Review Article **ISSN: 2349 – 7106**

Asian Journal of Research in Chemistry and Pharmaceutical Sciences
Journal home page: www.ajrcps.com

A REVIEW ON "GRAPHENEVS GRAPHENE-MOS$_2$ HYBRID MATERIALS: A ROLL IN ENERGY STORAGE DEVICE"

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ABSTRACT

The graphene, graphene-based as well as graphene/MoS$_2$ hybrid composite are promising for applications in energy storage devices due to the intriguing properties, such as, highly tunable surface area, outstanding electrical conductivity, good chemical stability and excellent mechanical behaviour. While graphene itself is chemically inert and a gapless semimetal, its isostructural analog, molydenumdisulfide (MoS$_2$) is chemically versatile with band gaps, thereby finding significant use in a myriad of applications. Although this 2D nanomaterial individually possesses tremendous authority for various applications, the combination of these materials in the recent past has created a new paradigm in emerging applications. Here, I try to attempt a comparative study between grapne/graphene-based vs graphene/MoS$_2$ hybrid materials in the applications as energy storage devices.

KEYWORDS

Graphene/MoS$_2$composite, Supercapacitors, Pseudocapacitance, Nanoflakes and Cycling stability.

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INTRODUCTON

Graphene is an allotrope (form) of carbon consisting of a single layer of carbon atoms arranged in a hexagonal lattice. It is the basic structural element of many other allotropes of carbon such as graphite, charcoal, carbon nanotubes, and fullerenes. It can be considered as indefinitely large atomic molecule, the ultimate case of the family of flat polycyclic aromatic hydrocarbons. Graphene has many unusual properties. It is the strongest material ever tested, efficiently conducts heat and electricity and is nearly transparent. Graphene shows a large and nonlinear diamagnetism[1], which is greater than that of graphite, and can be levitated by neodymium magnet. Scientists theorized about graphene for years. It had been unintentionally produced in small quantities for centuries, through the pencils and other similar graphite applications. It was originally observed in electron microscopes in 1962, but it was studied only while supported on metal surface[2]. The material was later rediscovered, isolated and characterized in 2004 by Andre Geim and Konstantin Novoselov at the University of Manchester[3,4]. Research was informed by existing theoretical description of its composition, structure and Properties[5]. This work resulted into the winning of noble prize in Physics in 2010 “for groundbreaking experiments regarding the two-dimensional material graphene”[6]. Graphene is a well-known two-dimensional carbon monolayers composed of all sp^2-hybridized carbons with some of the most intriguing properties, i.e., lightweight, high electrical and thermal conductivity, highly tuneable surface area (up to 2675 m^2/g), strong mechanical strength (1 TPa) and chemical stability[7-9]. The combination of these outstanding physical, mechanical and chemical properties make graphene-based materials more attractive for electrochemical energy strorage and sustainable energy generation, i.e, Li-ion batteries, fuel cells, supercapacitors, and photovoltaic and solar cells[10].

