Graphene and molybdenum disulfide hybrids: synthesis and applications

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Graphene and related inorganic two-dimensional (2D) nanomaterials are an exceptional class of compounds with exotic properties that are technologically intriguing. While graphene itself is chemically inert and a gapless semimetal, its isostructural analog, molybdenum disulfide (MOS_2) is chemically versatile with band gaps, thereby finding significant use in a myriad of applications. Although these 2D nanomaterials individually possess tremendous authority for various applications, the combination of these materials in the recent past has created a new paradigm in emerging applications. Here, we summarize the current state-of-the-art and progress over the past three years on the development of hybrids of these layered materials. We highlight their pivotal role in electrochemical energy storage, sensing, hydrogen generation by photochemical water splitting and electronic device applications such as field-effect transistors. Perspectives on the challenges and opportunities for the exploration of these 2D layered hybrid materials are put forward.

Introduction

Owing to its fascinating properties and potential applications, graphene is arguably the most studied two-dimensional (2D) layered nanomaterial today. The resounding success of graphene stemming from its extremely novel properties has led to renewed interest in the exploration of a whole new range of isostructural analogs of graphene, such as, hexagonal boron nitrides (BN) otherwise known as 'white graphene' and 2D transition metal dichalcogenides (TMDCs), whose layers are bound by a weak van der Waals forces with atomic scale thickness. Depending on the co-ordination and oxidation states of the metal atoms, TMDCs can be metals, semi-metals or semiconductors. Among the various types of TMDC materials, molybdenum disulfide (MoS_2) in particular, has garnered increasing attention, mainly because of its

appreciable band gap with exotic properties. Similar to graphite, the precursor for graphene, MoS_2 bulk crystals that are found in layered forms are naturally abundant as molybdenite. Besides being stable they can easily be exfoliated/prepared [1]. Over the past few years, like graphene, TMDCs individually have been used extensively in catalysis [2], energy storage [3,4], hydrogen generation [5], dehydrosulfurization [6] and nanoelectronics [7].

An inherent problem, however, is the restacking property of these nanomaterials when used individually, as it results in the decrease of activity and hampers its potential for various applications. Functionalization or hybridization of these materials with conductive templates or supports such as graphene is an established and effective way to improve the catalytic properties of individual materials and the hybrids as a whole. Although hybridization attempts between graphene and its 2D layered analogs, especially with MoS_2 is still in its nascent stage, the combined properties and their related applications have never gone unnoticed. Hybridization controls the physicochemical properties of individual component and also creates diverse functionality

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between each of the components via synergistic effects. Such a specific structure benefits from both properties, improves the dispersion of MoS$_2$, enhances mechanical properties [8] and the conductivity of the hybrid in general. Therefore, the combined intriguing properties endow the hybrids of graphene and TMDC nanomaterial in a host of applications, ranging from energy conversion and storage to electronics to sensing.

While more generalized accounts involving inorganic layered materials have appeared previously, in this review, we focus on the progress over the past three years involving hybrids of graphene and their inorganic layered counterparts with particular emphasis on graphene/MoS$_2$ based composites. Briefly summarizing on the variety of synthesis techniques reported thus far, we discuss the potential application of these hybrids in the field of energy conversion and storage, hydrogen generation, and device electronics to sensing. Current challenges and future perspectives are discussed in the latter sections.

Structural aspects and synthesis methodologies

Composed of carbon atoms arranged in a honeycomb lattice (Fig. 1a), graphene has been shown to possess unique properties. On the other hand, TMDCs, specifically MoS$_2$ is composed of three atom layers; a molybdenum layer sandwiched between two sulfur layers, with strong molecular intralayer bonds (coordination bonds) but weak interlayer bonds, giving rise to their layered structure. Similar in structure to graphene, MoS$_2$ is 2D and its single layer form is called 1H-MoS$_2$, with a typical thickness of ~0.65 nm (Fig. 1b) [9]. Unlike graphene, however, the 2D single layer form (1H-MoS$_2$) has a direct band-gap of the order of 1.9 eV, showing prospects for a wide range of applications. With individual 2D layers stacked upon each other by van der Waals forces, they form a three-dimensional bulk called 2H-MoS$_2$, with anisotropic properties. Recently, few-layered MoS$_2$ sheets have attracted considerable attention for to its promising semiconducting characteristics, thus showing potential for applications in nanoelectronics and optoelectronics. In general, the properties in these 2D materials are layer-dependent and greatly differ from the properties of the bulk materials.

Tremendous efforts have been devoted in the past few years to the development of methods in preparing 2D layered materials required for different applications. Generally, graphene and the corresponding mimics, particularly the layered TMDCs, can be obtained by several means involving top-down and bottom-up approaches. Besides chemical vapor deposition (CVD) [10,11],

liquid exfoliation, electrochemical exfoliation, lithium assisted intercalation and exfoliation [12], solvothermal/hydrothermal methods as well as microwave synthesis [13,14] have been successfully applied for generating graphene and its analog, namely MoS$_2$ [12,15–18,19].

Similar to graphene, TMDCs can also be mechanically exfoliated from a piece of naturally occurring bulk crystal [20]. Although mechanical exfoliation can be achieved in generating single to few-layers of the materials that are pristine and mostly defect free structures suitable for the fundamental studies, this technique is limited in terms of mass production. On the other hand, ultrasonication (liquid exfoliation) is a simple universal method used to synthesize dispersions of these layered materials from their bulk counterparts [21,22]. Such dispersions are useful in preparing novel hybrid and composite materials as they can easily blend with the solutions of other nanomaterials [22]. In addition to the aforementioned techniques, graphene can be mass-produced by oxidizing graphite to obtain a defect rich exfoliated structure, namely graphite/graphene oxide (GO) followed by deoxygenation, which removes some of the oxygen functionalities leading to a few-layered structure, so-called reduced graphene oxide (rGO).

Hybrids of graphene and transition metal dichalcogenides (MoS$_2$)

The construction of hybrid heterostructures by stacking different 2D layered materials such as MoS$_2$ and graphene or rGO together is an emerging research area (Fig. 1c) [23]. Benefitting primarily form the chemical interactions between hybridized components on their interface, these analogous nanostructured materials with enhanced specific surface area becomes promising building blocks for a diverse range of next generation of nanomaterial architectures.

Besides liquid exfoliation, chemical modification/functionalization strategies to produce these hybrid heterostructures, CVD grown graphene was used as a template to grow MoS$_2$ layers at a considerably low temperature of 400°C using ammonium thiomolybdate as a precursor [24]. Although a lattice mismatch between the graphene and MoS$_2$ was evident, this simple method provides a unique approach for the synthesis of graphene heterostructures as well as surface functionalization of graphene. Similarly, Lin et al. [10] demonstrated the direct growth of MoS$_2$ on epitaxial graphene. Therefore, the direct formations of MoS$_2$ on graphene substrates show great potential toward the development of new optical, electronic devices, transparent electrodes to name a
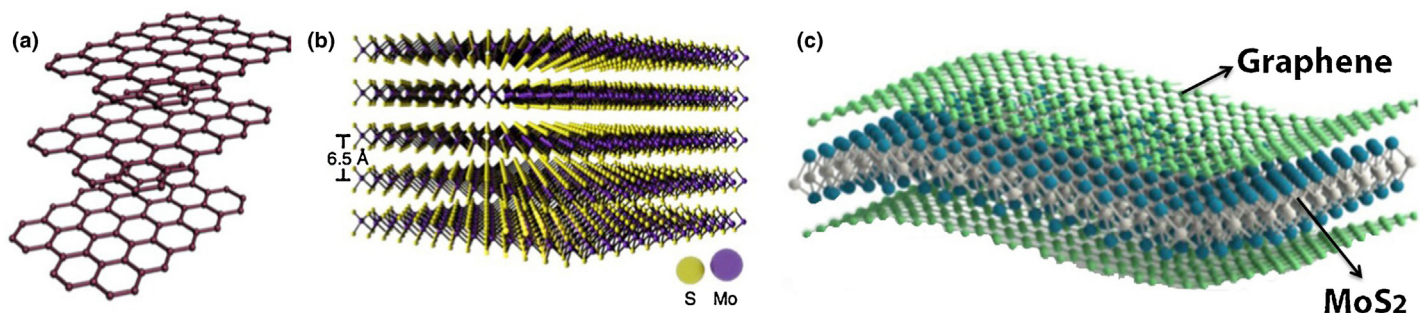

FIGURE 1

(a) Illustration of multilayered graphene sheets, (b) cross-section illustration of multilayered MoS$_2$ with an interlayer spacing of ~0.65 nm. Adapted from reference [9]. (c) Exfoliated few-layer MoS$_2$ and rGO flakes. Adapted from reference [23].

few. These are significant advances in pursuit of hybrid 2D materials.

