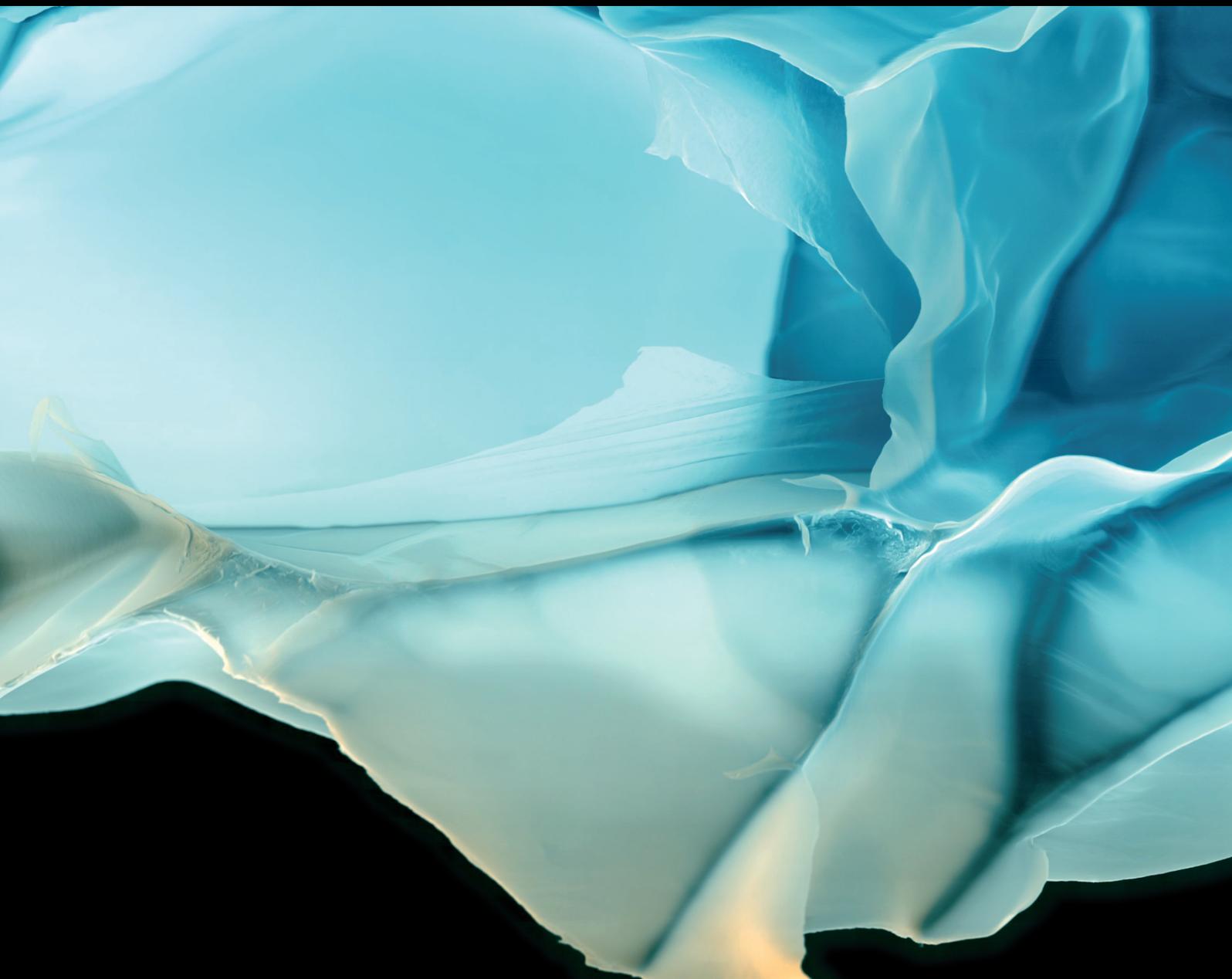


Advances in Polymer Technology

Synthesis and Applications of Two-Dimensional Polymer Materials in Energy Storage

Lead Guest Editor: Yong Ren

Guest Editors: Yuying Yan and Yue Chan





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Review Article (15 pages), Article ID 4294306, Volume 2019 (2019)

Review Article

Two-Dimensional Nanomaterials-Based Polymer Composites: Fabrication and Energy Storage Applications

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Polymers have been widely used for their low density, low cost, corrosion resistance, easy design, and processing. The addition of nanomaterials into polymer matrices has been studied for a long history due to their enhancement on properties of polymers, such as the electrical conductivity, thermal conductivity, corrosion resistance, and wear resistance. Two-dimensional materials, a new class of nanomaterials, have been intensively studied as a filler for polymer composites in recent years, which can significantly enhance the performance at even extremely small loading. In this review, firstly, the preparing and modifying method of 2D materials, such as graphene, graphene oxide, and hexagonal boron nitride, as a filler for polymer composites are organized. The related dispersion methods of 2D materials in the polymers, surface treatments of 2D materials, interface bonding between 2D materials and polymers are discussed alongside. Secondly, the applications of 2D materials/polymer composites for energy storage in lithium ion battery separators and supercapacitors are summarized. Finally, we have concluded the challenges in preparing 2D materials/polymer composites, and future perspectives for using this class of new composites have also been discussed.