Graphene-based materials have been extensively investigated as a conducting network to support the redox reactions of transition metal oxides, hydroxides and conducting polymers. Indeed, these nanohybrid electrodes consisting of graphene and nanoparticles of transition oxides/hydroxides or conductive polymers show the superior electrochemical performance, as a result of the synergistic effect which graphene layers facilitate the dispersion of metal oxide/hydroxide nanoparticles, and act as a highly conductive matrix for enhancing the electrical conductivity, and the metal oxide/hydroxide/conducting polymers offer the desired pseudo capacitance. Graphene has been synthesized in different ways and on different substrates. Graphene was first exfoliated mechanically from graphite in 2004[3]. This simple, low budget technique has been widely credited for the explosive growth of interest in graphene. Graphene flakes have been invaluable to the study and elucidation of graphene properties. Unfortunately, however, they are usually available at a size of several-microns (or tens of microns at best), have irregular shapes, and their azimuthal orientation is not deterministically controlled. Technological applications that take advantage of graphene's extraordinary electronic transport properties require structurally coherent graphene on a large scale (e.g., wafer-scale), or large arrays of graphene flakes positioned with a unique azimuthal orientation on a substrate. The latter structures have not yet been demonstrated with flakes and this technology is expected to have limited relevance to commercial high-end electronic applications. Graphene and few-layer graphene (FLG) have been grown by chemical vapor deposition (CVD) from C-containing gases on catalytic metal surfaces and/or by surface segregation of C dissolved in the bulk of such metals. Depending on the solubility of C in the metal, the former or the latter can be the dominant growth process, or they can coexist. A lot of work has been devoted since to the study of the formation of single or few layer graphite by surface segregation of C during annealing of various C-doped metals; The ability to select the host substrate independently of the sacrificial growth substrate is a major advantage for graphene grown on metals. At the same time, the transfer process often affects negatively graphene's integrity, properties, and performance. Wrinkle formation, impurities, graphene tearing, and other structural defects, can occur during transfer. Graphene growth on (not necessarily flat) substrates with sizes limited only by the size of the reactor, or in a continuous roll-to-roll process[11], enables graphene production at a large scale and lowers the cost per unit area. This will potentially enable several large area applications of graphene in the future. Graphene oxides (GO) are another important member in the graphene-graphite family, which are considered as derivatives of graphene. They that can be readily made from graphite, exhibit the layered structure and the surface related properties[12,13]. Depending on the synthesis techniques, three can be different surface groups in graphene oxides as well as their distribution on the surface. For instance, the oxygen-containing functional groups [hydroxyl (C-OH), carboxyl (C=O) and epoxy groups (C-O) locate around the edge of graphene sheets and stabilize the quasi two-dimensional sheets. Graphene oxides can easily be reduced into graphene by different reduction method. As a precursor for graphene, GO can easily be derived from the oxidisation of natural graphite at a large scale and low costs. The atomic layers of GO generally comprises phenol epoxy and epoxide groups on the basal plane and ionisable carboxylic acid groups around the edges[14,15]. The acid groups on the ionized edge enable the stabilization of GO in aqueous dispersion in the form of a single- sheet layer through weak dipole and van der waals interaction in the surrounding environment. This makes GO a high degree of processing and dispersion ability in solution, and offers the desired convenient method for producing graphene-based materials in a large scale. Among the various processes, graphene prepared by CVD (Chemical Vapour Deposition) offers the better properties, as a result of their large crystal domain, monolayer structure and less defects in the graphene sheet, which are beneficial for boosting carrier mobility in electronic applications[16]. Hernadez *et al*. Developed chemical method to exfoliate graphite in organic solvent[17]. Therefore, the production of graphe neat a low cost, a high yield and high quality have been taken into account in recent years. In general, the chemical exfoliation of graphite into GOs, followed by controllable reduction of GOs (with reduction agent such as hydrazine hydrate) into graphene is believed to the most efficient and low cost method[18]. To fabricate a highly reduced GO, two step method by Ajayan, *et al*[19] and one step method by Shi et al. [6] was described as well as to reduce the toxicity of reduction agent, Zhu *et al*. Synthesized graphene using sugar as a reduction agent[20] and Zhang *et al*. Employed ascorbic acid[21]. But, one-step hydrothermal method is a versatile and low cost process to produce the rGO. Shi et al. reported the reduction of GO via the one-step hydrothermal approach[22]. The rGO thus shows a high conductance of $5X10^{-3}$ S/cm and a high specific conductance of 175F/g with aqueous electrolyte. Nevertheless, it is rather challenging to completely reduce GO as some of the oxygen containing surface groups are rather difficult to be eliminated. Due to some limitations and disadvantages of graphene based materials, recently researchers concentrated themselves in the field of an emerging class of two-dimensional (2D) materials such as hybrid graphene and metal dichalconogenide, especially MoS_2. In this review, I try to attempt a comparative study on graphene-based material with hybrid graphene/MoS_2 composite. Owing to its fascinating properties and potential applications, graphene is arguably most studied two-dimensional (2D) layered materials 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 may 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[23]. Similar to graphite, the precursor for graphene, MoS_2 bulk crystal that are found in layered forms are naturally abundant as molybdenite. Besides being stable they can easily be exfoliated/prepared[24]. Over the past few years, like graphene, TMDCs individually have been used extensively in catalysis[25], energy storage[26,27], hydrogen generation[28], dehydrosulfurization[29], and nanoelectronics[30]. An inherent problem, however, is the restacking property of these nanomaterials when used individually, as it results in the decrease in activity and hampers its potential for various applications. Functionalization or hybridization of these materials with conductive templates or support such as graphene is an established and effective way to improve the catalytic properties of individual materials and the hybrid 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 between each of the component via synergistic effects. Such a specific structure benefits from both properties, improves the dispersion of MoS_2, enhances mechanical properties[31] 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. Composed of carbon atoms arranged in a honeycomb lattice, graphene has been shown to possess unique properties. On the other hand, TMDCs, especially MoS_2 is composed of three atom layers; a molybdenum layer is sandwiched between two sulphur 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 round 0.65 nm[32]. Unlike graphene, however, the 2D single layer form 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. Generally, graphene and corresponding mimics, particularly the layered TMDCs, can be obtained by several means involving top-down and bottom-up approaches. Besides chemical vapour deposition (CVD)[33,34], liquid exfoliation, electrochemical exfoliation, lithium assisted intercalation and exfoliation[35] solvothermal/hydrothermal methods as well as microwave synthesis[36,37] have been successfully applied for generating graphene and its analog, namely MoS_2[38-42]. 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[43]. Benefitting primarily from the chemical interaction between hybridized components on their interface, these analogs nanostructured materials with enhanced specific surface area become promising building blocks for a diverse range of next generation of nanomaterials architectures[23]. Beside 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^{o}C using ammonium thiomolybdate as a precursor[44]. 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*[33], demonstrated the direct growth of MoS_2 on epitaxial graphene. Therefore the direct formation of MoS_2 on graphene substrates show great potential toward the development of new optical, electronic devices, transport electrodes to name a few. These are significant advances of hybrid 2D materials[23]. Supercapacitors are one application for which 2D materials can greatly increase performance and efficiency. Supercapacitors are unique because they provide a much higher power density than conventional batteries while also having a higher energy density than regular capacitors while still maintaining almost limitless cycling durability. With the continued miniaturization of electronic devices the need of create similar miniature power sources is increasing, and supercapacitors based on 2D materials fulfil these requirements by having high specific capacitance for small active area and masses. The charge storage mechanism in supercapacitors can be divided into two groups; (1) electric double-layer capacitors (EDLCs) and (2) pseudocapacitors. EDLCs store energy through the accumulation ions at the interface between the electrode and electrolyte, and because of this, their performance is dependent on the surface area of the electrode, pore size and electrical conductivity[10]. Pseudocapacitors, on the other hand, use fast reversible redox reaction at the electrode-electrolyte interface, resulting in Faradaic charge transfer. EDLCs have the advantage of almost limitless cyclability with little degradation but comparatively low specific capacitance when compared to pseudocapacitors which have much higher specific capacitance but often suffer from performance degradation with respected charge-discharge cycles[45-47]. To enable comparision between different electrode materials, specific capacitance values are typically normalized by either the mass of the active material (F/g), the projected electrode area (mF/cm^2), or volume (F/cm^3). However care should be taken when comparing specific capacitance values reported in literature, as very low masses (μg) can give greatly overestimated values when extrapolated to the gram or even kilogram scale[48,49], as well as excluding the contribution of conductive additives (such as carbon black) or binding agents. Because of the difficulties in scaling up specific capacitance values for very small masses (μg or mg) of active material to large scale (g or kg) applications, the use of area normalized capacitance (mF/cm^2) is regarded as more accurately scalable[50-52] particularly for thin films of electrode material. Despite the increasing number of studies on the use of MoS_2 in supercapacitor electrodes, very little is understood about the fundamental electrochemical processes that contribute to its electron transfer characteristics and pseudocapacitance[53,54]. As well as Faradaic electron transfer resulting in the change in oxidation states of the Mo and S atoms at edge sites, several non-Faradaic charge storage mechanism have been proposed, including the adsorption of electrolyte ions onto the MoS_2 surface as well as the intercalation of ions between neighbouring layers[55-57]. Previous work on thin layer graphene based supercapacitors has reported a range of specific capacitance from 2 to 5 mF/cm^2 depending on the testing parameters, electrolyte and electrode architecture[58-60]. However, there have been fewer published values for MoS_2 based devices but they range from 2 to 3.1mF/cm^2 for solution exfoliated MoS_2[57,61] and 8mF/cm^2 for hydrothermally grown material[57]. Recently, the use of the metallic metastable IT-MoS_2 phase was demonstrated to be an ideal supercapacitor electrode material due to its high conductivity combined with ion intercalation pseudocapacitance[55]. With the obvious benefits of these 2D materials it is possible to combine graphene with MoS_2 to produce highly efficient composite electrochemical supercapacitor devices. These composite devices are able to produce high gravimetric specific capacitance between 205 and 282 F/g[62-64].