Applications

Graphene as well as MoS_2 exhibits remarkably unique and diverse range of properties, many of which were accounted previously [25–28]. Although MoS_2 has long been recognized as a lubricant [29,30] in many areas including aerospace industry (weak van der Waals bonds between the sulfur–molybdenum–sulfur leads to low friction properties), the diverse and exotic properties of this particular metal dichalcogenide can be tuned at will by functionalization/hybridization with graphene. Thus, the hybrids of graphene and MoS_2 are currently the focus of many research groups across the globe.

Apart from main application such as energy and water splitting, recently the hybrids of these materials with a conductive graphene have been increasingly explored to access a wealth of phenomena. For instance, Li et al. [14] have recently used MoS_2/rGO composites synthesized via a microwave-assisted method for visible-light photocatalytic degradation of methylene blue. The MoS_2/rGO composites enhanced the photocatalytic performance with a maximum degradation rate of 99% under visible light irradiation for 60 min. It was found that the excellent photocatalytic activity arose due to the contribution from the reduced electron–hole pair recombination, enhanced light absorption and increased dye adsorption with the introduction of rGO in the composite.

Using a similar microwave-assisted technique, MoS_2/graphene composites were proven to be an effective catalyst for hydrogenation of carbonyl sulfide (COS) or simply hydrodesulphurization. Up to 100% of COS conversion was achieved at 280°C using graphene based MoS_2 catalysts [6]. In recent years, graphene and graphene-based composites have been utilized in reducing fire hazards such as flame-retardants [31]. Graphene surfaces were hybridized with layered MoS_2 and epoxy resin using a hydrothermal method. Synergistic effects between MoS_2 and graphene nanosheets on thermal stability and fire hazards were investigated. By analyzing the char of MoS_2/graphene/epoxy composite, a noteworthy improvement of the flame retardant and smoke suppression properties were observed [32]. To understand the intrinsic properties of the 2D atomic crystals, direct imaging and identification of every atom is paramount. However, microscopic studies involving prolonged radiation can damage the crystals thus impeding important information. Recently, a single-layer MoS_2 sample was encapsulated between single graphene layers and their behavior under the electron beam was compared. It was found that the MoS_2 sample sandwiched between the graphene layers has the highest durability and lowest defect formation [33]. In the forthcoming sections, we highlight and discuss the top priority applications these hybrids render.

Energy

The energy crisis is a pressing problem today due to over use of fuels and depleting fossil reserves, bringing ecological problems and increased carbon dioxide emission. Thus, the energy issue becomes one of the most important concerns for researchers today. Energy conversion and storage devices such as lithium-ion batteries (LIBs), supercapacitors, fuel cells and solar cells are most popular electrochemical systems, which commonly store energy and deliver when required. However, most of these devices do not meet the colossal requirements of today's society. Therefore, the development of new renewable, environmentally friendly and energy efficient devices are paramount.

In the quest to novel electrode materials to build efficient energy systems, nanomaterials with merits of high efficiency and low cost are a prerequisite. Here, materials engineering plays a vital role. Graphene and related 2D TMDCs hybrids, especially MoS_2, with superior properties have emerged as alternative electrode materials in energy devices. Below, we showcase the most recent advances in field.

Rechargeable batteries

As one of the most promising energy storage system available today, the rechargeable LIB has been very popular in portable electronics owing to its high energy density but with limitations. Although capable of storing large quantities of energy, they usually suffer from poor power delivery. Graphite based materials are traditionally used as electrodes of these energy storage devices. However, its low theoretical capacity (373 mAh/g) does not fully meet the requirements for use in modern hybrid electric vehicles. In addition, because of the large lateral size dimensions they usually suffer from the long diffusion pathways of lithium into the material. It is now well understood that the performance of a typical LIB largely depends on the physical and chemical properties of the electrode material. While many research efforts are constantly conceived to design novel nanostructures as electrode materials, lately there has been strong interest on using graphene and MoS_2 based hybrid materials as anodes for LIBs.

While graphene itself is interesting and electrodes based on graphene for LIB applications are well documented, the aggregation problem is prevalent and embodies a number of disadvantages. To circumvent this issue and to use graphene alone as an electrode, several modifications are necessary. On the other hand, layered TMDCs, especially MoS_2, are highly promising materials as LIB electrodes due to its layered structure with fast ion conduction, and shorter path length, where Li^+ ions can easily intercalate and exfoliate.

Recent studies have demonstrated that graphene can enhance the surface area and provide conductive pathways, thereby improving the cycling stability of the electrodes, when hybridized with other electrochemically active materials to form composite electrodes for energy storage devices [34]. Detailing on the above principle, MoS_2/graphene composites were prepared by a one-step in situ solution phase method using GO and sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) and thiourea (NH_2CSNH_2) as precursors (Fig. 2a) [35]. The prepared composites were of a 2D nanoflake structure (Fig. 2b), in which the MoS_2 layers had an interlayer distance of 0.62 nm grown on the surface of graphene. It was found that about 4–5 layers of MoS_2 sheets were grown on the surface of graphene, which is quite smaller than pure MoS_2 that typically has tens of layers (Fig. 2c). This indicates that during the synthesis of MoS_2/graphene composites, MoS_2 is reduced in situ on the surface of graphene layers, and the graphene sheets inhibit the restacking of MoS_2 layers. When assembled as an anode for LIB, these composites exhibited improved reversible capacity of 1290 mAh/g at a current density of 100 mA/g and the capacity retained up to 50 cycles which is almost a little more than double for pristine MoS_2
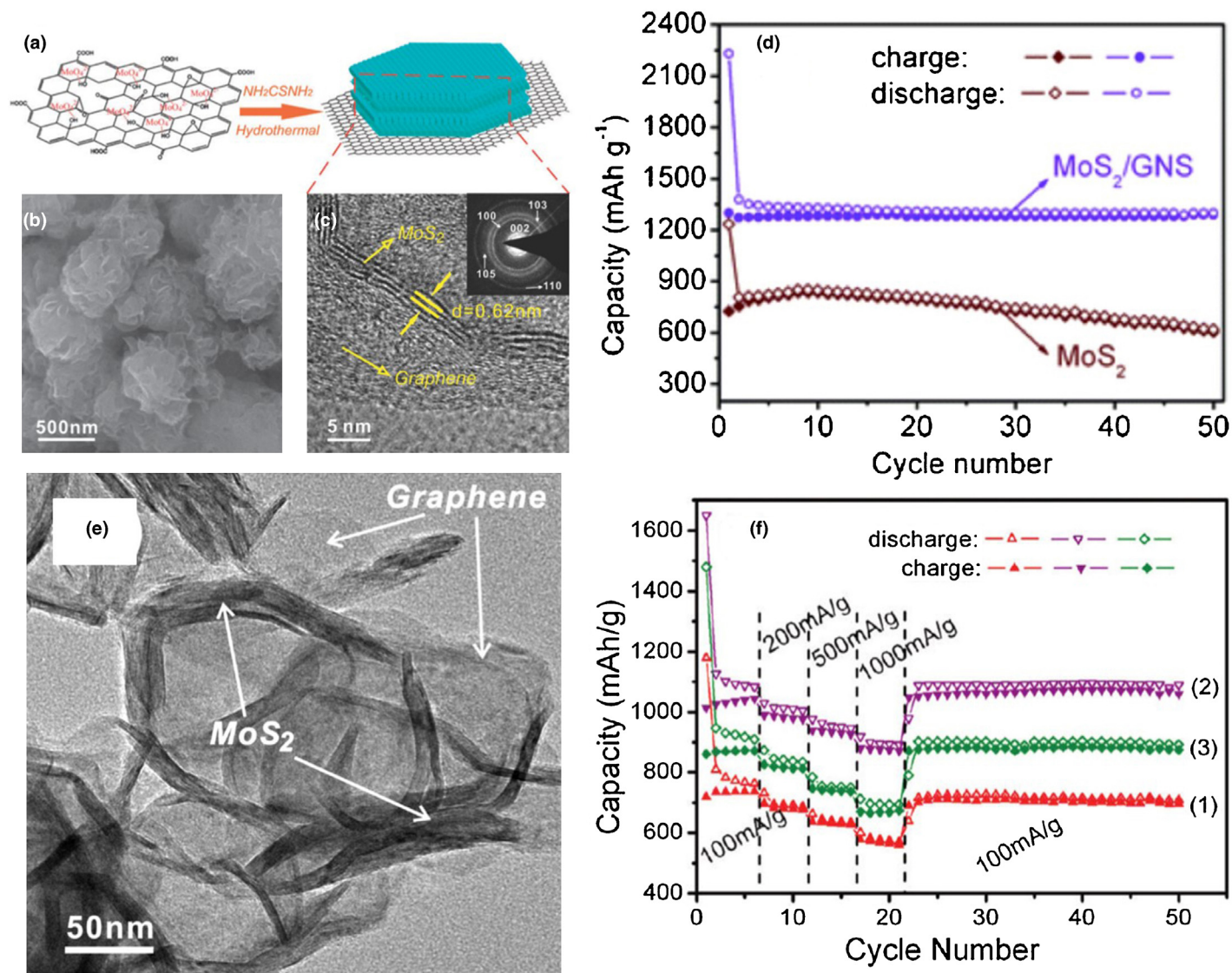
FIGURE 2

