulfide/reduced graphene oxide composite hollow microspheres as supercapacitor electrode material, Materials 9 (2016) 783, https://doi.org/10.3390/ma9090783.
[61] S. Dutta, S. De, MoS 2 nanosheet/rGO hybrid: an electrode material for high performance thin film supercapacitor, Mater. Today Proc. 5 (2018) 9771–9775, https://doi.org/10.1016/j.matpr.2017.10.165.
[62] Q. Liu, A. Gao, Y. Huang, F. Yi, H. Cheng, S. Zhao, H. Chen, R. Zeng, Z. Sun, D. Shu, X. Song, 3D sandwiched nanosheet of MoS_2/C@RGO achieved by supramolecular self-assembly method as high performance material in

supercapacitor, J. Alloy. Comp. 777 (2019) 1176–1183, https://doi.org/10.1016/j.jallcom.2018.11.108.
[63] R. Wang, S. Wang, D. Jin, Y. Zhanga, Y. Caia, J. Mab, L. Zhang, Engineering layer structure of MoS2-graphene composites with robust and fast lithium storage for high-performance Li-ion capacitors, Energy Storage Mater. 9 (2017) 195–205, https://doi.org/10.1016/j.ensm.2017.07.013.
[64] C. Zhan, W. Liu, M. Hu, Q. Liang, X. Yu, Y. Shen, R. Lv, F. Kang, Z. Huang, High-performance sodium-ion hybrid capacitors based on an interlayerexpanded MoS_2/rGO composite: surpassing the performance of lithium-ion capacitors in a uniform system, NPG Asia Mater. 10 (2018) 775–787, https://doi.org/10.1038/s41427-018-0073-y.
[65] K. Ramakrishnan, C. Nithya, R. Karvembu, Heterostructure of two different 2D materials based on MoS2 nanoflowers@rGO: an electrode material for sodium-ion capacitors, Nanoscale Adv. 1 (2019) 334–341, https://doi.org/10.1039/c8na00104a.
[66] J.-M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, in: Materials for Sustainable Energy, Co-Published with Macmillan Publishers Ltd, UK, 2010, pp. 171–179, https://doi.org/10.1142/9789814317665_0024.
[67] H. Li, Z. Wang, L. Chen, X. Huang, Research on advanced materials for Li-ion batteries, Adv. Mater. 21 (2009) 4593–4607, https://doi.org/10.1002/adma.200901710.
[68] J.B. Goodenough, Y. Kim, Challenges for rechargeable Li batteries †, Chem. Mater. 22 (2010) 587–603, https://doi.org/10.1021/cm901452z.
[69] R. Tian, Y. Zhang, Z. Chen, H. Duan, B. Xu, Y. Guo, H. Kang, H. Li, H. Liu, The effect of annealing on a 3D SnO2/graphene foam as an advanced lithium-ion battery anode, Sci. Rep. 6 (2016) 19195, https://doi.org/10.1038/srep19195.
[70] R. Wang, C. Xu, M. Du, J. Sun, L. Gao, P. Zhang, H. Yao, C. Lin, Solvothermal-induced self-assembly of Fe 2 O 3/GS aerogels for high Li-storage and excellent stability, Small 10 (2014) 2260–2269, https://doi.org/10.1002/smll.201303371.
[71] H. Duan, J. Gnanaraj, X. Chen, B. Li, J. Liang, Fabrication and characterization of Fe3O4-based Cu nanostructured electrode for Li-ion battery, J. Power Sources 185 (2008) 512–518, https://doi.org/10.1016/j.jpowsour.2008.06.078.
[72] Y. Sun, J. Wang, B. Zhao, R. Cai, R. Ran, Z. Shao, Binder-free α-MoO3 nanobelt electrode for lithium-ion batteries utilizing van der Waals forces for film formation and connection with current collector, J. Mater. Chem. 1 (2013) 4736, https://doi.org/10.1039/c3ta01285a.
[73] P. Wu, H. Wang, Y. Tang, Y. Zhou, T. Lu, Three-dimensional interconnected network of graphene-wrapped porous silicon spheres: in situ magnesiothermic-reduction synthesis and enhanced lithium-storage capabilities, ACS Appl. Mater. Interfaces 6 (2014) 3546–3552, https://doi.org/10.1021/am405725u.
[74] W.-J. Zhang, A review of the electrochemical performance of alloy anodes for lithium-ion batteries, J. Power Sources 196 (2011) 13–24, https://doi.org/10.1016/j.jpowsour.2010.07.020.
[75] X. Hu, W. Zhang, X. Liu, Y. Mei, Y. Huang, Nanostructured Mo-based electrode materials for electrochemical energy storage, Chem. Soc. Rev. 44 (2015) 2376–2404, https://doi.org/10.1039/C4CS00350K.