RESULTS AND DISCUSSION

Graphene as well as MoS_2 exhibits remarkably unique and diverse range of properties. Since 2004, the number of graphene-related academic publications has substantially increased. Till the date, there are a range of graphene and graphene/MoS_2production methods (as briefly discussed above), each of which carry their respective benefits, whilst at the same time producing different types of graphene (monolayer, multilayer etc.) and graphene/ MoS_2 which have different applications depending on the properties exhibited by each type of graphene and graphene/MoS_2 hybrid. Graphene and related inorganic TDMCs 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 anlog, 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.

High-speed electronics

The energy crisis is 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 energy 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 perquisite. 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[23]. One of the first proposed real world applications of graphene is related to the conductivity of graphene being extremely high. One would think that a high conductivity would be ideal for high speed electronics. While this is true, electronic devices consists of semiconductors which exhibit small yet significant band gaps which are required for ' on and off' states in an electronic device. Graphene is however a zero band gap material is and hence has yet to make its commercial debut in this manner[65]. Still, although scientists have work tirelessly to create a graphene derivative with a band gap[66-68], the efforts have proved ineffective in terms of application, though recent work has elucidated the origin of the lack of a band gap in bilayer graphene lies with the twisting of the graphene sheet[69]. In fact, a twist as much of 0.1^0 is thought to collapse the band gap. One particular problem with graphene based transistors originates from defects emerging upon the graphene sheet during the fabrication process of the device. Reducing the size of data storage devices, or increasing the capacity of data storage devices whilst maintaining, the size of a piece of hardware is an area which is lesser studied in the graphene world, yet has seen some impressive discoveries. Researchers investigating the storage properties of graphene oxides have shown that indium tin oxide electrodes modified with polymers and graphene oxide exhibit the write-read-erase-read-rewrite cycle for a non-volatile memory device[70]. But C. E. Banks, et al. argued that reducing the size of devices is not so much as an issue, considering USB flash drives are already small; however perhaps it would not be too long until a terabyte can be stored on a USB flash drive sized device whilst keeping the cost of the device to a minimum[65].