(a) Schematic of the *in situ* synthesis of MoS_2/graphene composites, (b) SEM image of MoS_2/graphene composites, (c) HRTEM image of MoS_2 layers on graphene in which the inset shows the electron diffraction pattern of the MoS_2 nanosheets on graphene, and (d) cycling behaviors of MoS_2 and MoS_2/graphene composites at a current density of 100 mA/g. Adapted from reference [35]. (e) HRTEM image of MoS_2/graphene (1:2) composite, and (f) rate capability of MoS_2/graphene samples at different current densities: (1) MoS_2/graphene (1:1); (2) MoS_2/graphene (1:2); (3) MoS_2/graphene (1:4). Adapted from reference [37].

electrode (Fig. 2d). In addition, the composites demonstrated good rate performance. At a high current density of 1000 mA/g, the specific capacity remains at 1040 mAh/g, which is still higher than that of free MoS_2 and graphene [35]. Similarly, the same group also prepared single-layer MoS_2/graphene composites dispersed in amorphous carbon [36]. It was found that the nanocomposites at (1:1) ratio delivered very high reversible capacity of 1116 mAh/g with excellent cyclic stability and high-rate capability as LIB anode materials. The superior electrochemical performances of the composites were attributed to their robust composite structure and the synergistic effect between MoS_2 and graphene layers in the previous example and the addition of amorphous carbon in the latter.

Similarly, Chang *et al.* [37] prepared few layered MoS_2/rGO hybrids via L-cysteine-assisted hydrothermal process in which L-cysteine was used along with sodium molybdate and GO as starting materials. Here, L-cysteine was used because it can act as a

sulfide source to form metal-sulfide nanoparticles and also act as a reducing agent to reduce GO to rGO, thereby enhancing the conductivity of the hybrid. Subsequently, the prepared samples were annealed in H_2/N_2 atmosphere at 800°C for 2 hours. It was shown that the MoS_2 layers were supported on the graphene surface (Fig. 2e). The composite samples in a molar ratio of 1:2 (Mo:C) when evaluated as anodes for LIBs, exhibited high reversible capacity for up to -1100 mAh/g at a current of 100 mA/g with excellent cyclic stability and high-rate capability. At a high current density of 1000 mA/g, the specific capacity of the 1:2 MoS_2/graphene composite remained at -900 mAh/g without any capacity loss (Fig. 2f).

Nitrogen-doped graphene, one of the important graphene-based derivatives, finds itself useful in several applications including LIBs as a template for synthesis of active electrode materials. Recently, a process for the synthesis of ultrathin MoS_2/N-doped

graphene revealed the growth mechanism of MoS_2 on the conductive surface of N-doped graphene [38]. The electrochemical surface area of the electrode increased after hybridization. During the lithiation process, the vacancies and defects trap a number of lithium ions and with increasing cycles, the vacancies are extended thus facilitating the insertion and removal of more lithium ions during the battery operation. Such a process contributes to high cycling stability. At a high current density of 1000 mA/g, the specific capacity remained at 850 mAh/g indicating that these architectures could serve as promising anode materials for high-performance LIBs.

It is known that the incorporation of polymer matrix to the crystal lattice such as PEO will stabilize the disordered structure of MoS_2 while improving the ionic conductivity of the whole composite. Therefore, nanocomposites comprised poly(ethylene oxide) (PEO), MoS_2, and graphene were prepared by the hydrolysis of lithiated MoS_2 in an aqueous solution of PEO and graphene. A significant increase of the reversible capacity was found in as-prepared MoS_2/PEO/graphene composite. An addition of 2 wt% of graphene to the nanocomposites greatly increased the rate capability with rates as high as 10,000 mA/g [39]. It was inferred that the interactions between the as-formed Mo and sulfur prevents dissolution of the intermediate polysulfide, thereby shedding clues about immobilization of the soluble species in a typical Li-sulfur battery.

Several other groups employed various techniques to prepare such hybrid composites especially during the past three years (2011–2014). Some of them include layer-by-layer technique [40], the use of cationic surfactants [41–43], liquid phase co-exfoliation of graphene and MoS_2 [44], simultaneous reduction of ammonium tetrathiomolybdate ($(NH_4)2MoS_4$) and GO with hydrazine hydrate in aqueous phase [45], hydrolysis of lithiated MoS_2 [46] and the combination of lithiation-assisted exfoliation followed hydrazine vapor reduction technique [47]. In addition to the above methods, novel composites of MoS_2-coated three-dimensional graphene networks were also synthesized by a facile CVD method [48] as well as employing one-step method, without the addition of any surfactants [49]. Similarly, a transfer-free method for the preparation of large-area, high-quality multilayered graphene/MoS_2 heterostructure films was also reported recently [50]. Owing to the shortened Li-ion diffusion pathway and the outstanding electronic conductivity of the hybrid, most of the above methods reported high reversible capacity and good cyclability for Li-ion storage.

It is strongly evident from all the above examples that graphene plays an important role in determining the electrochemical performance of the composites in a whole. With the robust composite structures, the capacities of these composites were tremendously enhanced, and the cycling stability and high rate capability were also significantly improved when compared to their pristine counterparts. More importantly, such a structure can prevent the agglomeration of the nanosheets.

Freestanding flexible films/paper electrodes play a crucial role in building next generation portable and wearable electronics as well as thin film LIBs so called 'flexible batteries'. Liu et al. [51] prepared a flexible MoS_2/graphene hybrid paper by the chemical bonding of MoS_2 and GO by the coordination of Cu^{2+} ions. This was further cross-linked by a polymer ligand namely PEO which improved the
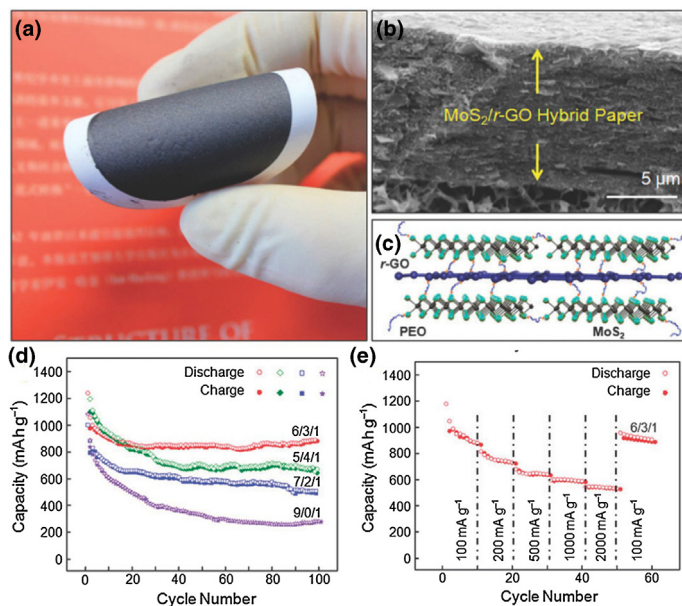

FIGURE 3

(a) Digital photograph, (b) cross-sectional SEM image and (c) structural scheme of a piece of flexible MoS_2/rGO hybrid paper chemically cross-linked by PEO, (d) cycling performance of different MoS_2/rGO/PEO film anodes at a current density of 100 mAh/g and (e) rate capability of the MoS_2/rGO/PEO film anode. Adapted from reference [51].

mechanical and electrical properties of the composite. After reduction and vacuum filtration, a piece of flexible MoS_2/rGO hybrid paper, consisting of orderly stacked nanosheets were obtained (Fig. 3a) with an average thickness of ~10 µm (Fig. 3b). The hybrid paper, peeled off from the PVDF, was directly attached to a copper foil and used as an electrode. The cycling behavior and rate capability of different MoS_2/rGO/PEO film anodes were evaluated (Fig. 3d,e). For the thin film anode without rGO (MoS_2/rGO/PEO-9:0:1), the discharge capacity fades rapidly to 24% at the 100th cycle due to the electrolyte decomposition and formation of a solid-electrolyte interface (SEI) layer. However, with an optimum composition of MoS_2/rGO/PEO in a proportion of 6:3:1, the films performed better exhibiting an initial discharge capacity of 1240 mAh/g, with only 29% irreversible loss to 890 mAh/g after 100 cycles. At a very high current density of 2000 mA/g, the reversible capacity was maintained at 545 mAh/g (Fig. 3d). Interestingly, when the current density was recovered from 2000 to 100 mA/g, the discharge capacity returns to 895 mAh/g, suggesting that the thin film anodes exhibit high cyclability.