1. Introduction of Polymer Composites

Polymer composite can be defined as the composite materials composed of more than two phases, which typically refer to polymer/polymer or filler (fiber, metal, etc.)-based polymer composite [1]. As compared to traditional materials such as ceramic and clay, the polymer composites were developed later. The polymer composites have important applications in various fields such as electronics [2], food packaging industry [3], and medicinal industry [4], etc. With the rapid development of science and technology, the demands for better performance of materials are also increasing. Traditional polymer materials made of a single component cannot satisfy the increasing demands on high comprehensive performances. For example, polymers usually have a melting temperature range of 100–250°C, which means that most of them are not suitable for use at high temperature. Therefore, the idea for incorporating additives into the polymer matrix was proposed, which could greatly improve the performance of the polymers. For example, Wakabayashi et al. [5] reported a significant improvement in Young's modulus by adding graphite (2.5 wt%, 1870 MPa)

into the neat PP matrix (910 MPa). Based on the progress made in various application fields, this conceptual innovation by adding inorganic materials/metals into polymer matrix has attracted broad research interests.

Compared with conventional neat polymers, polymer composites exhibit enhanced properties in various fields [6–8]. A large number of studies showed high improvement in mechanical properties [9, 10], electrical conductivity [11–13], thermal conductivity [14], corrosion resistance [15], and wear resistance [16], by incorporating even a little amount of additives into the polymer matrix. These properties make them suitable for commercialization in diverse fields, such as thermal conduction and dissipation devices [17], resist-memory devices [18], energy storage [19], etc. Traditional fillers such as metals and minerals are in macroscale, which have been widely used in various applications. However, these additives can not remarkably improve the properties due to the limited interfacial structure between them and the matrix. To further improve the performance of the composites, reducing the size of fillers into microscale and nanoscale should be one of the main strategies because of their large surface areas and good

contact with the polymers [20]. Roy and Komarneni firstly proposed the idea of polymer nanocomposite in 1984, which was defined as the composite materials in which at least one of the dispersed phases was within 100 nm, including carbon nanotubes (CNTs), fullerenes, nanosized particles, etc. [21]. These materials are very suitable for mixing with polymers to form polymer nanocomposites. Actually, the earliest report on polymer nanocomposites can be dated back to the midterm of the 1800s when carbon black was blended into vulcanized rubber in the application of automobile tires. In comparison, blending with other polymers or macro-scale materials into one polymer, polymer nanocomposites exhibit enhanced mechanical [22], optical [23], and electrical properties [24]. Meanwhile, as the sizes of conventional fillers reduced to nano-scale, such as nano-SiO₂ [25] and nano-CaCO₃ [26], they showed better dispersity into polymer compared to macro-scale particles, and much better property enhancement effect. Therefore, only a small amount of nanomaterials needs to be used for the properties, which can reduce the cost on the fillers and avoid many side effects ascribed to the high contents of fillers.

Two-dimensional (2D) materials are a new type of sheet-like nanomaterials, typically showing lateral size from hundreds of nanometers to few micrometers and their average thickness is <5 nm [27]. These materials have a large surface area with a high percentage of atoms exposed to the surface, which make them have a good interaction with the matrix and even a little amount of them can greatly increase the performance of polymers. In addition, their abundant species make them suitable fillers for different application purposes [28]. It has been reported that with a small loading (<1–5 wt%) of 2D materials, such as the layered silicates or graphene, into a polymer matrix, the mechanical properties of the resulted polymer composites improved up to ~200% compared to the neat polymers [2]. So far, a variety of 2D materials have been prepared and used in the polymer composites, including grapheme [29], graphene oxide (GO) [30], hexagonal boron nitride (h-BN) [31], transitional metal dichalcogenides (TMDCs) [32], metal organic frameworks (MOFs) [33], etc. In this review, we will focus on the recent progress in the fabrication of 2D materials-based polymer composites. Their applications in energy storage aspects will also be discussed.