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 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 (373mAh/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 anode 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[23]. 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[71].

The prepared composites by one step method were of a 2D nanoflake structure, in which the MoS_2 layer had an interlayer distance of 0.62 nm grown on the surface of graphene[72]. 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. 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 1290mAh/g at a current density of 100mA/g and the capacity retained up to 50 cycles. In addition, the composites demonstrated good rate performance. At a high current density of 1000mA/g, the specific capacity remains at 1040mA/g, which is still higher than that of free MoS_2 and graphene[72]. To enhance the performance of the semiconducting 2H-MoS_2, M. A. Bissett, *et al*[73] produced composites of MoS_2 and graphene in differing ratios and characterized the resulting membranes by Raman and XPS before electrochemical testing. Composite membranes were synthesized by mixing dispersions of MoS_2 and graphene in differing weight ratios: 1:1, 1:3, 3:1 (MoS_2/graphene). The performance of each of these composite membranes was then compared to the respective “pure” membranes (data not shown). It was found that each of the composites had improved performance over the pure membranes, but the 1:3 composite membranes exhibited the highest specific capacitance and so they focused on that ratio[73]. The superior performance of the 1:3 ratio composite is attributed to the balance between the high concentration of highly conductive graphene combined with a smaller amount of MoS_2 flakes to prevent restacking and provide extra surface area. To determine the distribution of MoS_2 and graphene within the composite membranes M. A. Bissett, *et al* used Raman spectroscopy to take a map over a large area. Their study clearly indicated that at all areas measured there was a combination of both graphene and MoS_2 signal. This indicates that during the mixing of the each of the dispersion and subsequent membrane formation, the two materials are thoroughly mixed and evenly distributed. The high surface roughness shown was ideal for thin layer capacitor devices, although some highly reflective larger restacked flakes were visible and the performance of the membrane could be further improved by minimizing those large aggregates. To further investigate the morphology of each membrane, SEM analysis was performed by M. A. Bissett, *et al* and typical SEM images of each membrane was shown and for graphene it was clearly indicated that it consists of many large sheets (3-5μm) forming a highly wrinkled surface and for MoS_2, due to smaller flake size (0.2-1 μm), that forms a smoother continuous film with several cracks formed due to manipulation during the sample preparation. The composite film, because of the combination of the larger graphene sheets and the smaller MoS_2 flakes, they observed a rougher surface with increased surface area which perform better compared to either of the “pure” membranes[73]. 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. 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[74]. By vacuum filtration of GO and MoS_2 sheets dispersed in water/isopropyl alcohol (1:1) solution, the obtained paper was annealed to obtain MoS_2/rGO composite paper with an approximate thickness of 10-20 μm that varied with the weight percentage of MoS_2 in GO. High resolution imaging showed that graphene wraps few layers of MoS_2 forming a very good electron conductive layer.

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 230mAh/g, with respect to total electrode weight and the coulombic efficiency nearing 99%. Here the graphene based freestanding paper electrode provided 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 200mA/g, the hybrid paper electrode shows stable charge/discharge without abnormalities, an indication of high mechanical stability (2-3 MPa) of the electrode probably due to the interleaved structure. Diassembling 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 temperature is expected to open new avenues for use of such film at flexible electrodes for rechargeable battery applications[75].Y. Wang, *et al*, demonstrated[75] in their work vertical graphene nanosheet (VGNS) as an effective platform for the loading of MoS_2 without additional conductive agents and binders[76,77]. VGNS consists of few-layered graphene sheets self-organized in a vertical orientation with an inherently open and interconnected array structure. The structural rigidity of VGNS can prevent the restacking of graphene nanosheets, a commonly observed problem in horizontal graphene[78-80]. Using a simple solvothermal method, they also showed that MoS_2 nano-leaves with a thickness of ~3 nm can be directly grown on VGNS with a controllable mass loading and pore size distribution. This unique nanoarchitecture design offers several attributes for effective energy storage and conversion. First, MoS_2 nano-leaves firmly grow on surface of VGNS, which not only act as the growth backbone for MoS_2 nano-leaves but also provide outstanding electronic conductivity to improve the electron transfer rate. Second, the vertically aligned VGNS's rigid nanostructure could effectively inhibit the MoS_2 restacking issue and mechanical failure during cycling testing, leading to stable performance for energy storage and conversion evaluation. Third, the ultrathin layered structure of MoS_2 nano-leaves, which provide large surface area and defect sites, can effectively enhance the ion accessibility and reduce the ion diffusion length. Owing to these advantages, the resultant binder-free MoS_2/VGNS hybrid electrodes exhibit excellent specific capacity, rate capability and cycling stability for LIBs and greatly improve the electro catalytic efficiency in HER-related applications.