Although in the developmental phase, the sodium-ion (Na ion) battery seems to be a cheap alternative to the existing LIBs, primarily because of the abundance of Na metal (the earth's crust makes up 2.6% of sodium by weight). Recent work has been instrumental in the understanding the role of hybrid films as a self-standing flexible electrode in Na-ion batteries. Singh and co-workers made a breakthrough in such an application by interleaving acid exfoliated few layer MoS_2 and GO nanosheets to form a hybrid composite paper [23]. By vacuum filtration of GO and MoS_2 sheets dispersed in water/isopropyl alcohol (1:1) solution (Fig. 4a), the obtained paper was annealed to obtain MoS_2/rGO composite paper (Fig. 4b) with an approximate thickness of 10–20 µm that
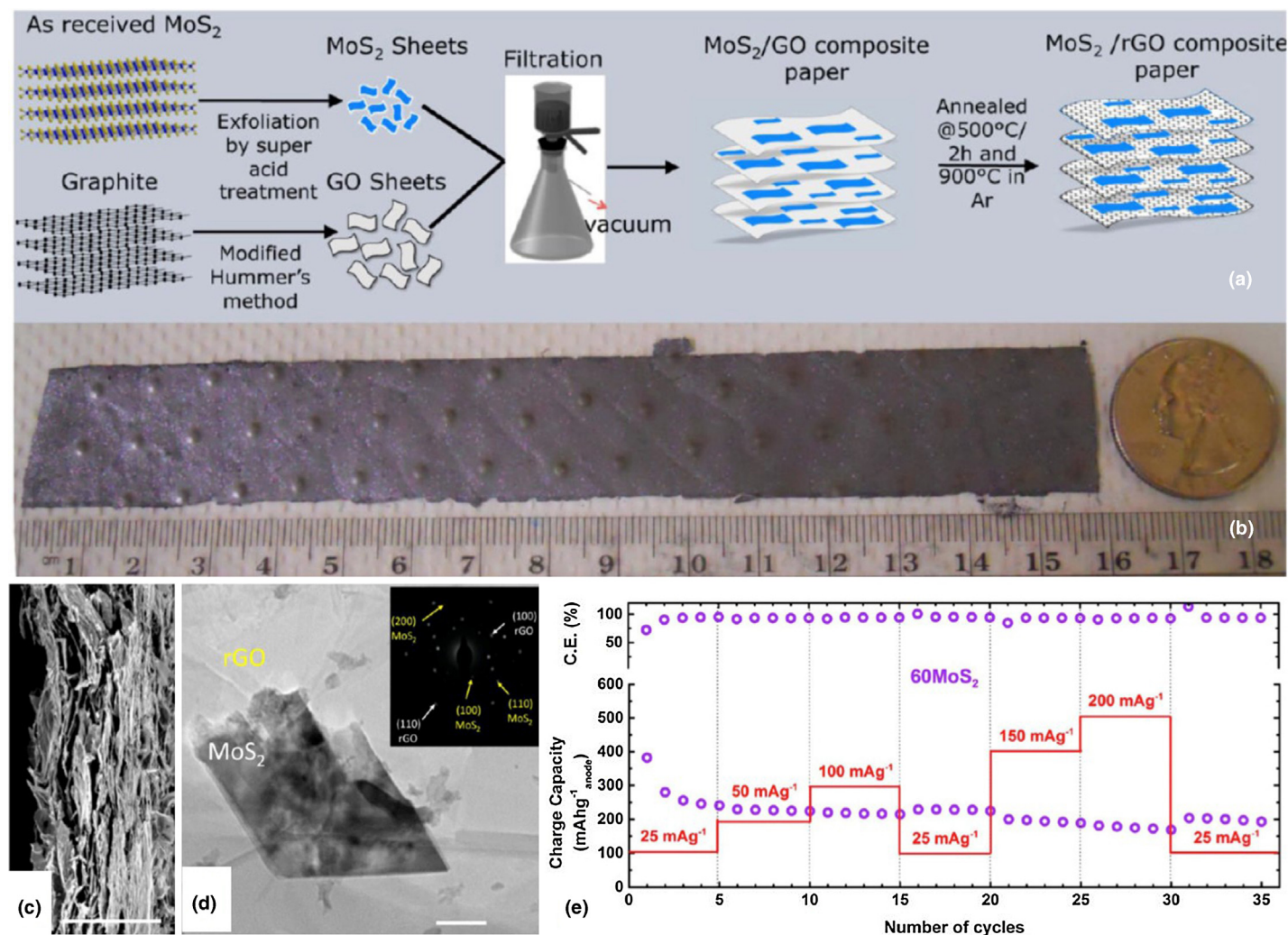
FIGURE 4

(a) Schematic cartoon depicting the synthesis of rGO/MoS$_2$ composite paper, (b) digital picture showing large-area composite paper, (c) SEM cross-sectional image of the paper, (d) TEM image and SAED pattern of MoS$_2$ (inset). Scale bar is 100 nm. (e) Sodium charge capacity and corresponding coulombic efficiency of the electrode cycled at varying current densities. Adapted from reference [23].

varied with the weight percentage of MoS$_2$ in GO (Fig. 4c). High-resolution imaging shows that graphene wraps few layers of MoS$_2$ forming a very good electron conductive layer (Fig. 4d).

Acting as both an active material and a current collector, the composite paper when used as a negative electrode, offered a stable charge capacity of 230 mAh/g, with respect to total electrode weight and the coulombic efficiency nearing 99%. Here, the graphene-based freestanding paper electrode provides a porous and flexible support structure for MoS$_2$ to undergo a reversible conversion-type reaction with Na ions. At a high current density of 200 mA/g, the hybrid paper electrode shows stable charge/discharge cycle without abnormalities (Fig. 4e), an indication of high mechanical stability (2–3 MPa) of the electrode probably due to the interleaved structure. Disassembling the cell post electrochemical tests revealed no cracks or volume changes. This first experimental evidence of reversible electrochemical storage of Na in a layered freestanding composite electrode at room temperatures is expected to open new avenues for use of such films as flexible electrodes for rechargeable battery applications.

Supercapacitors

Electrochemical supercapacitors, a class of next generation energy-storage devices, with high power and energy densities are urgently required to feed power-hungry portable devices. Generally, divided into two types, electrochemical double-layer capacitors (EDLCs) and pseudocapacitors, these devices find application in ambitious hybrid electric vehicle and backup power grids mainly due to the prolonged cycle life and wide thermal operating range. In addition, supercapacitors can be expected to complement todays LIBs. For example, an asymmetric structure where one supercapacitor like electrode and other battery type electrode is combined to provide enhanced capacitance for many devices.

For both EDLC and pseudocapacitors, electrodes materials with large surface area and high electrical conductivity are required. Carbon-based electrodes especially graphene-based typically fulfill these requirements. MoS$_2$, having a layered structure similar to graphite with a basal and an edge plane, is known to be electrochemically active on its edges. Although having unique features resembling graphene, MoS$_2$ nanosheets are rarely used as an electrode material of supercapacitors [52] due to their intrinsically

low electrical conductivity and its tendency to form fullerene like structures during processing. To fabricate a high performance supercapacitor using such metal sulfides, a conducting substrate is often necessary which will inhibit unusual growth of the crystal and instead which results in the formation of layers of MoS_2 over graphene layers [53]. This will indeed facilitate electron transport through MoS_2 nanostructures, providing an easier and faster ion diffusion between MoS_2 layers and the electrolyte to yield high specific capacitance in a whole.

Utilizing a microwave technique, recently Liete and co-workers prepared supercapacitor electrodes by directly bonding layered MoS_2 on GO substrate without the need for any further treatment because GO is partially reduced due to microwave irradiation [54]. Electrochemical measurements were carried out on samples with low, medium, and high concentrations of MoS_2. As a result, the specific capacitance values of the MoS_2/rGO composites at 10 mV/s were 128, 265 and 148 F/g, respectively. In low concentrations of MoS_2 in the composites, the electrode delivered an energy density of 63 Wh/kg. 92% of the specific capacitance was retained after 1000 cycles indicating superior cyclability.

Detailing on the L-cysteine assisted solution-phase method as discussed previously [37], Huang and co-workers prepared MoS_2/rGO composites recently and used them as electrodes for supercapacitors [55]. A capacitance of 243 F/g was achieved at a current density of 1 A/g with energy density of 73.5 Wh/kg at a power density of 19.8 kW/kg. The above studies suggest that these hybrid composites are suitable and promising electrode materials for high-performance supercapacitors.

