



Graphene and molybdenum disulphide hybrids for energy applications: an update

N.R. Chodankar ^a, A.K. Nanjundan ^{b,*}, D. Losic ^c, D.P. Dubal ^{d,**}, J.-B. Baek ^{e,***}

^a Department of Energy & Materials Engineering, Dongguk University, Seoul, 100-715, Republic of Korea

^b School of Chemical Engineering, The University of Queensland, St. Lucia, Brisbane 4072, Australia

^c School of Chemical Engineering, The University of Adelaide, ARC Research Hub for Graphene Enabled Industry Transformation, Adelaide, South Australia 5005, Australia

^d School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George Street, Brisbane, QLD, 4001, Australia

^e School of Energy and Chemical Engineering/Center for Dimension-Controllable Organic Frameworks, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST, Ulsan 44919, South Korea

ARTICLE INFO

Article history:

Received 14 November 2019

Received in revised form

9 December 2019

Accepted 11 December 2019

Available online 6 February 2020

Keywords:

Graphene

MoS₂

Battery

Supercapacitor

Water splitting

ABSTRACT

Graphene and its analog, two-dimensional (2D) layered molybdenum disulphide (MoS₂), 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 MoS₂ 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-MoS₂ hybrids for energy-oriented applications. In particular, a summary of recent developments in the synthesis of the graphene-MoS₂ 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.

© 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

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 (MoS₂), 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 MoS₂ 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 MoS₂ has been used in various energy-related applications including supercapacitors [13,14], batteries [15,16], and water splitting for hydrogen production [17,18].

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: chodankarnilesh311@gmail.com (N.R. Chodankar), ashoknanjundan@uq.edu.au, ashoknanjundan@yahoo.com (A.K. Nanjundan), dusan.losic@adelaide.edu.au (D. Losic), deepak.dubal@qut.edu.au (D.P. Dubal), jbbaek@unist.ac.kr (J.-B. Baek).

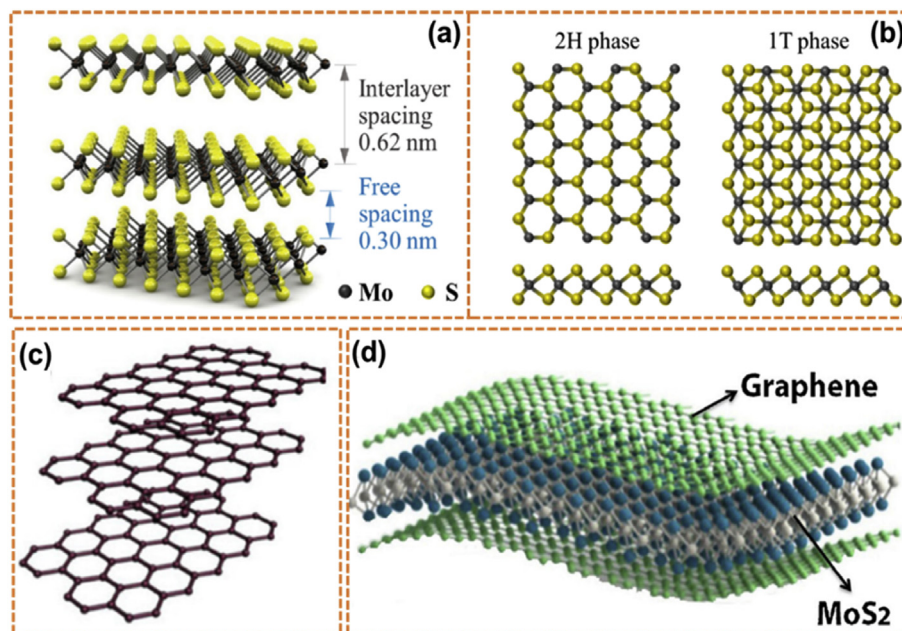


Fig. 1. (a) 3D illustration of MoS₂ structure, adapted with permission from the study by Radisavljevic et al [29]. Atomic positions in (b) the 2H phase with trigonal prismatic coordination and the 1T phase with octahedral coordination. Adopted from the study by Wang and Mi[30] (c) The structure of graphene and (d) Exfoliated few layer MoS₂ and rGO flakes. Adapted from the study by David et al [31].