Supercapacitors

Graphene-based fibres and yarns have a great application potential due to the combined merits of tiny volume, high flexibility and weave-ability, which promise some applications in the next generation supercapacitors for wearable and portable devices and electrical vehicles[81]. The carbon based materials, i.e., carbon fibres, CNTs, graphene and mesoporous carbon can be made into various fibre and yarn forms. They can be also hybridized with selected electrical active materials with Faradaic pseudocapacitance, i.e., metal oxides, hydroxides and conducting polymers (e.g., poly-pyrrole, PANI, poly (3,4) ethylenendioxythiophene, PEDOT)[82-85]. A solid electrochemical capacitor made of fibre-shaped rGO coated on Au wire was reported, exhibiting a high specific capacitance of 101.9uF/cm (6.49mF/cm^2) with a rather small capacitance loss (lower than 1%), even when is bent to 120^0 or twisted into an S-shaped structure. To achieve a lighter electrode material, Meng *et al,* developed an all-graphene yarn supercapacitor, where Au wires as a core were replaced with rGO and a sheath of graphene was electrochemically deposited onto the graphene framework. The graphene fibres (GFs) produced show a density of 0.23 g/cm^3, which is 7 times and 85 times lower than that of conventional carbon fibres (> 1.7 g/cm^3) and Au wire (ca. 20 g/cm^3), respectively[81]. The all-graphene yarn exhibit a high electrical conductivity and a great surface area due to the 3D interpenetrating porous networks of graphene. The solid state of such materials made of all graphene fibres using H_2SO_4-PVA gel electrolyte could be processed to spring-shaped supercapacitors, which possess highly compressible and stretchable mechanical performance and show an areal capacitance of 1.2-1.7 mF/cm^2[86]. Although the graphene fibres are light weight, highly flexible and electrically conductive, the restacking interaction between individual graphene sheets dramatically lower the large initial surface area of graphene sheets. Recent studies showed that hybrid materials combining 2D graphene sheets with 1D CNTs have a synergistic effect with greatly improved electrical, thermal conductivities and mechanical flexibility, compared to either of the single component alone. Cheng *et al*. developed hybrid fibres (CNT-G) by CVD growth of 1D carbon nanotubes (CNTs) on 2D graphene. The CNT-graphene hybrid fibres prepared exhibit an areal capacitance of 1.2-1.3 mF/cm^2 with a stable CV performance even after 200 bending cycles in the textile structure[87].

On the other hand, among the graphene-based 2D films, graphene papers have attracted much attention due to the tuneable thickness, structural flexibility, lightweight and electrical properties, which are the essential qualities required for flexible supercapacitors[88]. Considerable research efforts have therefore been dedicated to exploring novel processing methods for graphene-based films and papers, including spin-coating[89], Langmuir-Blodgett, layer-by-layer deposition, interfacial self-assembly, and vacuum filtration[90-92]. In similar situation as with other graphene-based materials, the processing of graphene thin films and papers is hindered due to the agglomeration and restacking of graphene sheets resulting from the inter-planar π-π interaction and van der Waals forces, which can greatly reduce the surface area and limit the diffusion of electrolyte ions between graphene layers[93-95]. There were numerous attempts to break the processing bottleneck, i.e., adding spacers, template-assisted growth, and crumpling of the graphene sheets[96-98]. Separation by appropriate spacers is an approach effective to improve the stacking of graphene sheets. The most widely investigated spacers are carbonaceous materials (e.g., carbon particle, CNT), metals (e.g., Pt, Au) or metal oxides (e.g., SnO_2) and other pseudocapacitive materials (e.g., transition metal oxides, hydroxides and conducting polymers)[99-102]. Besides the development of solid-spacer intercalation in graphene, solution-based spacing was also developed to reduce the agglomeration of graphene sheets. Li et al. investigated water as a "spacer" to prevent the restacking of graphene sheets[103]. The grphene-water hybrid is generated through the balance between the repulsive interaction and inter-sheet π-π interaction among the solvated graphene layers. It is self-stacked into graphene film rather than restacked into the graphite structure. The solvated graphene film is demonstrated with a high specific capacitance of 215 F/g and a good retention ability, where the capacitance of 156.5 F/g can be retained at a high current density of 1080 A/g and >97% cycling ability being retained after 10,000 cycles at the current density of 100 A/g. The solution based spacing approach can be extended to other type of liquids also such as Nafion[104]. To further address this and other related issues, considerable efforts were made to develop graphene-based macrostructure with 3D networks, i.e., aerogels, graphene foams, and sponges[105-109]. These 3D graphene-based materials, consisting micro- meso- and macro-interconnected pores, high surface areas and fast ion/electron transport channels, are highly desirable for exploring both high energy and power density, and overall super capacitance performance[110-118]. Several processing techniques were reported for the preparation of the 3D graphene-based supercapacitor electrodes. For instance, a template-directed assembly technique was developed to fabricate 3D macro porous bubble graphene foam. Cheng *et al*, used monodisperse polymethyl methacrylate (PMMA) spheres as hard templates, which were then removed via calcinations at 800^{o}C[118]. The resultant 3D bubble graphene structure provides controllable and rather uniform macropores and tailorable overall microstructure, therefore leading to a high capacitance retention of 67.9% with increasing a scanning rate up to 1000mV/S. However, the annealing procedure at high temperature (~ 800^{o}C) can cause aggregation of graphene sheets, resulting in a decreased specific area to128.2 m^2/g. In the fabrication processes discussed above, the resultant graphene foams are of chemically reduced graphene oxides, which can include structural defects and chemical moieties introduced in the synthesis procedures[15]. Therefore, the electrical conductivity of the as-prepared graphene foams can be largely comprised. In addition to 3D graphene foams using polymer spheres as a sacrifice template, chemical vapour deposition (CVD) on Ni foam is also used as an efficient process to synthesise graphene foams, which can be seamlessly continuous and highly conductive with fewer defects for fabrication of monolithic 3D nanocomposite-type electrode. Graphene aerogels (Gas) and hydrogels are a novel class of ultralight and porous carbon-based materials exhibiting both high-strength-to-weight and surface-area-to-volume ratios[118-120]. The 3D porous frameworks of Gas can provide multidimensional ion/electron transport pathways, offering easy access even to solid-state electrolytes, and minimize transport distance between bulk electrode and electrolytes[121-124]. These features enable Gas to be potentially used as additive/binder free electrodes in electrochemical applications. Although these bulk 3D bulk graphene hydrogels can be facilely prepared by a one-step hydrothermal method, their inflexible structures and low mechanical strength restrict their applications as a flexible electrode[110]. Recently, Duan *et al*, demonstrated a free-standing holey Graphene (HGF) framework developed via pressing bulk hydrogel into a high density hydrogel film that is attached onto a flexible current collector. It was assembled into an all-solid-state flexible supercapacitor with polyvinyl alcohol (PVA) gel electrolyte[125]. The HGF electrode material was demonstrated with a gravimetric capacitance of 298 F/g and volumetric capacitance of 212 F/cm^3 in organic electrolytes, and stable capacitance retention of 87% after 10,000 cycles.