Photovoltaics (dye-sensitized solar cells-DSSCs)

The conversion of sunlight directly into electrical energy (light-to-energy conversion) through the photovoltaic effect is an efficient strategy to address the looming energy crisis and looked at as a viable alternative. A solar cell, also known as photovoltaic cell (PV) is one such device that has long been in research for this reason. Including silicon-based solar cells, several other types such as dye-sensitized solar cells (DSSCs), hybrid solar cells, and organic solar cells, have been in focus. Among them, the DSSC is most promising device due to their ease in fabrication, low cost, environmental friendliness and high efficiency. Consisting of a photoanode, a redox couple based electrolyte and a counter electrode; the latter is one of a crucial component in a DSSC that serves as a catalyst in reducing the redox couple. Thus far, platinum (Pt) is predominantly used as a counter electrode. However, the use of expensive and rare Pt severely impedes large-scale manufacturing of DSSCs. Developing an alternative lightweight, low cost counter electrode along with high electrocatalytic activity and stability is therefore an important challenge.

In the race to replace Pt, graphene has emerged as a wonder material owing to its large surface area, high electron mobility and more importantly due to its strong electron accepting capability. In addition, graphene being an excellent sunlight absorber, achieving 2.3% visible light absorbance in just 3.3 Å thickness, holds strong promise for ultrathin photovoltaics [56]. Modifications of graphene-based materials such as doping, functionalization and hybridization with foreign moieties have been fruitful in achieving enhanced efficiencies [57]. Although possessing the essential characteristics for an ideal DSSC, the efficiency of

graphene-based counter electrodes are far from satisfaction and are mostly embodied with merits and de-merits. MoS_2 with similar layered structure is known to have potential as a counter electrode because of its indirect band gap of -1.2 eV in the bulk form. Up to day, however, only a handful of studies report on the use of MoS_2/graphene hybrids for solar cell applications.

Taking advantage of the exotic properties of both the layered materials, Liu et al. [58] fabricated such composites by using GO and ammonium tetrathiomolybdate as precursors followed by reduction to produce MoS_2/rGO composites. Here, the high surface area of graphene promotes uniform deposition of MoS_2 nanoparticles across the surface of the rGO sheets. Because of the high conductivity of rGO, the electrons are easily shuttled across the material to the catalytic sites in MoS_2 aiding in the reduction of tri-iodide species (Fig. 5a). An efficiency of 6.04% comparable to that of sputtered Pt counter electrode was obtained (Fig. 5b). The same group embedded graphene flakes into MoS_2 matrix via an in situ hydrothermal route [59]. It was found that the hybrid counter electrode with 1.5 wt% of graphene demonstrated the relatively enhanced electrocatalytic activity with a high power conversion efficiency of 6.07% under standard illumination, up to 95% of the level obtained using conventional Pt CE, which was roughly 6.41% (Fig. 5d). In both the above cases, the high electrocatalytic activity for iodide reduction was attributed to the synergistic effect between the components that provide fast electron transport network (Fig. 5c). The above numbers in terms of power conversion efficiency was very similar to that obtained by the same group earlier (5.98%) using such composite films with a graphene content of 1.5% [60]. The authors claimed that the thickness of the film and graphene content in the hybrid influenced the photovoltaic efficiency of DSSC.

Optical transparency in DSSCs is of substantial benefit for location-based needs such as roof panels, windows or various decorative facilities involving metal-foil-supported plastic solar cells. Hence the need for counter electrodes with high transparency coupled with fast electron transfer kinetics is paramount. Transparent counter electrode comprising MoS_2 and graphene nanosheets were reported using an electrophoretic deposition technique [61]. The resultant composite counter electrode demonstrated high transmittance up to 70% at visible wavelengths. This Pt free counter electrode exhibited an impressive photovoltaic conversion efficiency of 5.81%, which is around 93% of that obtained using a conventional Pt counter electrode (6.24%). It is important to note that such transparent characteristic provides promising potential for power-producing windows. All the above results indicate that the hybrids of MoS_2/graphene are promising counter electrode catalysts for low-cost and highly efficient DSSCs.

Hydrogen generation by splitting water (hydrogen evolution reaction)

Hydrogen generation by the conversion of solar fuel (sun light) or simply splitting water is a prime and important source for clean energy. Since the remarkable breakthrough by the Japanese scientists Fujishima and Honda in 1972 [62] there has been a surge in the development of catalysts for water splitting. It is envisioned that hydrogen can play a major role in the development of sustainable energy and clean environment thereby providing a solution to both energy shortage and environmental problems.
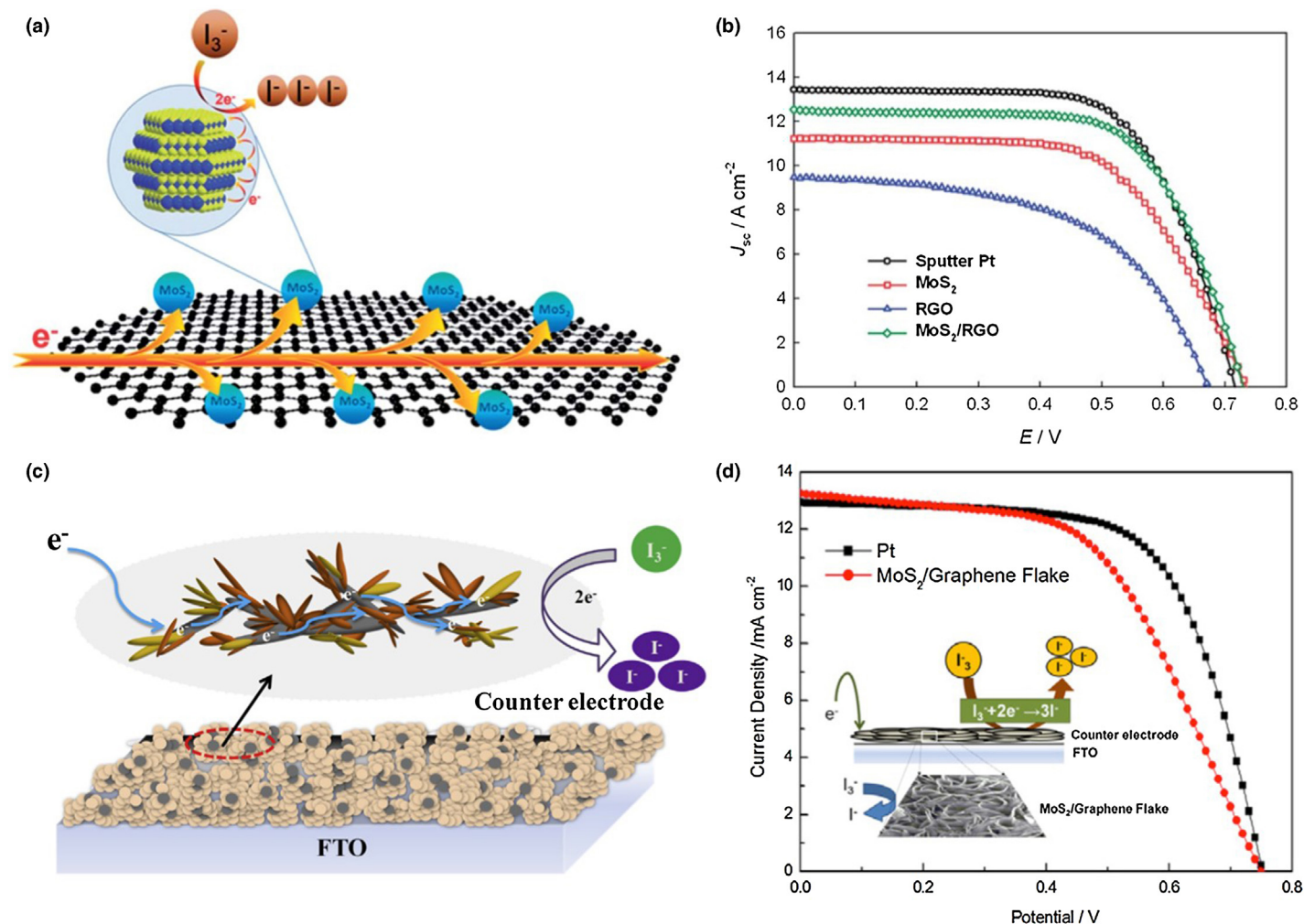
FIGURE 5

(a) Schematic depicting catalytic mechanisms of MoS$_2$/rGO hybrid, (b) photovoltaic performances of DSSCs based on MoS$_2$, rGO, MoS$_2$/rGO composites and sputtered Pt CEs. Adapted from reference 58. (c) Schematic for the possible synergistic effect of the hybrids produced by hydrothermal route and (d) photovoltaic characteristics of the cells using various CEs under the standard illumination. Adapted from reference [59].

Until now, water splitting is the best-known methodology for the mass production of hydrogen.

Water splitting can be divided into two half-reactions, namely, the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The latter step ($2H^+ + 2e^- \rightarrow H_2$) is the reduction half-reaction that needs an excellent catalyst to reduce the over-potential, thereby increasing the efficiency of splitting water into hydrogen and oxygen. While platinum with near zero over-potential is known to be the most effective catalyst under acidic conditions, again, the cost and depleting natural reserves inhibits its use not only for water splitting reaction, but also for several other important reactions such as oxygen reduction reaction (ORR) in fuel cells and counter electrodes used in solar cells etcetera as discussed in the previous sections. Therefore, it is highly imperative to develop alternative catalysts that are abundant and cost-effective and simultaneously have a high current density.