The typical process to prepare 2D materials-based polymer composites comprises the preparation of exfoliated 2D materials and their dispersion into the polymer matrix. For the preparation of 2D materials, the exfoliation process is to weaken the interaction or break the bonds between layers [34]. With the expansion of interlayer space by intercalation, the slippage happens between layers by applying a shear force. Until now, there are various methods to exfoliate layered materials including intercalation-assisted exfoliation [35, 36], liquid phase exfoliation [36], etching assisted exfoliation [37], ball milling [38], electrochemical exfoliation [39], ion exchange-assisted exfoliation [40], etc. After the exfoliation of 2D materials, the essential task is to ensure their even dispersion into the polymer matrix. The commonly used method is dissolving the polymer in solvents and then putting the 2D materials into the dissolved polymer solution. However, the complicated fabrication process makes the final products expensive and

the organic solvents are poisonous and harmful, which are the big challenges for the scalable use of 2D materials based polymer composites. Further refinement of the fabrication process is necessary to cut down the price and reduce environmental pollution. Therefore, a review on the current state of this field and the most updated strategies to solve the challenges is very necessary for the real use of 2D materials based polymer composites. In the following section, we will first introduce the preparation methods of various 2D materials-based polymer composites. Then, properties enhancement of different types of 2D materials-based polymer composites (graphene, h-BN, MoS₂, and MOF) will be summarized. Third, the applications of 2D materials/polymer composites for lithium ion batteries and supercapacitors will be summarized. Finally, the challenge for exfoliating and preparing polymer nanocomposites will be discussed and the future perspective on how to improve the performance of polymer composites will be concluded.

2. Graphene-, GO-Based Polymer Composites

The history of graphene can track back to 2004 when Novoselov et al. [41] firstly obtained the few-layered graphenes by scotch tape transferring technique and characterized their excellent electrical performance. This milestone work inspired the basic research and commercialization of graphene. The graphene is composed of carbon atoms tightly packed into 2D honeycomb lattice structure through sp² hybridization. Such a structure displays versatile physical and chemical properties, such as high carrier mobility at room temperature (~10,000 cm² V⁻¹ s⁻¹) [41], high Young's modulus (~1 TPa) [42], large theoretical specific surface area (2630 m² g⁻¹) [43], low light absorption (~2.3%) [44], and high thermal conductivity (~5000 Wm⁻¹ K⁻¹) [45]. GO is an essential derivative of graphene, which was obtained by strong oxidation of the graphite with oxidative agents. During the oxidation process, various oxygen-containing functional groups such as carboxyl, hydroxyl, epoxy groups, etc., are introduced on the surface of grapheme [43]. Despite a similar 2D structure, graphene and GO have totally different properties. For example, GO has a much poorer electrical conductivity than graphene due to the transformation of C–C bonds from sp² to sp³ hybridization by the strong oxidation process. The graphene is insoluble in water, and GO exhibits excellent dispersity in water due to the large amount of hydrophilic oxygen-containing groups on the surface. Therefore, graphene and GO show different application purpose for polymer composites.

Before the development of graphene and GO, CNTs were commonly used as fillers for polymer composites. The high cost of preparing CNTs and their aggregation were the bottlenecks restricting their applications in polymer composites [46]. Currently, the mass production of graphene and GO has been well solved and their costs were also acceptable for commercial applications [47, 48]. Therefore, they are considered as suitable fillers to replace CNTs for polymer composites. To optimize the properties of the polymer composites, it is essential to make the filler well dispersed in the polymer matrix and interact tightly with them. So far, various methods for the

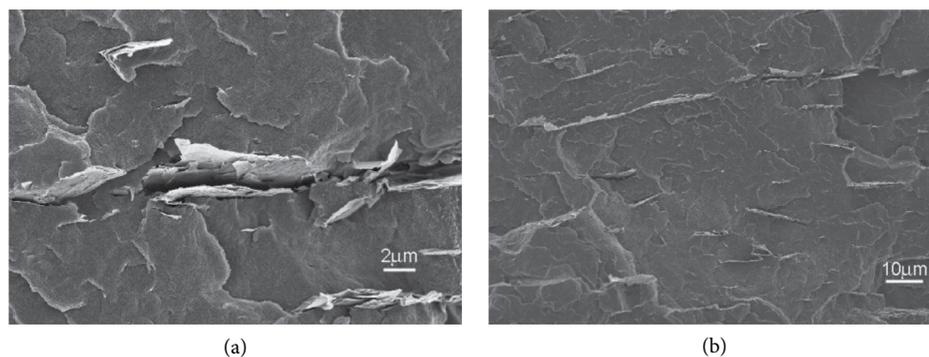


FIGURE 1: SEM images of (a) expanded graphite (EG)-PVDF and (b) functionalized graphene sheets (FGS)-PVDF showing the surface integrity. Adapted from [61].

preparation of graphene and GO-based polymer nanocomposites have been well established, including solution mixing [49–51], ball milling [38, 52], in situ polymerization [53–56], etc. In the following subsections, the mechanism and principles of these methods will be introduced in detail and enhanced properties from the experimental data will be reviewed.