Graphene-based materials in different forms of 0D, 1D, 2D to 3D have proven to be excellent candidates of electrode materials in electrochemical energy storage systems, such as supercapacitors. In recent years, considerable efforts have been made on the structural design, material fabrication, performance evaluation, as well as understanding of the key electrochemical phenomena observed. To realize the expected full-scale practical application, the quality and reproducible quantity of the electrode materials both will to be further improved, in particular with the development of the most desired structures tuneable in nano- micro- meso- and macro-scales. The low cost and effective process to produce graphene-based materials is the chemical exfoliation of graphite into GO and the subsequent reasonable reduction of GO to rGO. However, before the large scale application of this facile processing method in electrochemical energy storage devices, the stabilization of single or few-layer graphene sheets in various solvents and the preservation of their intrinsic properties must be addressed in order to break the bottleneck of re-stacking of graphene sheets. According to the authors Q. Ke and J. Wang[126], to fabricate supercapacitors with free-standing graphene particles, slurry casting method was generally employed, in which the active material powders were mixed with polymer binder and conductive additives to connect electrode material with current collectors. However, these polymers and conductive additives generally make little contribution to the overall capacitance and decrease both the volumetric and gravimetric capacitance of electrodes. Compared to the free-standing graphene particles, supercapacitors made of 1D fibre-type or yarn-type and 2D graphene-based film as electrode can be made binder- and collector-free. These 1D and 2D structures possess a high electrical conductivity and a superior mechanical flexibility. However, the structures with moderate rate stability and power density are achieved due to the porous structure and varying degrees of graphene sheet aggregation, which can affect the effective diffusion of electrolyte ions. The interconnected graphene networks and tuneable porous structure in varying scales, which can be achieved in 3D graphene foam/hydrogels, can lead to better control in the re-stacking of graphene sheets, thereby having the improved rate and power performance, although their mechanical strength can be compromised. To develop the graphene-based materials as super capacitor electrodes and boarden their applications into other energy storage devices, the following future aspects was suggested by the authors Q. Ke and J. Wang[126]:

1. Graphene-based electrode materials with different architectures exhibit varying physical, mechanical and chemical behaviours, thereof affecting their performance in energy storage. Compared to

the 0D, 1D and 2D structures, more attention should be paid to further exploring the the tuneable 3D graphene networks with interconnected porous structure, which can be manipulated for large internal surface area, ion/change pathways, and avoiding the dead volume and collapse of the overall structures.

2. The nanocomposites consisting of graphene-based and pseudocapacitive materials, i.e., those graphene/conductive polymers, graphene/metal oxides or hydroxides, are promising for achieving for long awaited requirement of both power density and high energy density. Therefore, there is a need to future exploring efforts on the clarification of the nanohybrid structures and the control of the interfacial interaction between graphene and psedocapacitive materials in order to improve the overall Faradaic processes across the interface.
3. The rapid development of flexible electronics requires flexible and deformable energy storage devices. Therefore, future studies focus on the development of mechanical flexibility of graphene-based materials for supercapacitors and other energy storage devices.
4. The multifunctional of self-powered hybrid systems will be of considerable interests for future development. Recent pioneer work on the combination of flexible supercapacitors with other electronic and energy devices (i.e., solar cells, Li-ion batteries, electrochromic devices and nano-generators) were reported. Therefore, the integration of graphene-based supercapacitors with these devices will be of considerable values and a challenge as well.