Recent advances [5,63] in TMDC research highlight few layered MoS$_2$ to be promising and inexpensive alternative for HER owing to its ample number of active edge sites and higher specific surface area [63]. Although MoS$_2$ is regarded as an excellent candidate for water splitting having a moderate over-potential of 0.1–0.2 V, the hybrids of graphene derivatives with MoS$_2$ could serve as new type of co-catalyst owing to the unusual synergetic effect between MoS$_2$ and conductive graphene. As an example, solvothermal synthesis of MoS$_2$ nanoparticles on rGO sheets resulted in better HER activity with a low onset potential compared to MoS$_2$ (Fig. 6a) [64]. Because of the ample number of MoS$_2$ crystals dispersed uniformly on the graphene (rGO) support (which forms an inter-connected conducting network to afford rapid electron transport) (Fig. 6b), the high concentrations of exposed edge-plane structures of MoS$_2$ significantly elevated the catalytic activity. The polarization curves show an over-potential as small as of ~0.1 V (Fig. 6c) with large cathodic currents and a Tafel slope of −41 mV/decade was measured (Fig. 6d).

Similarly, selective synthetic routes including hydrothermal methods and solvent-evaporation-assisted intercalation followed by solvothermal treatments to process MoS$_2$/rGO hybrid composites were carried out [53,65,66]. In all cases, it was shown that graphene provides good electrical coupling to the hybrid electrodes for efficiently transferring electrons, thereby leading to high electrocatalytic activity in HER. In another instance, Jaroniec and co-workers prepared TiO$_2$ nanoparticles on such hybrids following
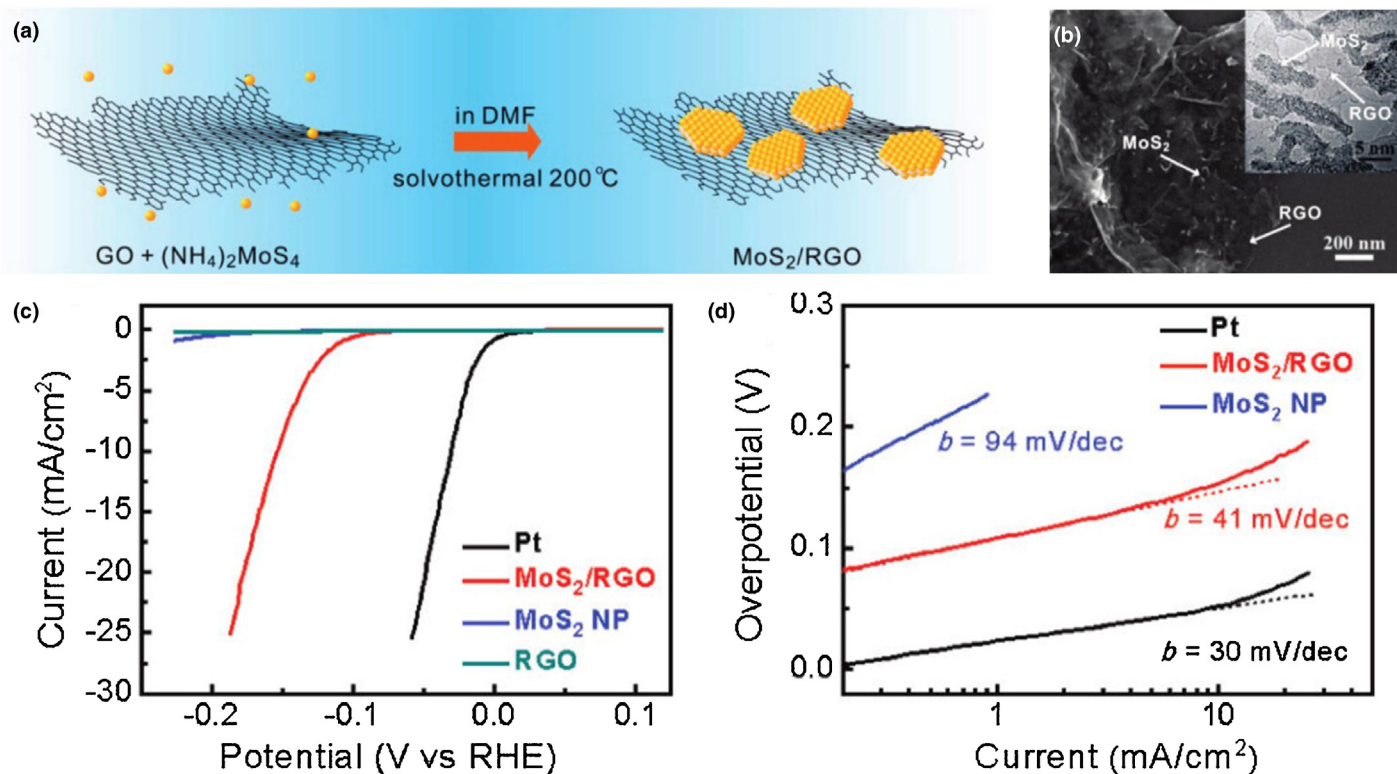
FIGURE 6

(a) Schematic solvothermal synthesis with GO sheets to afford the MoS$_2$/rGO hybrid, (b) SEM and TEM images (inset) of the hybrid, (c) polarization curves obtained with several catalysts as indicated and (d) corresponding Tafel plots recorded on glassy carbon electrodes with a catalyst loading of 0.28 mg/cm^2. Adapted from reference [64].

a two-step hydrothermal process to enhance photocatalytic hydrogen production [67]. With only a small content of graphene (5 wt%) close proximity of TiO$_2$, MoS$_2$, and graphene components were achieved. This positive synergetic effect between the components in the hybrid co-catalyst favored the transfer of photogenerated electrons from TiO$_2$ to MoS$_2$ and/or graphene sheets, thus enhancing the charge separation and photocatalytic efficiency.

Nitrogen-doped graphene not only plays a crucial role in many of the applications described above, but also finds significant relevance in hydrogen generation as nitrogen incorporation in graphene leads to improved catalytic activity of the composite by enhancing the electron donating ability of the graphene. Recently, Rao et al. [68] demonstrated the HER activity of heavily nitrogenated graphene composited with few-layer 2H-MoS$_2$. They found that the composite exhibited much better H$_2$ evolution compared to 2H-MoS$_2$ alone.

Because 3D architectures have several known merits over 2D ones, such as preventing graphene from restacking and increasing the specific surface area, MoS$_2$ nanoparticles were formed on mesoporous 3D graphene foams (MoS$_2$/MGF) via a hydrothermal route [69]. The 3D architectural graphene not only allowed the intimate growth of highly dispersed ultrafine MoS$_2$ nanoparticles onto its surfaces, free of aggregation, but also facilitated rapid electron transfer. The hybrid exhibited excellent electrocatalytic activity for HER, with a Tafel slope of 42 mV/decade. Prior to this report, Chang et al. showed that graphene sheets grown on 3D Ni foams at relatively low temperature (120°C) could efficiently

increase the MoS$_x$ catalyst loading. Such a configuration provides robust protection of Ni against corrosion and therefore was highly stable in acid environment, leading to the enhancement in electrocatalytic HER efficiency. A Tafel slope of 42.8 mV/decade was measured [70].
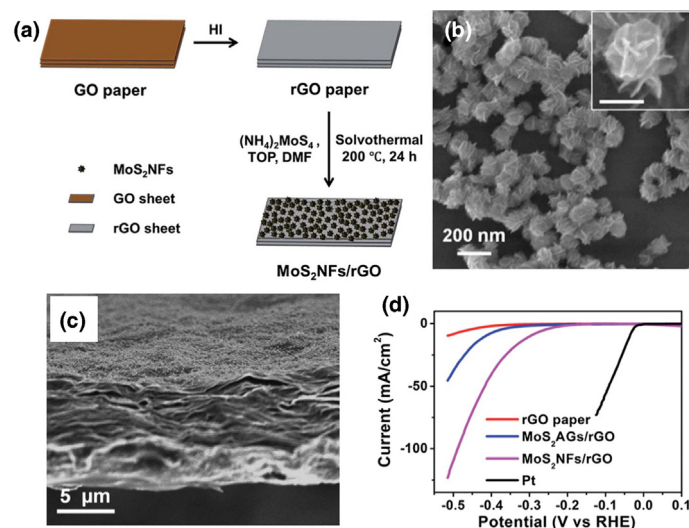

FIGURE 7

(a) Schematic of the fabrication process of MoS$_2$NF/rGO paper, (b) SEM and high magnification SEM image (inset), (c) cross-section of MoS$_2$NF/rGO, and (d) polarization curves of MoS$_2$NF/rGO, MoS$_2$AG/rGO, rGO paper and Pt (AG – aggregates). Adapted from reference [71].