Because of its distinctive structure and conductivity, MoS₂ 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 MoS₂ 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 MoS₂, it was recently suggested that it be combined as a nanocomposite with another conducting material such as carbon black or graphene. Metallic MoS₂, 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, MoS₂ nanosheets have a tendency to restack. This restacking of the 2D MoS₂ 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 MoS₂-based materials. Another promising way to overcome the restacking issue is to functionalize or hybridize the 2D MoS₂ with another highly conducting material such as graphene. The controlled hybridization of MoS₂ 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-MoS₂ hybrids for energy storage and water splitting applications. To begin with, we briefly summarize the diverse synthesis routes used to prepare the graphene-MoS₂ 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-MoS₂ 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, MoS₂, 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 MoS₂ [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 MoS₂. 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 (NH₄)₂MoS₄ 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 MoS₂. Similarly, Zhan and co-workers [35] developed MoS₂ thin films by sulfurization of the Mo substrate. Despite these developments, the preparation of large area and uniform 2D MoS₂ 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 MoS₂ 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 MoS₂ material [37].

Another approach, the aqueous solution-based hydrothermal process has also been proposed to prepare MoS₂-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 MoS₂ nanostructure.

The lithium intercalation and exfoliation method is another effective approach for preparing metallic MoS₂. In organic solvents, the bulk MoS₂ and strong reducing agents (n-butyl lithium or LiBH₄) react with each other to form a Li-intercalated MoS₂. Later, the dispersion of Li-MoS₂ in aqueous solvent with subsequent sonication process gives 2D metallic MoS₂ [39].

Similar synthesis routes can be used to prepare graphene-MoS₂ hybrid materials. Typically, graphene or reduced graphene oxide (rGO) is used as a supporting material or substrate to develop the MoS₂-based nanostructures. For example, Zhang et al. [40] prepared the rGO-MoS₂ hybrid using the solvothermal method, in which the graphene oxide was dispersed in DMF with (NH₄)₂MoS₄ 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 MoS₂. 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, MoS₂, and their hybrid combinations. How the structural and surface properties (such as morphology, surface areas etc.) of the MoS₂-graphene hybrid affect particular applications is discussed.

3. Applications

With their 2D layered structure, excellent electrical conductivity, and well-developed synthesis procedure, graphene-MoS₂ 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-MoS₂ 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 MoS₂ 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 MoS₂ 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 MoS₂ on a three-dimensional (3D) conducting substrate, which can enhance the electron transport process. For instance, a graphene-MoS₂ hybrid was reported by Zhang et al. [53] for supercapacitor and lithium-ion battery applications. They prepared highly conducting 3D graphene decorated with a MoS₂ flocculent nanostructure and determined it was promising electrode material, as shown in Fig. 2. The combined effect of the graphene and MoS₂ led to excellent energy storage capacity in both energy storing systems.

In the supercapacitor, the prepared graphene-MoS₂ 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-MoS₂-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 MoS₂/polyaniline (MoS₂/PANI/rGO). The MoS₂/PANI was well dispersed on graphene oxide and