2.1. Graphene-Based Polymer Composites

2.1.1. Fabrication Methods of Graphene-Based Polymer Composites.

There are two main strategies to fabricate the graphene-based polymer composites: in situ polymerization and melt intercalation [9]. In situ polymerization is a popular method for preparation of graphene-based polymer nanocomposites. Generally, in situ polymerization for graphene is started with suitable monomers, such as epoxy and aniline. For a typical process, by the loading of a suitable initiator such as room temperature ionic liquids (RTILs) [57], polymerization is initiated with the strong shear force exerted on the untreated flaky graphene and epoxy. The as-exfoliated few-layered graphene nanosheets are directly dispersed into the epoxy. On the other hand, appropriate initiators need to be selected for different polymers. For example, ammonium persulfate served as a free-radical agent to initiate the oxidative polymerization of aniline [58]. Besides the applied high-shear force to the composites, heat, electrochemical polymerization, and radiation are the other useful ways to initiate the polymerization of monomers to prepare graphene-based polymer composites [59, 60]. For example, anodic electropolymerization has been used to polymerize aniline onto graphene papers by directly applying a voltage in an aniline solution with the graphene papers as an electrode. This method has been applied to prepare various graphene-based polymer nanocomposites, i.e., epoxy/graphene [53], poly(vinylidene fluoride) (PVDF)/graphene (Figure 1) [56], poly(vinyl alcohol) (PVA)/graphene [62], etc.

In the melt intercalation method, strong shear force and high temperature are simultaneously used to blend the graphene and polymer matrix in the molten state without using organic solvents [9]. Firstly, the thermoplastic polymer melts at high temperature. Then, with the help of high shear force, graphene is intercalated by the polymer chains to form

polymer nanocomposites [63]. It is worth noticing that only thermoplastic polymer could be processed using this method. It has the advantage to prepare polymer composites for those can not be in situ polymerized. Meanwhile, it is worth noticing that the molecular weight of polymer and 2D material-polymer interaction are two important factors in the melt intercalation method. For example, to ensure the good dispersion of graphene into a polymer matrix, it is necessary to reduce the molecular weight of the polymer and increase the graphene-polymer interaction. Otherwise, the high entropy in composite with high molecular weight will forbid the dispersion of the filler [64]. From previous reports, a wide range of polymer composites has been successfully prepared using this method, such as polystyrene (PS)/graphene [65] and PP/EG [66, 67].

2.1.2. Properties of the Graphene-Based Polymer Composites.

For a polymer composite, the filler influences the electrical conductivity, thermal conductivity, mechanical properties, and even the dielectric properties. The graphene has a large surface area and good interactions with the polymer matrix, which means a very small amount of them can lead to a significant change in their performance (Table 1). Taking graphene/PVDF composite as an example, the dielectric constant reached 340 with 0.2 vol% of graphene at 100 Hz and the highest dielectric constant was achieved up to 7940 with 1.2 vol% of graphene at 100 Hz [56]. On the other hand, to obtain polymer composites with the same dielectric constant, the loading of conventional ceramic powder needs to be extremely high, i.e., over 50 vol%. As another example, PET-graphene composite with 3.0 vol% graphene loading exhibited a high electrical conductivity of $\sim 2.11 \text{ Sm}^{-1}$ (Figure 2) [73]. The thermal stability of the polymers can also be greatly enhanced by a small loading of graphene. Loading 0.05 wt% of FGS into PMMA shows the increase of glass transition temperature (T_g) to 30°C. With a loading of 1 wt%, FGS into the poly(acrylonitrile) (PAN) increased T_g to 46°C [76]. Compared with the conventional carbon-based fillers, such as CNTs and EG, the enhancement of T_g was much higher by adding the same amount of graphene into the polymer matrix due to their 2D structure and the large percentage of surface atoms to interact with the polymer matrix.

TABLE 1: Electrical conductivity enhancement in PS polymer nanocomposites.

S/N	Authors	Year	Loading content	Preparation method	Electrical conductivity (S/m)	Ref
1	Nadia Grossiord et al.	2007	1.5 wt% (SWCNT)	Solution mixing	≈ 1	[68]
2	Mathur et al.	2008	2.0 vol% (MWCNT)	Solution mixing	2.5	[69]
3	Guo Hua Chen et al.	2001	2.8–3.0 vol% (EG)	In situ polymerization	1	[70]
4	Na Liu et al.	2008	4.2 vol% (graphene)	Electrochemical polymerization	13.8	[71]
5	Xian Yong Qi et al.	2011	PS	—	$\approx 6.7\text{E-}14$	[72]