[76] C.N.R. Rao, H.S.S. Ramakrishna Matte, U. Maitra, Graphene analogues of inorganic layered materials, Angew. Chem. Int. Ed. 52 (2013) 13162–13185, https://doi.org/10.1002/anie.201301548.
[77] R. Tian, W. Wang, Y. Huang, H. Duan, Y. Guo, H. Kang, H. Li, H. Liu, 3D composites of layered MoS 2 and graphene nanoribbons for high performance lithium-ion battery anodes, J. Mater. Chem. 4 (2016) 13148–13154, https://doi.org/10.1039/C6TA04331C.
[78] H. Xue, J. Wang, S. Wang, S. Muhammad, C. Feng, Q. Wu, H. Li, D. Shi, Q. Jiao, Y. Zhao, Core–shell MoS 2 @graphene composite microspheres as stable anodes for Li-ion batteries, New J. Chem. 42 (2018) 15340–15345, https://doi.org/10.1039/C8NJ01100A.
[79] S. Li, P. Liu, X. Huang, Y. Tang, H. Wang, Reviving bulky MoS 2 as an advanced anode for lithium-ion batteries, J. Mater. Chem. 7 (2019) 10988–10997, https://doi.org/10.1039/C9TA01089K.
[80] W.S.V. Lee, E. Peng, T.A.J. Loh, X. Huang, J.M. Xue, Few-layer MoS 2 -anchored graphene aerogel paper for free-standing electrode materials, Nanoscale 8 (2016) 8042–8047, https://doi.org/10.1039/C6NR00340K.
[81] Y.-Z. Wang, X.-Y. Shan, D.-W. Wang, Z.-H. Sun, H.-M. Cheng, F. Li, A rechargeable quasi-symmetrical MoS_2 battery, Joule 2 (2018) 1278–1286, https://doi.org/10.1016/j.joule.2018.04.007.
[82] L. Li, Y. Zheng, S. Zhang, J. Yang, Z. Shao, Z. Guo, Recent progress on sodium ion batteries: potential high-performance anodes, Energy Environ. Sci. 11 (2018) 2310–2340, https://doi.org/10.1039/c8ee01023d.
[83] J. Li, H. Wang, W. Wei, L. Meng, Advanced MoS 2 and graphene heterostructures as high-performance anode for sodium-ion batteries, Nanotechnology 30 (2019) 104003, https://doi.org/10.1088/1361-6528/aaf76c.
[84] E. Brown, P. Yan, H. Tekik, A. Elangovan, J. Wang, D. Lin, J. Li, 3D printing of hybrid MoS_2-graphene aerogels as highly porous electrode materials for sodium ion battery anodes, Mater. Des. 170 (2019) 107689, https://doi.org/10.1016/j.matdes.2019.107689.
[85] T. Wang, X. Shen, J. Huang, Q. Xi, Y. Zhao, Q. Guo, X. Wang, Z. Xu, Tulip-like MoS 2 with a single sheet tapered structure anchored on N-doped graphene substrates via C–O–Mo bonds for superior sodium storage, J. Mater. Chem. 6 (2018) 24433–24440, https://doi.org/10.1039/C8TA09221D.
[86] G. Li, D. Luo, X. Wang, M.H. Seo, S. Hemmati, A. Yu, Z. Chen, Enhanced reversible sodium-ion intercalation by synergistic coupling of few-layered MoS_2 and S-doped graphene, Adv. Funct. Mater. 27 (2017) 1702562–1702570, https://doi.org/10.1002/adfm.201702562.
[87] H. Wang, D. Tran, J. Qian, F. Ding, D. Losic, MoS2/Graphene composites as promising materials for energy storage and conversion applications, Adv. Mater. Interfaces 6 (2019) 1900915–1900938, https://doi.org/10.1002/admi.201900915.
[88] R. Kumar, S. Sahoo, E. Joanni, R. Singh, R. Yadav, R. Kumar, D.P. Singh, W.K. Tan, A. Pérez del Pino, S.A. Moshkalev, A. Matsuda, Nano Res 12 (11) (2019) 2655–2694, https://doi.org/10.1007/s12274-019-2467-8.
[89] Y. Gong, Z. Xu, H. Pan, Y. Lin, Z. Yang, X. Du, Hierarchical Ni 3 S 2 nanosheets coated on Co 3 O 4 nanoneedle arrays on 3D nickel foam as an efficient electrocatalyst for the oxygen evolution reaction, J. Mater. Chem. 6 (2018) 5098–5106, https://doi.org/10.1039/C7TA11104E.
[90] J.A. Turner, Sustainable hydrogen production, Science 305 (2004) 972–974, https://doi.org/10.1126/science.1103197.
[91] M.G. Walter, E.L. Warren, J.R. McKone, S.W. Boettcher, Q. Mi, E.A. Santori, N.S. Lewis, Solar water splitting cells, Chem. Rev. 110 (2010) 6446–6473, https://doi.org/10.1021/cr1002326.
[92] Y.-J. Yuan, D. Chen, J. Zhong, L.-X. Yang, J. Wang, M.-J. Liu, W.-G. Tu, Z.-T. Yu, Z.-G. Zou, Interface engineering of a noble-metal-free 2D–2D MoS 2/Cu-ZnIn 2 S 4 photocatalyst for enhanced photocatalytic H 2 production, J. Mater. Chem. 5 (2017) 15771–15779, https://doi.org/10.1039/C7TA04410K.