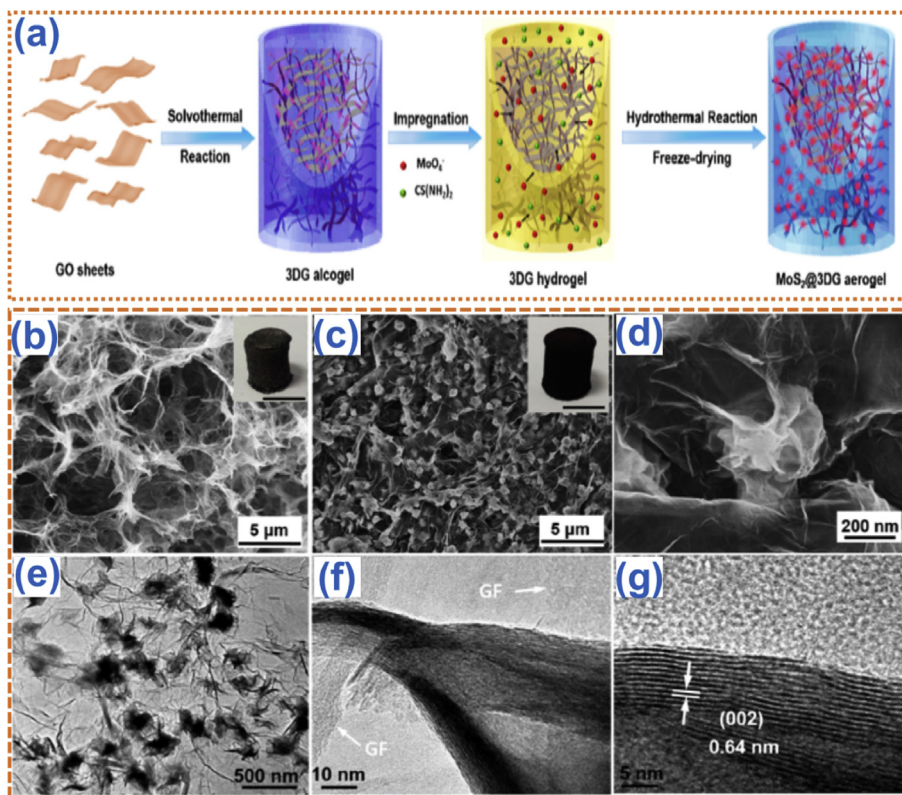


Fig. 2. (a) Schematic of fabrication of the MoS₂-graphene hybrid structure, (b) Scanning electron microscopy (SEM) image of the porous graphene sample, (c) SEM image of the MoS₂-graphene hybrid (inset: optical photograph of MoS₂-graphene bulk sample, scale bar: 1 cm), (d) SEM image of MoS₂-graphene hybrid at higher magnification, (e, f) Transmission electron microscopy (TEM) images of the MoS₂-graphene hybrid at different magnifications, (g) High-resolution transmission electron microscopy (HRTEM) image of the MoS₂-graphene composite showing lattice fringes of MoS₂ 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 MoS₂/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 MoS₂/PANI/rGO ratio was 1:1. Using a hydrothermal technique, Saraf et al [56] prepared an rGO-MoS₂ hybrid for the supercapacitor application. The prepared rGO-MoS₂ hybrid electrodes showed satisfactory electrochemical performance because of the synergetic effect of both components. The rGO-MoS₂ hybrid exhibited a capacitance value of 387.6 F/g at 1.2 A/g, which was much higher than the pristine rGO and MoS₂ 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 MoS₂-nitrogen-doped graphene (MoS₂-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-MoS₂ hybrids for the supercapacitor applications [58–62]. The aforementioned studies demonstrate the enhanced electrochemical performance of graphene-MoS₂ hybrids in supercapacitor applications, where the complementary features of the graphene and MoS₂ 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-MoS₂ 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 Li₄Ti₅O₁₂ (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-MoS₂ 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.