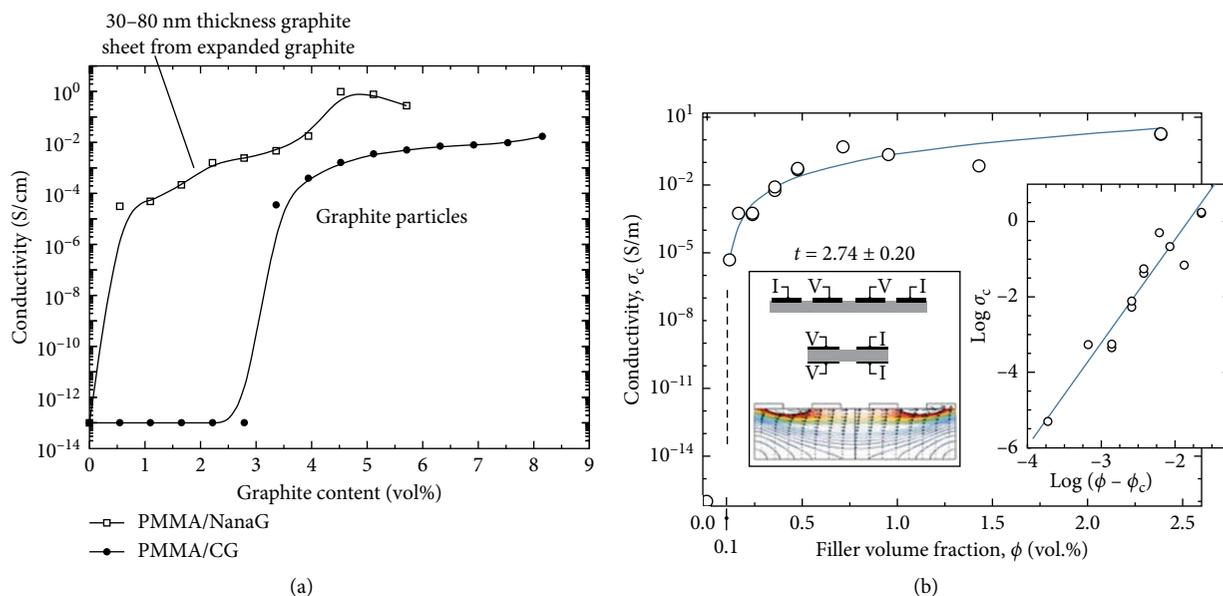


FIGURE 2: (a) Electrical conductivity of polymethyl methacrylate (PMMA)/graphite with different graphite contents. Adapted from [74]. (b) Electrical conductivity of polystyrene/graphene with different filler volume fractions. Adapted from [75].

2.2. GO-Based Polymers

2.2.1. Fabrication Methods of GO-Based Polymer Composites.

The graphene-based polymer composites have very low loading limit due to the low solubility of graphene in the polymer solutions or melts. To solve these problems, the functionalized GOs, which have good stability in the solvents or melts, have been used as fillers to prepare polymer composites. For the preparation of GO-based polymer composites, solution-based mixing is one of the most convenient methods [77]. Due to the rich oxygen-containing functional groups on the surface, GOs can be easily dispersed in suitable solvents, such as dimethyl formamide (DMF) and N-methyl pyrrolidone (NMP). The polymers, such as thermoplastic polyurethane (TPU) and PVDF, can be dissolved in these organic solvents. Therefore, GO nanosheets and the polymers can be directly mixed in these solvents. By evaporating the solvents, GOs can be homogeneously dispersed in the polymer matrix. However, using costly and toxic organic solvents, this method for preparing the polymer composites is expensive, complicated, and time consuming. To avoid the scalable use of organic solvents, other methods, such as in situ exfoliations of layered materials inside a polymer matrix, have been developed.

Ball milling is one of the popular methods to exfoliate 2D materials. For a typical process, graphite oxides are used as starting materials, which are exfoliated by the shear force or great momentum provided by balls with different diameters to overcome the interlayer Van der Waals interaction of layered materials. The graphite oxides are exfoliated to GOs and then evenly dispersed in polymers [78]. The high energy generated from the collision activates the chemical activity of the polymer, helping the recombination of the atoms on the surface and modifying the surface of GO. During the process, the addition of suitable catalysts can improve the dispersion of the GO inside the matrix. For example, the oxalic acid was used for GO-phenolic resin (PF) composites to increase the interaction between the 2D materials and polymer matrix [79]. The 2D materials could be obtained in large quantities and functional groups could be grafted at the same time by such a method.

2.2.2. Properties of GO-Based Polymer Composites. GOs have rich oxidative functional groups on their surfaces, which can have good interactions with the polymer matrix [80, 81]. Therefore, only a small loading can significantly improve the performance of the polymers. By using the solution mixing technique, the formed PVA/GO composite exhibited a high