[93] E.J. Popczun, C.G. Read, C.W. Roske, N.S. Lewis, R.E. Schaak, Highly active electrocatalysis of the hydrogen evolution reaction by cobalt phosphide nanoparticles, Angew. Chem. Int. Ed. 53 (2014) 5427–5430, https://doi.org/10.1002/anie.201402646.
[94] J.-F. Lin, O. Pitkänen, J. Mäklin, R. Puskas, A. Kukovecz, A. Dombovari, G. Toth, K. Kordas, Synthesis of tungsten carbide and tungsten disulfide on vertically aligned multi-walled carbon nanotube forests and their application as non-Pt electrocatalysts for the hydrogen evolution reaction, J. Mater. Chem. 3 (2015) 14609–14616, https://doi.org/10.1039/C5TA02908B.
[95] S. Zhang, B.V.R. Chowdari, Z. Wen, J. Jin, J. Yang, Constructing highly oriented configuration by few-layer MoS 2 : toward high-performance lithium-ion batteries and hydrogen evolution reactions, ACS Nano 9 (2015) 12464–12472, https://doi.org/10.1021/acsnano.5b05891.
[96] N. Zhang, S. Gan, T. Wu, W. Ma, D. Han, L. Niu, Growth control of MoS 2 nanosheets on carbon cloth for maximum active edges exposed: an excellent hydrogen evolution 3D cathode, ACS Appl. Mater. Interfaces 7 (2015) 12193–12202, https://doi.org/10.1021/acsami.5b02586.
[97] F. Li, J. Li, X. Lin, X. Li, Y. Fang, L. Jiao, X. An, Y. Fu, J. Jin, R. Li, Designed synthesis of multi-walled carbon nanotubes@Cu@MoS_2 hybrid as advanced electrocatalyst for highly efficient hydrogen evolution reaction, J. Power Sources 300 (2015) 301–308, https://doi.org/10.1016/j.jpowsour.2015.09.084.
[98] Y. Zhao, X. Xie, J. Zhang, H. Liu, H.-J. Ahn, K. Sun, G. Wang, MoS 2 nanosheets supported on 3D graphene aerogel as a highly efficient catalyst for hydrogen evolution, Chem. Eur J. 21 (2015) 15908–15913, https://doi.org/10.1002/chem.201501964.
[99] C. Tsai, F. Abild-Pedersen, J.K. Nørskov, Tuning the MoS 2 edge-site activity for hydrogen evolution via support interactions, Nano Lett. 14 (2014) 1381–1387, https://doi.org/10.1021/nl404444k.
[100] M.A. Lukowski, A.S. Daniel, F. Meng, A. Forticaux, L. Li, S. Jin, Enhanced hydrogen evolution catalysis from chemically exfoliated metallic MoS 2 nanosheets, J. Am. Chem. Soc. 135 (2013) 10274–10277, https://doi.org/10.1021/ja404523s.
[101] J. Deng, H. Li, J. Xiao, Y. Tu, D. Deng, H. Yang, H. Tian, J. Li, P. Ren, X. Bao, Triggering the electrocatalytic hydrogen evolution activity of the inert two-dimensional MoS 2 surface via single-atom metal doping, Energy Environ. Sci. 8 (2015) 1594–1601, https://doi.org/10.1039/C5EE00751H.
[102] L. Liao, J. Zhu, X. Bian, L. Zhu, M.D. Scanlon, H.H. Girault, B. Liu, MoS 2 formed on mesoporous graphene as a highly active catalyst for hydrogen evolution, Adv. Funct. Mater. 23 (2013) 5326–5333, https://doi.org/10.1002/adfm.201300318.
[103] D.J. Li, U.N. Maiti, J. Lim, D.S. Choi, W.J. Lee, Y. Oh, G.Y. Lee, S.O. Kim, Molybdenum sulfide/N-doped CNT forest hybrid catalysts for high-performance hydrogen evolution reaction, Nano Lett. 14 (2014) 1228–1233, https://doi.org/10.1021/nl404108a.
[104] F. Li, J. Li, Z. Cao, X. Lin, X. Li, Y. Fang, X. An, Y. Fu, J. Jin, R. Li, MoS 2 quantum dot decorated RGO: a designed electrocatalyst with high active site density for the hydrogen evolution reaction, J. Mater. Chem. 3 (2015) 21772–21778, https://doi.org/10.1039/C5TA05219J.
[105] Z.H. Deng, L. Li, W. Ding, K. Xiong, Z.D. Wei, Synthesized ultrathin MoS 2 nanosheets perpendicular to graphene for catalysis of hydrogen evolution reaction, Chem. Commun. 51 (2015) 1893–1896, https://doi.org/10.1039/C4CC08491H.
[106] Z. Zhang, W. Li, M.F. Yuen, T.-W. Ng, Y. Tang, C.-S. Lee, X. Chen, W. Zhang, Hierarchical composite structure of few-layers MoS 2 nanosheets supported by vertical graphene on carbon cloth for high-performance hydrogen evolution reaction, Nano Energy 18 (2015) 196–204, https://doi.org/10.1016/j.nanoen.2015.10.014.