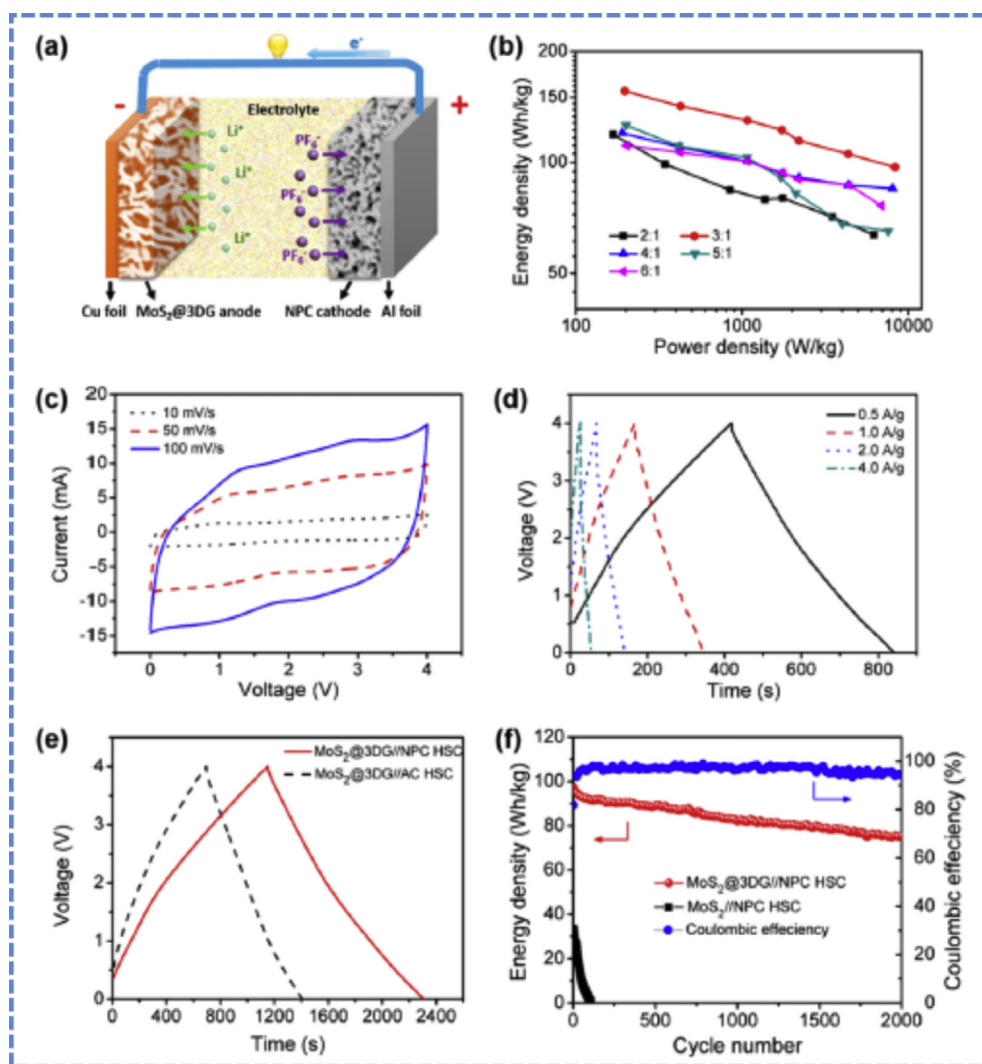


Fig. 3. (a) Schematic illustration of the working mechanism of the MoS₂-graphene nanoporous carbon hybrid supercapacitor (b) The Ragone plot of the hybrid supercapacitor using MoS₂-graphene as a negative electrode and nanoporous carbon as a positive electrode with various mass ratios from 2:1 to 6:1 (positive electrode: negative electrode) over a voltage window of 0.0–4.0 V. (c) CV curves of the MoS₂-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 MoS₂-graphene nanoporous carbon hybrid supercapacitor at different current densities from 0.5 to 4.0 A/g. (e) Galvanostatic charge/discharge curves of the MoS₂-graphene nanoporous carbon hybrid supercapacitor and the MoS₂ nanoporous carbon hybrid supercapacitor as contrast at a current density of 0.2 A/g. (f) Cycling performance of the MoS₂-graphene nanoporous carbon hybrid supercapacitor and MoS₂ 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 MoS₂-rGO has been used as an anode material for the sodium-ion capacitor (NICs) by Zhan et al. [64]. In the MoS₂-rGO hybrid electrode, the graphene frame delivered sufficient enough charges and the highly expanded MoS₂ achieved fast ion diffusion. As a result, the MoS₂-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 MoS₂ nano-flowers@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 SnO₂ [69], Fe₂O₃ [70], Fe₃O₄ [71], MoO₃ [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-MoS₂ 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 MoS₂ 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 MoS₂ 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 MoS₂ electrode after long-term cycling, Xue et al. [78] proposed a carbon encapsulation strategy. The core-shell-structured MoS₂@graphene composite, with MoS₂ spheres as the core and ultrathin graphene sheets as the shell, was synthesized using a novel spray drying method. In the MoS₂@graphene composite, the graphene layer helped to enhance the cycling stability of the MoS₂ 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 MoS₂@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 MoS₂ 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 micro-sized MoS₂. Commercially available micron-sized MoS₂ 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 MoS₂ was performed by etching process in 6 wt% H₂O₂. Then, the MoS₂ was coated with polydopamine and graphene oxide. Hydrothermal and sintering processes were carried out to produce the final MoS₂@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 MoS₂.

Combining the MoS₂ 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 MoS₂-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 MoS₂ sheets and later as a free-standing support for the current collector. Fig. 5(a) shows a schematic diagram of the preparation of the MoS₂-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 MoS₂-graphene, as seen in Fig. 5. A MoS₂/graphene composite has been also used for the quasi-symmetrical MoS₂ battery, in which an electrochemical activity modulation strategy was used to activate redox in the electro-negative and electro-positive parts [81]. Several similar approaches to enhance the Li-ion storage capacity of MoS₂-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 MoS₂ 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, MoS₂ 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 MoS₂ 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 MoS₂@liquid-phase exfoliated graphene (LEGr) composite as an anode electrode. The microwave-assisted solvothermal method was used to prepare the MoS₂@LEGr composite electrode, in which the LEGr was used as a support for the MoS₂. 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 MoS₂-graphene aerogels for NIB application. The prepared hybrid MoS₂-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 MoS₂ was anchored over the N-doped graphene substrate (tulip-MoS₂/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 MoS₂-NG electrodes exhibited good capacity retention and long cycling stability, with over 1000 charge/