Young's modulus of 3.45 GPa with an extremely low loading of 0.7 wt% GO, which was 62% higher than the neat PVA polymer matrix [62]. For poly(allylamine hydrochloride) (PAH) with GO nanosheets as a filler, the formed thin crosslinked film exhibited a huge increase in elastic modulus, i.e., from 3.64 to 18.31 GPa [82]. The modulus of the GO/epoxy resin composites reached its maximum value of ~4.2 GPa when the expanded GO concentration was 1.5 wt% [83]. Noteworthy, even for the same filler, the resulting properties can be significantly different due to the dispersity and interactions between matrices and fillers. Here, we will use the GO/epoxy resin as an example. By using the in situ polymerization method, the resultant GO/epoxy composite showed an increase of 103% in thermal conductivity as compared with the neat epoxy ($0.25 \text{ Wm}^{-1}\text{K}^{-1}$), with a loading of 2 wt% GO [84]. Similar enhancement was presented in another experiment but even with lower loading of GO [48] by using the tetraethylenepentamine (TEPA) to modify the GO sheets. The TEPA functionalized GO sheets were polymerized by a three-roll mixing method. With 0.5 wt% of GO loading, this multifunctional composites of TEPA modified GO/epoxy showed an enhancement of thermal conductivity by 103% [85].

2.3. 3D Graphene/Polymer Composites

2.3.1. Fabrication methods of 3D Graphene/Polymer Composites. Although properties' enhancements are reported in various fields, there are several drawbacks of 2D graphene nanosheets, which restrict the development of graphene-based polymer composites. For example, the π - π interaction between each graphene sheet cause the agglomeration and uneven dispersion of them, which reduce the specific surface area and active sites [86]. In addition, the graphene sheets in the matrix have poor contact with each other since they are well dispersed in the polymer solvents/melts. Therefore, organizing the 2D graphene sheets into a connected macroporous 3D structure, i.e. 3D graphene, and then fill this structure with polymers is a good method to overcome the agglomeration problems [87]. Compared with 2D materials in the composites prepared by adding them into the polymer matrix, the 2D materials in this preformed 3D structure showed much better contact. This good contact will improve the properties of the composites, such as electrical conductivity and thermal conductivity. Therefore, many studies have been reported about the synthesis of 3D graphene structures and their applications in polymers [88].

The freeze-drying process is the most straight forward way for the preparation of 3D graphene-based composites [89]. At extremely low temperature, the solvents in the 2D graphene dispersion become solids, which could be sublimated under vacuum condition. During the sublimation process, the graphene would not aggregate due to the small interfacial energy between the solids and the graphene. By using this strategy, the resulting 3D structured graphene does not stack or aggregate together, leading to a large surface area. Polymers could be filled with resulting 3D graphene-based fillers. For example, Wang et al. [90] reported the synthesis of graphene

aerogel started with aqueous GO under the freeze-drying method. After constructing the 3D structure of graphene, epoxy resin was directly added and infiltrated into the as-formed aerogel under vacuum condition, forming the graphene aerogel/epoxy polymer composite.

The hydrothermal method is another convenient method to get 3D graphene filled polymers [91]. The fundamental procedure is based on the in situ polymerization. Firstly, polymers are added into the aqueous solution of GO to obtain the well-dispersed suspension. By sealing the mixture into an autoclave, the graphene will be converted to 3D graphene with the structure containing polymer. The 3D-graphene-based polymer can be obtained by using this technique and the resulting product could also be directly applied in the practical devices [92].

Chemical vapor deposition (CVD) is another method to prepare the 3D graphene with interconnected network structure. During the CVD process, the Ni foam was firstly used to grow graphene at high temperature (1000°C), and then filled with polymers. After removing the solvent and etching the template, 3D graphene-polymer composites were obtained [93]. Because of the high quality of the graphene and the good interconnection in the 3D structure, the materials showed excellent electrical, thermal conductivity, and superior mechanical properties. However, the high cost of graphene preparation via CVD restricts its practical applications.

2.3.2. Properties of 3D Graphene/Polymer Composites. Liu et al. prepared a 3D graphene-polypyrrole (PPy) composite by polymerization of graphene with PPy after heat conversion, which showed promising electrochemical properties. The specific capacitance measured from this composite achieved 186 F/g, which was roughly three times larger than that of the neat PPy [91]. Compared with the 3D graphene, the specific capacitance increases 33% for the 3D graphene-PPy. The as-fabricated supercapacitors showed very strong actuation response as an electrochemical actuator, demonstrating its ability for practical applications. As another important property parameter for polymers, the electrical conductivity of the 3D graphene/polymer composites has been widely discussed. Jia et al. found properties enhancements in various aspects, including the electrical conductivity by embedding CVD grown 3D graphene into epoxy [93]. With only 0.2 wt% loading of 3D graphene, the electrical conductivity of the composite increased 55% compared to neat epoxy [93]. The glass transition temperature has also shown a significant increase by 31°C (0.2 wt% of 3D graphene), which was ascribed to the excellent dispersity and the strong bonding interaction of the 3D graphene in the epoxy resin (Figure 3). 3D GO-based composites are the important derivative of 3D graphene. With the loading of 1.3 wt% 3D GO into epoxy, the thermal conductivity of the composite increased 148%, up to $0.62 \text{ Wm}^{-1}\text{K}^{-1}$ [94]. The 3D structure and the low thermal resistance resulted in a high enhancement in thermal conductivity for the composites. These 3D graphenes showed a significant potential compared to the conventional CNTs and graphenes as fillers for polymers.