Eletrochemical 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. For boyh EDLC and pseudocapacitors, electrodes with large surface area and high electrical conductivity are required. Carbon-based electrodes especially graphene-based typically fulfil these requirements. MoS_2, having a layered structure similar to graphite with a basal and edge plane, is known to be electrochemically active on its edge[23]. Although having unique features resembling graphene, MoS_2 nanosheets are rarely used as an electrode material of supercapacitors[127] 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 sulphides, 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 graphenelayers[128]. 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[62]. Electrochemical measurements were carried out on samples with low, medium and high concentration of MoS_2. As a result, the specific capacitance values of the MoS_2/rGO composites at 10mV/s were 128, 265 and 148 F/g, respectively. In low concentration 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 prepared by hydrothermal process in which L-cysteine was used along with sodium molybdate and GO as a starting materials, where L-cysteine was used because it can act as a sulphide source to form metal-sulfide nanoparticles and also act as a reducing agent to reduce GO to rGO[129], Huang and co-workers prepared MoS_2/rGO composites recently and used them as electrodes for supercapacitors[130]. 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 19.8kW/kg. The above studies suggest that these hybrid composites are suitable and promising electrode materials for high-performance supercapacitors.

Cycling stability

One of the most metrics for comparing supercapacitor electrodes is the cycling stability. Ideal EDLC supercapacitors should possess extremely high stability with minimal degradation in performance with repeated charge/discharge cycles, while pseudocapacitors typically sacrifice cycling stability for increased energy density[131]. Typically when MoS_2 or graphene supercapacitor electrodes are cycled continuously, there is a gradual degradation in capacitance due to increased resistance between flakes, collapse of the porous structure, as well as desorption of active material from the current collector. Thus, the cycling stability is a good indication of the materials suitability for real world supercapacitor applications. Previously, reported literature values for graphene supercapacitor cycling stability vary depending on the testing conditions but can range from 30% loss to almost no loss after 10,000 cycles[132]. This is compared to a 30% decrease in capacitance for solution exfoliated MoS_2 after only 200 cycles[133] and an 8% decrease over 1000 cycles for laser patterned MoS_2[134]. Mark A. Bissett and co-workers[74] studied the cycling stability of the MoS_2, graphene and composite membranes over 10,000 charge/discharge cycles at a current density of $1mA/cm^2$. The intermediate discharge cycles (every 2000 cycles) were shown for each membrane. In the case of MoS_2 membrane instead of a gradual degradation of the specific capacitance with repeated cycling as seen typically for such devices[133,62,135], there was an initial large increase (800%) in the performance over the first ~3000 cycles before stabilizing for the remaining 7000 cycles. Upon assembly electrochemical cells required "preconditioning" (several charge/discharge cycles) to ensure the electrolyte has permeated throughout the porous structure and the cell has stabilized[136]. For all results presented by Mark. A. Bessett and co-workers[73] each system was preconditioned by charging/discharging for ~200 cycles ($1mA/cm^2$) prior to further characterization. Thus, the observed increased with repeated cycling only occurs when > 1000 charge/discharge cycles are applied. An approximate doubling of the specific capacitance ($10mF/cm^2$) was measured for graphene membrane over the first~500 cycles, after which the performance increased only slightly over the remaining cycles. The composite membrane exhibits a different behaviour, increasing gradually over the duration to ~250% of the initial value ($11mF/cm^2$) after 10,000 cycles. The lack of any decrease with continued cycling demonstrates the applicability of these membranes to devices. The large initial increase in capacitance of the MoS_2 membrane can be attributed to a combination of (1) a transition in the charge storage mechanism from EDLC to pseudocapacitive ion intercalation and deintercalation, combined with (2) increased surface area due to partial exfoliation. Initial the predominant charge storage mechanism of the MoS_2 membrane is accumulation of ions at the double layer interface between the flakes and the electrolyte. Comparing the CV data for individual graphene and MoS_2 as well as Composite by the authors Mark A. Bessett[73], it was indicated that the composite of both graphene and MoS_2 together was better to able to resist structural changes that occurred with continual charge and discharge cycles. Typically, when dispersion s of 2D materials are deposited into a film, the van der Waals attraction between neighbouring sheets cause restacking to occur, and this limits the available surface area, thus reducing the specific capacitance. Thus, it is deduced that differences in flake dimensions and surface energy in the case of the MoS_2/graphene composites form disordered heterostructures and prevent restacking. It is this physical prevention of restacking, effectively increased the specific surface area, that is likely responsible for the ideal EDLC charge storage behaviour observed. Although very important when discussing application of supercapacitor designs, the self-discharge behaviour is often neglected when characterizing the performance of a given material[130,51]. Self-discharging of supercapacitors can severely limit their applicability to real world applications and thus are an important figure of merit when comparing electrode designs. The spontaneous voltage decrease that occurs when a charged supercapacitor under open circuit conditions, often referred to as self-discharge, can occur because of three mechanisms: Faradaic processes, leakage current, and charge redistribution[137,138]. These Faradaic processes that can occur, when aqueous electrolyte solutions are used, are thought to be predominantly oxygen reduction at the negative electrode[139]. Leakage current occurs when charged ions or impurities within the electrolyte spontaneously migrate from each electrode, thereby reducing the cell potential[138]. Charge redistribution occurs when selective areas of the active material are unevenly charged, leading to areas that are overcharged while others have lower charge. This charge redistribution between these areas then leads to an overall decrease in cell potential. Thus when a supercapacitor electrode material is characterized, minimizing the self-discharge rate is important to maximize performance. In the case of EDLC devices the voltage decrease initially from its initial value quickly and the rate decrease with time[137]. Over this initial rapid decrease in potential the device is exhibiting noncapacitive behaviour (due to Faradaic processes and charge redistribution); after this the linear decrease in potential is typical of a dielectric capacitive response due to current leakage[137]. The rate of self-discharge has also been shown to be strongly dependent on the charging duration as well as method (galvanostatic and potentiostatic). Mark A. Bessett and co-workers[73] studied the open-circuit voltage of the three symmetrical cells (postcycling); each underwent 15 min of potentiostatic charging to 1V before the open-circuit potential over 1 h. It was seen that the graphene membrane suffers from the highest rate of self-discharge, followed closely by the MoS_2 membrane. The composite membrane, however, displays much better charge retention (37% greater than the graphene, 25% greater than MoS_2). The increased charge retention performance of the composite membrane indicates that the synergistic effect of combining the highly conductive graphene with the pseudocapacitive MoS_2 allows for reduced Faradaic leakage and charge redistribution across the membrane. This work suggests that composites of various 2D materials (TMDs, graphene, hBN, etc.) can easily be combined and used to enhance the performance of single component materials for electrochemical storage.