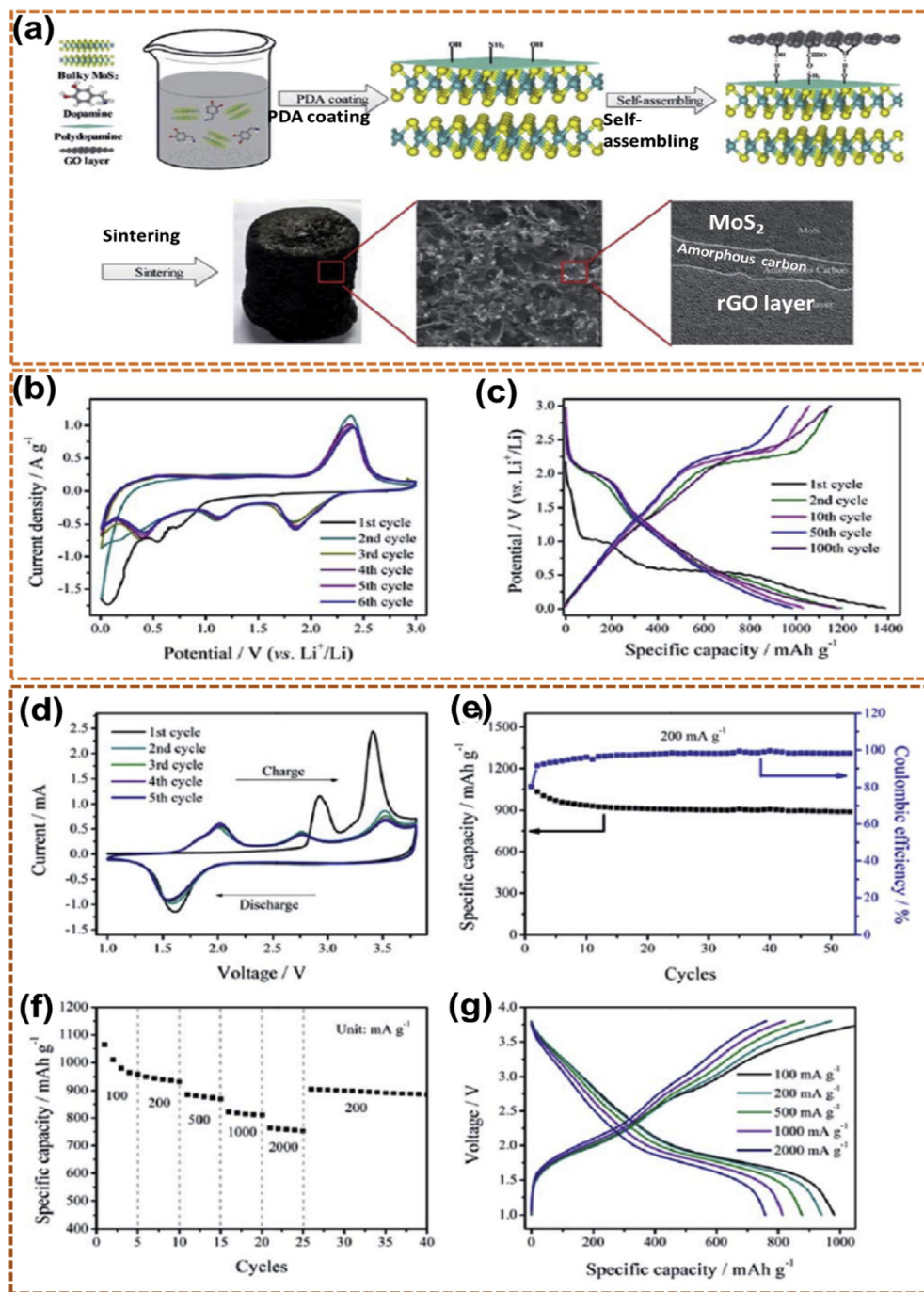


Fig. 4. (a) Schematic of the synthesis strategy and electrochemical performance of the MoS₂@C/RGO composite, electrochemical performance of the MoS₂@C/RGO composite. (b) CV curves from 0.01 to 3.00 V at 0.2 mV/s, (c) typical charge-discharge profiles for different cycles and electrochemical properties of the MoS₂@C/RGO//LiCoO₂ 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 MoS₂@C/RGO (approximately 1200 mA h/g) and commercial LiCoO₂ (150 mA h/g) with 5% cathode excess to achieve full utilization of MoS₂@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 MoS₂-decorated sulfur-doped graphene nanosheets (MoS₂-SG). The MoS₂-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 MoS₂ 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