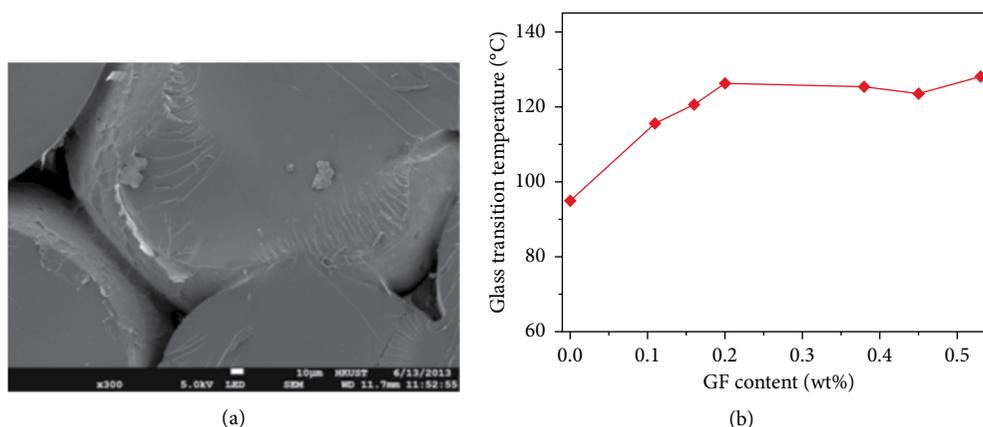


FIGURE 3: (a) SEM image of 3D graphene (0.2 wt%)/epoxy composite. (b) Glass transition temperature reaches its threshold at the loading of 0.2 wt% 3D graphene. Adapted from [93].

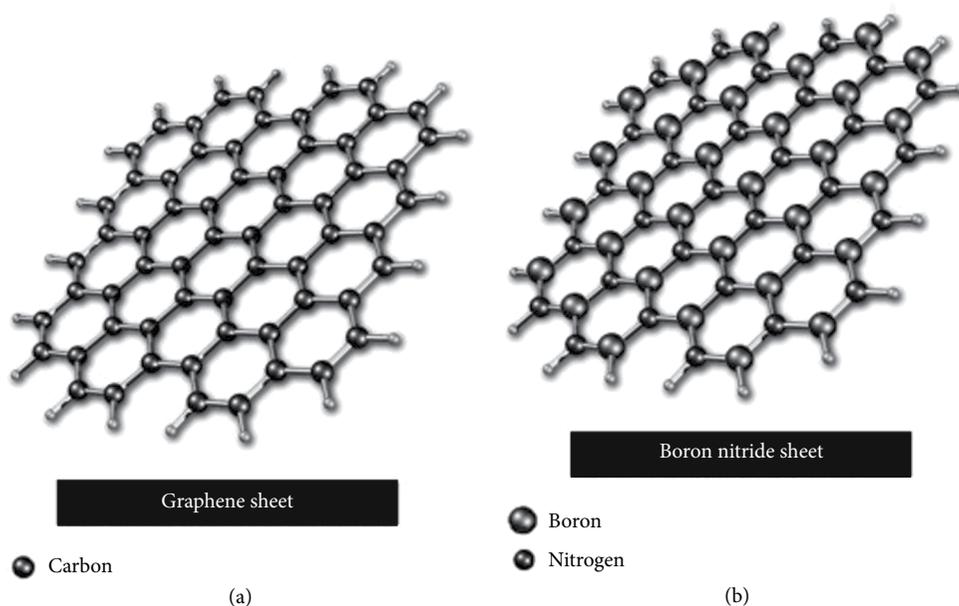


FIGURE 4: Schematic representation of the structure of graphene (a) and boron nitride (b). Adapted from [95].

3. Other 2D Materials/Polymer Composites

3.1. h-BN/Polymer Composites. The 2D h-BN has a similar structure with graphene (Figure 4), which shows high thermal conductivity, low dielectric constant and poor electrical conductivity. Therefore, it has a potential to be used in conditions where good thermal conductivity and insulating properties are needed, such as electronic devices, and thermal interface management. Their polymer composites have also been widely considered for these applications. For h-BN-based composites as a thermal interface management material, the increase of the loading will significantly improve the properties. Taking the enhancement in thermal conductivity as an example, various studies showed the potential of h-BN as a thermal conductive filler with different types of polymer [17, 96–98]. When the loading of h-BN is 30 wt%, polyimide composite films achieved a thermal conductivity of