Flower like morphologies of MoS_2 (MoS_2NF) coated on rGO paper were prepared through a one-pot solvothermal method (Fig. 7a,b) [71]. Again, here, the rGO paper serves as a conductive and flexible substrate to support the MoS_2NFs. These free standing and durable working electrodes were directly used for HER. Although a small over-potential of -0.19 V was recorded, a Tafel slope of ~95 mV per decade was measured [71], which was more than double than previously reported values [64,69,70]. The electrodes, however, exhibited good stability with negligible current loss after 300 cycles suggesting that the electrodes were highly durable.

Since most of the techniques to prepare such hybrid composites involve GO or rGO as a precursor, there is always an element of doubt that is created, as both the components are prone to restacking. Therefore, introducing another conductive and electrocatalytically active component to the MoS_2/graphene hybrid to produce a ternary composite is an effective idea or at least to prevent re-aggregation of sheets. Thus, Yan et al. introduced tungsten monocarbide (WC) to the hybrid in a one-step solvothermal process. The resultant MoS_2/WC/rGO composite with highly exposed reactive sites stabilized by the binary support enhanced the electrocatalytic activity in the HER process. The authors attributed the synergism between the co-catalyst and high conductivity of the ternary composite for the high HER activity [72]. On a similar note, very recently, CdS nanocrystals were grown on the surface of a nanosized MoS_2/graphene hybrid by solution-chemistry approach to yield a 3D hierarchical configuration. These noble metal-free photocatalysts were evaluated for H_2 evolution under visible light irradiation [73]. The authors claimed that by optimizing each component proportion in the MoS_2/graphene/CdS composite, the hybrids exhibited enhanced photocatalytic activity for H_2 production.

Sensing

Sensors are of paramount importance in medical diagnostics, security, forensic sciences as well as environmental monitoring. Platforms of 2D layered materials play a vital role in this arena of science. It is well known that the high surface-to-volume ratio of these 2D materials enables better adsorption of gas molecules and thus lead to lower electrical noise and better detection limit. In addition to surface-to-volume ratio, semiconducting properties and the availability of reactive sites for redox reactions are especially important for enhanced sensitivity. Functionalizing graphene surfaces with other 2D materials, particularly MoS_2, provides a promising platform for the development of a viable and effective sensor because of the band-gap, which leads to synergistic effect with selective reactivity upon exposure to a range of analytes.

On the above basis, layered MoS_2/graphene composites synthesized by L-cysteine-assisted solution-phase method as reported previously [37] were used to modify glassy carbon electrodes for the construction of an electrochemical sensor [74]. Such an electrode favored electron transfer kinetics for acetaminophen detection. Later, the same group used these hybrids to construct an electrochemiluminescence aptasensor based biosensor. Glassy carbon electrodes trickled with MoS_2/graphene hybrids were immersed in gold nanoparticles (AuNPs) containing colloidal solution, where AuNPs assemble on the electrode following the

famous gold-thiol chemistry. These modified electrodes were used for the detection of thrombin, an important blood enzyme responsible for coagulation [75]. The aptasensor with a sandwich structure had good stability with high electrochemiluminescence response. In another instance, AuNPs were assembled on the surface of poly(diallyldimethylammonium chloride)(PDDA) functionalized graphene/MoS_2, which had a flower like morphology using the gold-thiol chemistry. Here, the positively charged polyelectrolyte PDDA, plays a dual role: it prevents restacking of graphene via noncovalent functionalization and enhances the dispersion properties. The hybrid modified glassy carbon electrodes were used for the detection of eugenol, a semivolatile phenolic compound found in herbal species and widely used in cosmetic industries. The authors claim that the modified electrode displayed a wide linear range and a low detection limit with outstanding stability and reproducibility [76]. Similarly, hydrogen peroxide (H_2O_2) detection is also very important chemical, biological and industrial samples for a clean environment. Very recently, it was demonstrated that a biosensor constructed by the combination of the negatively charged MoS_2/graphene hybrid and positively charged horseradish peroxidase (HRP) enzyme (electrostatic attraction) could detect trace amounts of H_2O_2 [77].

Detection of specific DNA or peptide sequences is of significant importance in forensic sciences as well as disease diagnostics and other bio-medical applications. Existing methods in DNA profiling are tedious and costly. Graphene/rGO-based field-effect transistors have shown potential in label-free DNA detection in sub-femtomolar levels [78]. The large surface area and unique electrical properties of such a layered material render them suitable to interface with biomolecules. Loan et al. [79] recently developed a graphene/MoS_2 hetero-structured film for the detection of DNA hybridization. Here, graphene serves as a compatible interface layer to host DNA molecules on its surfaces as well as a protection layer to prevent the reaction between MoS_2 and the ambient environment. The authors claimed that the photoluminescence (PL) intensity of the MoS_2 layer in the hybrid stack increased with the concentration of the added target DNA. A confocal laser system was used to probe the PL signal of the heterostructures (Fig. 8a). The integrated PL peak area mappings collected before and after the probe DNA immobilization, and after the addition of the DNA analyte solutions with various concentrations revealed that the graphene/MoS_2 stacks responds to the target DNA but not to the mismatched DNA, thus demonstrating the capability of this technique to differentiate these DNA molecules (Fig. 8b,c). The authors' findings revealed that fast response time and real time detection at a concentration as low as 1 attomolar (10^{-18} mol/ dm^3) levels could be reached with such an ultrasensitive platform.

Device applications and field emitting properties

Because of the high carrier mobility of up to 10^6 $cm^2V\,s^{-1}$, graphene-based field effect transistors (FETs) have been studied with great interest and reviewed recently [80]. In general, graphene being a semimetal with no band gap, these FETs could not be used for conventional transistors or logic circuits for low-power electronic switching at room temperatures, because of the small current on/off ratio [81]. Several techniques such as doping, chemical functionalization, application of high electric field on graphene, and even tailoring a graphene like nanoribbon were
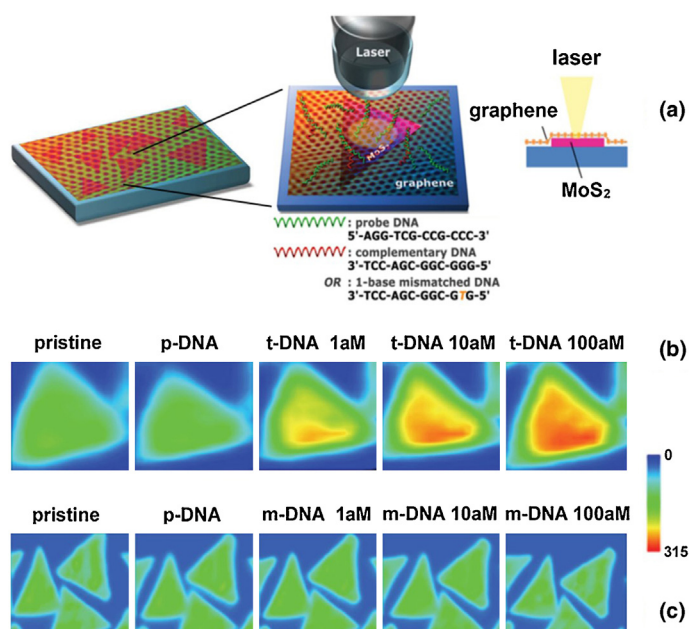
FIGURE 8

(a) Illustration of the DNA detection method using a microscope and the graphene/MoS$_2$ heterostructure sensor, (b) photoluminescence peak area mappings of the graphene/MoS$_2$ heterostructure hybridized with the complementary target DNA and (c) mismatched DNA. Adapted from reference [79].

done to modulate the band gap of graphene. Although boron/nitrogen co-doping exhibited a band gap of 3.3 eV and a 10.7 on/off ratio [81], most of the other aforementioned modifications might diminish mobility in the process. Inspired by the advances of graphene based FETs, recently, the atomically think TMDCs, especially MoS$_2$ possessing semiconducting characteristics have exhibited extensive applications in transistors, sensors, memory devices, and optoelectronic devices. The direct band gap of around 1–2 eV renders MoS$_2$ suitable as channel materials in FETs. Therefore, there has been a substantial interest in utilizing these 2D TMDCs in electronics and optoelectronics as reviewed in greater detail elsewhere [82,83].