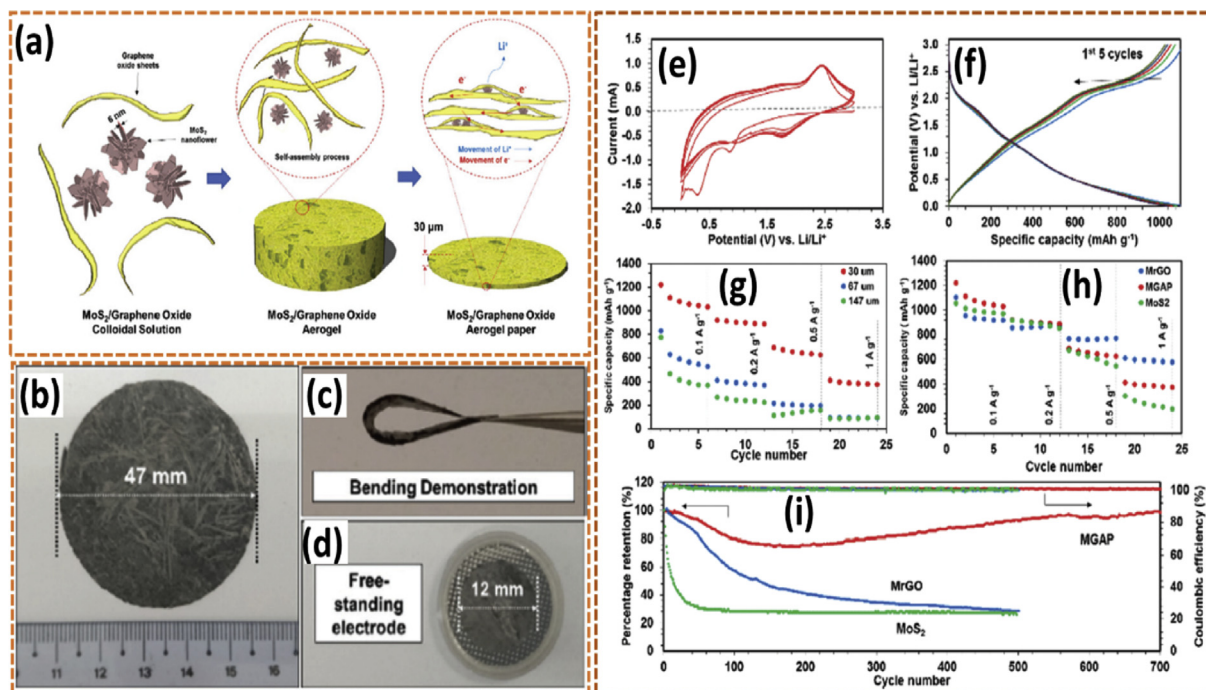


Fig. 5. (a) Schematic diagram to prepare the free-standing MoS₂-graphene aerogel paper electrode, (b) fabricated free-standing MoS₂-graphene aerogel paper electrode, (c) flexibility test for the MoS₂-graphene aerogel paper electrode, (d) 12 mm diameter free-standing electrode used directly for LIB testing. The electrochemical performance for the MoS₂-graphene aerogel paper electrode as an anode for the LIBs. (e) First 5 CV curves of MoS₂-graphene aerogel paper electrode; (f) first 5 galvanostatic charge/discharge profiles of MoS₂-graphene aerogel paper electrode at 0.1 A g⁻¹; (g) specific capacity of MoS₂-graphene aerogel paper electrode (MGAP) with various thicknesses at various current densities; (h) specific capacities of MGAP, MoS₂-graphene oxide powder (MrGO), and pristine MoS₂ at various current densities; and (i) cyclic performance and coulombic efficiency of MGAP, MrGO, and pristine MoS₂ 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 CO₂. 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-TiO₂ 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 MoS₂ 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 MoS₂-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 MoS₂ quantum dots (MoS₂ 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/cm²) and a Tafel slope as small as 63 mV per decade. The catalytic activity resulted from the zero-dimensional

MoS₂ 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 MoS₂ occurred because of the high electrical conductivity of the MoS₂ edges.

Deng et al. [105] prepared ultrathin nanosheets composed of MoS₂ perpendicular to rGO (MoS₂-rGO) for the HER application

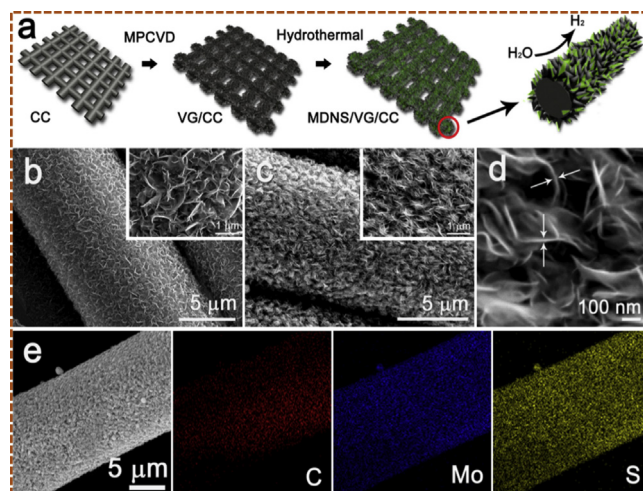


Fig. 6. (a) Schematic illustration of the fabrication of MDNS/VG/CC for the HER application, the low and high-magnified (insets) for the (b) VG/CC, (c, d) few-layers molybdenum disulfide nanosheets supported by vertical graphene on conductive carbon cloth (MDNS/VG/CC), (e) Energy-dispersive X-ray spectroscopy (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 MoS₂ on rGO enhanced the electron transport through each MoS₂ nanosheets, resulting in an overpotential of 172 mV at 10 mA/cm² current density.