[107] J. Cao, J. Zhou, Y. Zhang, Y. Zou, X. Liu, MoS_2 nanosheets direct supported on reduced graphene oxide: an advanced electrocatalyst for hydrogen evolution reaction, PLoS One 12 (2017), https://doi.org/10.1371/journal.pone.0177258 e0177258.

[108] J. Zhou, H. Xiao, B. Zhou, F. Huang, S. Zhou, W. Xiao, D. Wang, Hierarchical MoS_2−rGO nanosheets with high MoS_2 loading with enhanced electrocatalytic performance, Appl. Surf. Sci. 358 (2015) 152−158, https://doi.org/10.1016/j.apsusc.2015.07.187.

[109] J. Guo, K. Zhang, Y. Sun, Y. Zong, Z. Guo, Q. Liu, X. Zhang, Y. Xia, Enhanced hydrogen evolution of MoS 2/RGO: vanadium, nitrogen dopants triggered new active sites and expanded interlayer, Inorgan. Chem. Front. 5 (2018) 2092−2099, https://doi.org/10.1039/C8QI00488A.

[110] F. Li, L. Zhang, J. Li, X. Lin, X. Li, Y. Fang, J. Huang, W. Li, M. Tian, J. Jin, R. Li, Synthesis of Cu−MoS_2/rGO hybrid as non-noble metal electrocatalysts for the hydrogen evolution reaction, J. Power Sources 292 (2015) 15−22, https://doi.org/10.1016/j.jpowsour.2015.04.173.

[111] L. Wu, X. Xu, Y. Zhao, K. Zhang, Y. Sun, T. Wang, Y. Wang, W. Zhong, Y. Du, Mn doped MoS 2/reduced graphene oxide hybrid for enhanced hydrogen evolution, Appl. Surf. Sci. 425 (2017) 470−477, https://doi.org/10.1016/j.apsusc.2017.06.223.

[112] X. Xu, W. Zhong, L. Wu, Y. Sun, T. Wang, Y. Wang, Y. Du, Highly efficient hydrogen evolution based on Ni 3 S 4 @MoS 2 hybrids supported on N-doped reduced graphene oxide, Appl. Surf. Sci. 428 (2018) 1046−1055, https://doi.org/10.1016/j.apsusc.2017.09.250.

[113] H. Dong, C. Liu, H. Ye, L. Hu, B. Fugetsu, W. Dai, Y. Cao, X. Qi, H. Lu, X. Zhang, Three-dimensional nitrogen-doped graphene supported molybdenum disulfide nanoparticles as an advanced catalyst for hydrogen evolution reaction, Sci. Rep. 5 (2015) 17542, https://doi.org/10.1038/srep17542.