Solar cells

Photovoltaic cells, or solar cells, are another potential application of graphene. Current solar cell technologies contain platinum based electrodes which carries at least two problems: The abundance of platinum on earth one would think is too low to create a planet's worth of solar cells, which is related to the second drawback-the cost. With graphene being an excellent conductor there is potential for graphene electrode design which would reduce cost and weight whilst maintaining efficiency, as described by Wang *et al*[140]. Their graphene electrode in a dye-sensitized solar cell actually exhibited an efficiency of 7.8% which is 0.2% less than a platinum-based counter electrode, but produced at a fraction of the cost. Clearly it would be better to improve efficiency but cutting the cost is as much an issue as improving efficiency for modern day technology. Nevertheless, any contribution to green will undoubtedly win over governments, activist groups, and home owners who feel they pay too much for their utility bills[65]. However, solar cell research in general has been a slow process for many years, although any sign of progress is still progress nevertheless. 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 the 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[23]. 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 A^0 thickness, holds strong promise for ultrathin photovoltaics[141]. Modifications of graphene-based materials such as doping, functionalization and hybridization with foreign moieties have been fruitful in achieving enhanced efficiencies[142]. Although processing 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. Talking advantage of the exotic properties of both the layered materials, Liu *et al*[143], 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 adding in the reduction of tri-iodide species. An efficiency of 6.04% comparable to that of sputtered Pt counter electrode was obtained. The same group embedded graphene flakes into MoS_2 matrix via an *in situ* hydrothermal route[144]. 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, upto 95% of the level obtained using conventional Pt CE, which was roughly 6.41%. 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. 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%[145]. 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[146]. 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[23].

CONCLUSION

Graphene-a one atom thin sheet of carbon atoms arranged in a hexagonal format or a flat monolayer of carbon atoms that are tightly packed into a 2D honeycomb lattice is the 'new wonder material' that is expected to shape almost all aspects of future technologies. Being a great conductor of electricity, although it does not have a band gap (can't be switched off). One the other hand, hybrids of graphene and related metal dichalcogenide, especially MoS2, are an emerging class of next generation nano-materials. 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 few years. Graphene-based materials in different forms of 0D, 1D, 2D to 3D have proven to be excellent candidates of electrode materials in electrochemical energy storage systems, such as supercapacitors. The low cost and effective process to produce graphene-based materials is the chemical exfoliation of graphite into GO and the subsequent reasonable reduction of GO to rGO. Because of the direct band-gap, MoS2 was widely used as channel materials in logic transistors. Heterostructures based on graphene and MoS2 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 MoS2 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[24]. However, before the large scale application of this facile processing method in electrochemical energy storage devices, the stabilization of single or few-layer grapheme sheets in various solvents and the preservation of their intrinsic properties must be addressed in order to break the bottleneck of re-stacking of graphene sheets[129]. Certainly, the future of such hybrid materials, in general, should be exciting as new opportunities are uncovered.

ACKNOWLEDGEMENT

The author is very grateful to the Institute and the Department of Chemistry for supporting me to write the article. The author is also thankful to his family members for their encouragement.

CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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Please cite this article in press as: Parikshit Mandal. A review on “graphenevs graphene-mos$_2$ hybrid materials: a roll in energy storage device”, *Asian Journal of Research in Chemistry and Pharmaceutical Sciences,* 7(1), 2019, 80-101.