Similarly, Zhang et al. [106] reported a MoS₂-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, MoS₂ 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/cm² (η_{10}), and a Tafel slope of 53 mV/dec (Fig. 7). The low overpotential was attributed to the abundant active edges provided by the vertical MoS₂ 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 MoS₂ nanosheets/rGO with a small Tafel slope of 57 mV/dec and an overpotential of 130 mV at 10 mA/cm² current density.

Zhou et al. [108] studied the effect of MoS₂ mass loading on the catalytic performance of a MoS₂-rGO electrode. The mass loading of the redox-active material played an essential role in the catalysis process. The prepared MoS₂-rGO composite electrode contained 94 wt% MoS₂ and 6 wt% rGO. Compared with the bare MoS₂ electrode, the MoS₂-rGO composite had ten-fold higher catalytic activity.

Doping can also change the catalytic activity of the MoS₂ hybrid electrode. Recently, Guo et al. [109] studied the effect of vanadium and nitrogen codoped MoS₂ on rGO for HER application. Doping can expand interlayer spacing, with enhanced defect sites at the edges of the MoS₂ to boost the catalytic activity. As a result, the prepared

vanadium and nitrogen codoped MoS₂ on an rGO electrode showed the extremely low overpotential of 68 mV at 10 mA/cm² and a Tafel slope of 41 mV/dec.

Li et al. [110] studied the effect of a Cu-doped MoS₂-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 MoS₂-rGO composite for the HER application. They found that the Mn-doped MoS₂-rGO composite had higher catalytic activity than the MoS₂-rGO and MoS₂ 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 Ni₃S₄/MoS₂ (Ni₃S₄/MoS₂@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 MoS₂-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, MoS₂ 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-MoS₂-based hybrids, using various synthesis methods. In the energy storage and