Because graphene is semi-metallic, it could form the ideal contact to 2D semiconductors, capable of supporting large current densities for large-scale 2D electronics [84]. Here, we highlight, in brief, the designing of MoS$_2$ and graphene heterostructures in
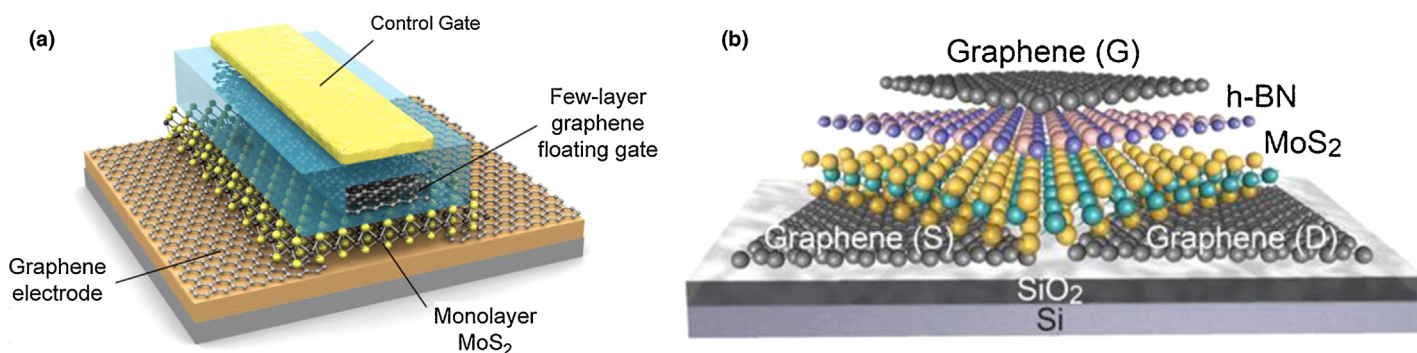
pursuit of novel devices over the past three years. Using a vertically stacked graphene/MoS$_2$/graphene sandwich structure, Britnell et al. [85] demonstrated a tunneling transistor with MoS$_2$ acting as an ultrathin tunneling barrier between two graphene electrode layers. Later it was shown that such a vertical integration of layered materials could enable the design of novel electronic and photonic devices for efficient photon harvesting [86]. Myoung et al. further studied such vertical heterostructure tunneling transistors. The transistors prepared by sandwiching MoS$_2$ layers between graphene layers not only show high on/off ratios, but also spin dependent tunneling showing potential in spintronics [87].

Highly flexible and transparent FETs constructed with single-layer MoS$_2$ channels, were fabricated by a mechanical stacking process with hBN as dielectric and graphene as gate electrodes, exhibited field-effect motilities in the range of 45 cm^2 V^{-1} s^{-1} with a low operating gate voltage below 10 V with greatly reduced hysteresis [88]. Similarly, a highly flexible and transparent transistor was also developed based on an exfoliated MoS$_2$ channel and CVD-grown graphene source/drain electrodes without hBN [89]. The authors claimed that the introduction of 2D nanomaterials provided a high mechanical flexibility, optical transmittance of −74%, and current on/off ratio (>10^4) with an average field effect mobility of −4.7 cm^2 V^{-1} s^{-1}.

The unique electronic properties of semiconducting monolayer MoS$_2$ with the high conductivity of graphene when combined leads to a 2D heterostructure capable of information storage [90]. These non-volatile memory cells with monolayer MoS$_2$ as the channel semiconductor and single-layer graphene as the floating gate (Fig. 9a) [90] showed very stable operation resulting in a factor of 10^4 difference between memory program and erase states. Later Roy et al. [91,92] demonstrated the optoelectronic functionalities of these hybrids, including highly sensitive photodetection and gate-tunable persistent photoconductivity showing promise in photoresponsive memory devices. Unlike the previously prepared heterostructures, metallization was carried out with Ti/Au [93] and only a single layer of graphene was part of the structure [91]. By contrast, such a structure was constructed using rGO and MoS$_2$ nanosheets recently. Preferable photoresponse activity under the illumination of ultraviolet light was observed [94].

Shih and co-workers studied the electron transfer, photoluminescence, and gate-controlled carrier transport in such a heterostructure. They found that the junction is a Schottky barrier, whose height can be artificially controlled by gating or doping

FIGURE 9

(a) Three-dimensional schematic view of the memory device based on single-layer MoS$_2$/graphene heterostructure. Adapted from reference [90]. (b) Illustration of FETs built on all 2D material components. Adapted from reference [96].

graphene. A very high room temperature on/off current ratio (−36) was obtained. The authors also showed that the on/off current ratio could be tuned to be as high as −100, without sacrificing the field-effect mobility of graphene at room temperature [95]. Roy *et al.* [96] went another step further to heterogeneously stack 2D materials for all of the components, including the semiconductor, insulator, and metal layer (Fig. 9b). Specifically, MoS_2 was used as the active channel material, hexagonal-BN as the top-gate dielectric, and graphene as the source/drain and the top-gate contacts [96]. This transistor exhibited n-type behavior with an on/off current ratio of $>10^6$, and an electron mobility of −33 cm^2/V s.

Several other groups demonstrated the use of such hybrid heterostructures for various purposes. For example, Tan *et al.* [97] fabricated a small-signal generator based graphene/MoS_2 heterojunction. Zhang *et al.* [98] demonstrate that graphene was transferable onto large-area and continuous MoS_2 monolayer grown by a CVD method. Photodetectors based on the heterostructures was able to provide a high photogain. Electrical characteristics of multilayer MoS_2 FET's with MoS_2/graphene heterojunction contacts were also investigated. The charge transport mechanism in both junctions was determined to be either thermionic-field emission or field emission depending on bias voltage and temperature [99].

In addition to high-performance FETs and logic devices, such hybrids produced in large scale, in solution are also ideal for large-area electronics that are flexible and transparent. Recently, Finn *et al.* demonstrated that a range of 2D materials could be printed in combinations to form integrated structures. The authors found the interface between MoS_2 and graphene to be extremely uniform and to give apparent Ohmic behavior. The resultant structure was found to display reasonable photoconductive properties [100].

Summary and outlook

Clearly, hybrids of graphene and related metal dichalcogenide, especially MoS_2, are an emerging class of next generation nanomaterials. There has been a substantial interest in utilizing these nanomaterials for a range of applications from energy to sensing and electronics, which have been well documented in the past three years. Above, we have provided an up to date account and highlighted important advances involving these heterostructures over the past three years. Opportunities and challenges exist equally in various fields as detailed above. In the field of energy conversion and storage, such hybrids show tremendous potential as anodes in LIBs as the interlayer spacings provide a convenient environment for the accommodation of guest species, for example lithium ions; literally, this structure facilitates lithiation and de-lithiation. While lithiation could lead to structural instability during exfoliation, this factor did not affect LIBs studies [23]. Further insight would be fruitful for other purposes. Due to the electrolyte decomposition the formation of a solid-electrolyte interface and the loss occurring during the first cycle poses a major concern. Attempts to minimize this loss or overcome this issue should be beneficial. Although many efforts are focused on LIB and water splitting using graphene/MOS_2 hybrids, relatively a few studies have been reported on their use as supercapacitors. Recent research indicates that high-performance supercapacitors can be prepared by using these hybrid electrodes [54,55]. Impressive

capacitive behavior reported for the hybrid material was attributed to the combination of faradic and non-faradic processes of the active MoS_2 layers coupled with highly conductive graphene sheets. With global energy consumption increasing at an alarming rate, improving supercapacitor performance should be a future direction. Bringing in a ternary conductive material to form composite hybrids can further enhance device performance. One minority view is that the oxygen dissolved in aqueous electrolyte, in general, can easily oxidize TMDCs, which can lead to unstable structures. Fortunately, these have not been noticed in the reports thus far. This factor should be looked in to. Application of these hybrid materials in solar cells, especially DSSCs, are very rare and therefore future research should urgently scrutinize this topic.

Stupendous improvements have been achieved in the field of hydrogen generation. Future research should elucidate the mechanisms of HER activity. As the catalytic activity is layer and morphology dependent, close attention should be paid to designing novel architectures and methods to improve the surface area should be looked in to, as 3D porous structures are known to improve the specific surface area as well as prevent aggregation. In addition, functionalization or doping is one strategy that can be built on. Thus, it is possible to produce new hybrid materials with unprecedented functionalities not only for HER enhancement, but also for energy storage.

Because of the direct band-gap, MoS_2 was widely used as channel materials in logic transistors. Heterostructures based on graphene and MoS_2 have been used to construct non-volatile memory cells, signal generators as well as photodetectors. For such applications, large area and high quality crystals are crucial. Therefore, controllable synthesis of these hybrids is of both great significance and a challenge which needs to be further explored. On one hand research could focus on the scalable production of such materials, while by contrast, efficient exfoliation and CVD methods and thickness control techniques need to be developed. Although, hybrids of graphene and MoS_2 are excellent substrates for energy storage, sensing, hydrogen generation and electronics, there is much room for scientific advancement, and therefore a great deal of effort is still needed to explore for practical applications. Certainly, the future of such hybrid materials, in general, should be exciting as new opportunities are uncovered.

Acknowledgements

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