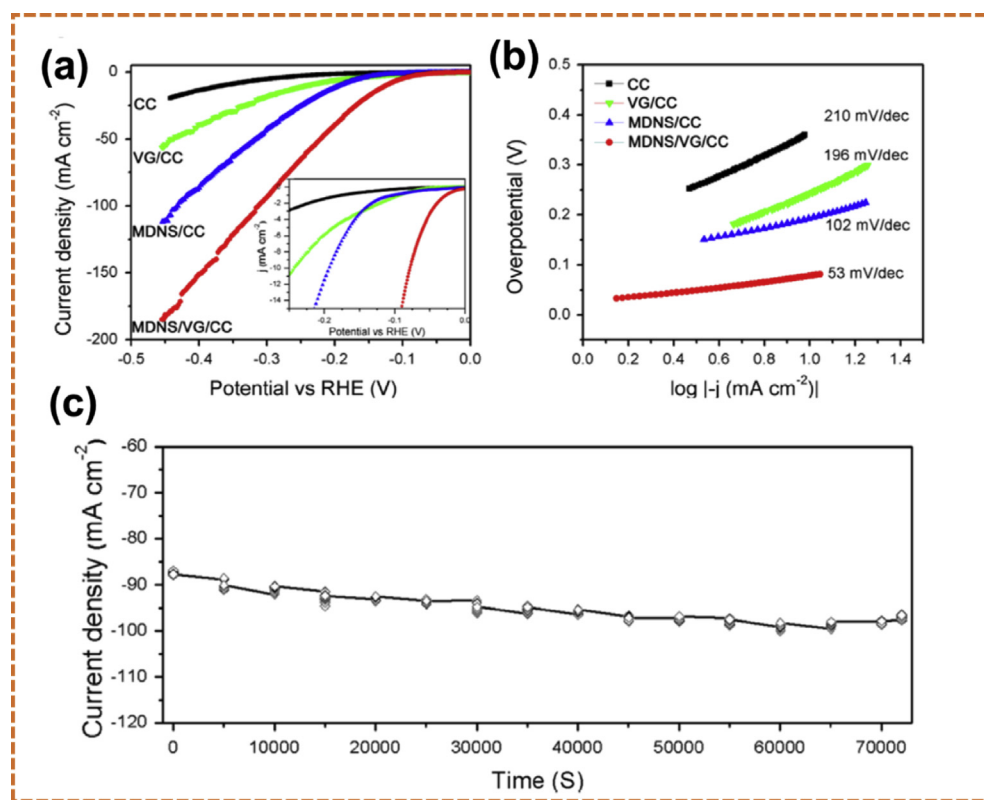


Fig. 7. (a) The polarization curves corresponding (b) Tafel plots for the carbon cloth (CC), vertical graphene/carbon cloth (VG/CC), few-layers molybdenum disulfide nanosheets supported by vertical graphene on conductive carbon cloth (MDNS/VG/CC), MDNS/CC electrodes, (c) the stability for the MDNS/VG/CC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

generation field, graphene-MoS₂ 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 MoS₂. Many encouraging concepts and results have recently been reported for energy storage applications using graphene-MoS₂ 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-MoS₂ 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 MoS₂-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/cm²). 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/cm². 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/MoS₂-based electrodes that needs to be overcome.

Finally, great progress in the development of graphene-MoS₂ 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.

Acknowledgments

D.P.D. acknowledges the Queensland University of Technology and Australian Research Council (ARC), Australia for the Future Fellowship (FT180100058). D.L. acknowledges the support from the Australian Research Council, ARC Research Hub for Graphene Enabled Industry Transformation, (IH150100003). J.-B.B. acknowledges the Creative Research Initiative (CRI, 2014R1A3A2069102) and Science Research Centre (SRC, 2016R1A5A1009405) programs through the National Research Foundation (NRF) of Korea funded by the Ministry of Education.

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 MoS₂ 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 MoS₂ 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 MoS₂ 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 MoS₂ for hydrogen evolution, *J. Am. Chem. Soc.* 138 (2016) 16632–16638, <https://doi.org/10.1021/jacs.6b05940>.
- [13] A. Paravannoor, A. Babu, MoS₂/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 MoS₂-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. Koeh, J. Liu, J.P. Lemmon, Exfoliated MoS₂ 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 MoS₂ 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 MoS₂ 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 MoS₂ 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-MoS₂ 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 MoS₂ 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-MoS₂ 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 MoS₂-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 MoS₂ 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 (MoS₂) nanosheets, *Environ. Sci. Technol.* 51 (2017) 8229–8244, <https://doi.org/10.1021/acs.est.7b01466>.
- [31] L. David, R. Bhandavat, G. Singh, MoS₂/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 MoS₂ 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 MoS₂ atomic layers on a SiO₂ substrate, *Small* 8 (2012) 966–971, <https://doi.org/10.1002/sml.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. Theuvsissen, 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, MoS₂ 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 Na₃V_{2-x}Ga_x(PO₄)₃ (0 ≤ x ≤ 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 MoS₂/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/MnO₂ nanostructured electrodes by conductive wrapping, *Nano Lett.* 11 (2011) 4438–4442, <https://doi.org/10.1021/nl202663u>.
- [51] L. Li, Z.A. Hu, N. An, Y.Y. Yang, Z.M. Li, H.Y. Wu, Facile synthesis of MnO₂/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 MoS₂-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 MoS₂ 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. Prasantkumar, J. Joyner, S. Ozden, D.S. Galvao, P.M. Ajayan, Enhanced supercapacitor performance of a 3D architecture tailored using atomically thin rGO-MoS₂ 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, MoS₂ 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 MoS₂/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 interlayer-expanded MoS₂/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 Fe₂O₃/GS aerogels for high Li-storage and excellent stability, *Small* 10 (2014) 2260–2269, <https://doi.org/10.1002/sml.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 MoS₂ 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 MoS₂@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 MoS₂ 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 MoS₂-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 MoS₂ 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 MoS₂ 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 MoS₂-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 MoS₂ 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 MoS₂ 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 Ni₃S₂ nanosheets coated on Co₃O₄ 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 MoS₂/Cu–ZnIn₂S₄ photocatalyst for enhanced photocatalytic H₂ 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. Mäklän, R. Puskas, A. Kukovec, A. Dombóvári, 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 MoS₂: 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 MoS₂ 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/acsnano.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@MoS₂ 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, MoS₂ 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 MoS₂ 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 MoS₂ 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 MoS₂ 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, MoS₂ 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, MoS₂ 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 MoS₂ 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 MoS₂ 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, MoS₂ 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 MoS₂-rGO nanosheets with high MoS₂ 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 MoS₂/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-MoS₂/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 MoS₂/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 Ni₃S₄@MoS₂ 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>.