$0.47 \text{ Wm}^{-1} \text{K}^{-1}$ [99]. The same polymer composite has been prepared by other methods, showing thermal conductivity of 3 and $7 \text{ Wm}^{-1} \text{K}^{-1}$ with a loading of 30 and 60 vol% of h-BN [100]. Similar result for h-BN/epoxy composites was also obtained but with a slightly low loading of 33 vol% [101]. Despite the high thermal conductivity, the higher loading of filler does not mean good properties, good dispersity and strong interaction with the polymers are also critical for the performance of the composites. Due to the inert surface, 2D h-BN has poor interfacial adhesion with the polymer matrix. To overcome this challenge, it is necessary to modify the surface of h-BN to improve the interfacial adhesion. Several strategies have been employed to functionalize the 2D h-BN, for example, PS and PMMA were used to coat h-BN particles, resulting in an enhanced interfacial adhesion [101]. Lee et al. [102] demonstrated thermal conductivity enhancement with modified h-BN/polyetherimide (PEI). Following the same idea

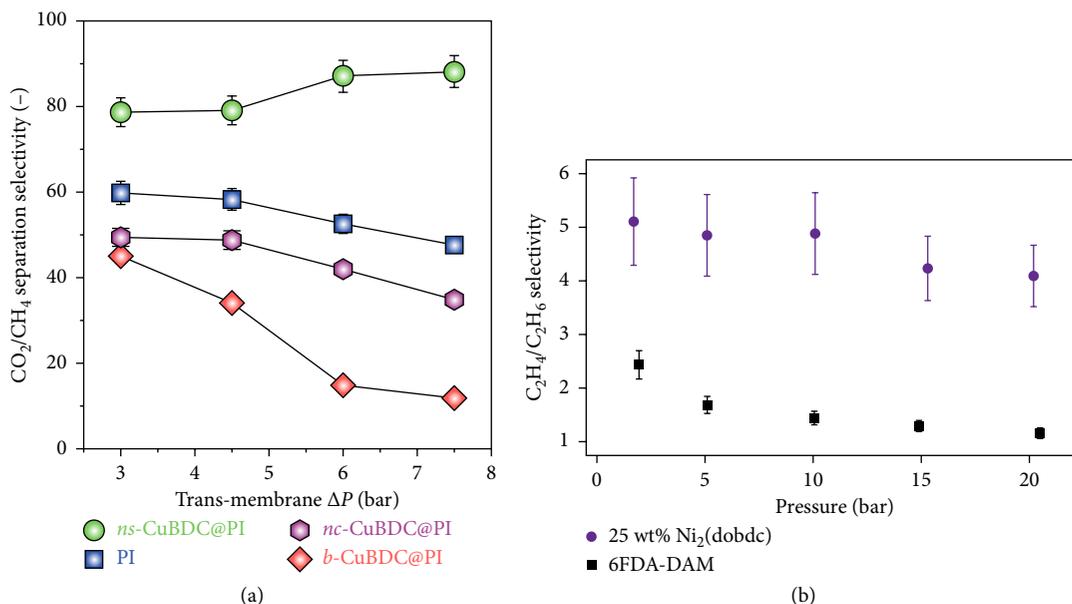


FIGURE 5: (a) Difference of separation selectivity of CO₂/CH₄ when employing several types of MOF/polymer composites. Adapted from [33]. (b) Selectivity of C₂H₄/C₂H₆ vs. pressure for Ni₂(dobdc) (25 wt%)/6FDA-DAM composite. Adapted from [117].

of coating modification, h-BN particles were pretreated by polyimide (PI). Then the PI-coated h-BN was mixed with PEI matrix to form a composite. The thermal conductivity of the composite achieved $3.3 \text{ W m}^{-1} \text{ K}^{-1}$ with 60 wt% loading, while the result was $2.6 \text{ W m}^{-1} \text{ K}^{-1}$ without modification. Apparently, due to the improved interfacial adhesion, the connection between polymer and h-BN is stronger after modification of the h-BN.

3.2. MoS₂/Polymer Composites. MoS₂ is another popular layered material, which is structurally analogous to graphene. It can be exfoliated into 2D materials using the physical or chemical methods to break the interlayered interaction, i.e., the Van der Waals force [103, 104]. As a well-known functional material, MoS₂ has a good electrochemical capacitance and catalytic property, which are used for energy storage and catalysis applications [105, 106]. Among these applications, there is a research hot spot on the lithium ion batteries (LIBs) by using MoS₂ as a cathode material. To obtain a good performance of the LIBs, it is necessary to intercalate a suitable polymer into the host gallery of MoS₂, making it easy for the insertion and extraction of Li⁺ ions. Ma et al. [107] reported a large-scale preparation strategy for synthesizing MoS₂/PPy composites. During the process of in situ polymerization, MoS₂ was pretreated with *p*-toluenesulfonic acid and then pyrrole monomer was added. Pyrrole monomer was well dispersed in MoS₂ suspension with the assistance of stirring. Later, oxidants were dropped into the mixture to get oxidative chemical composites. From the report, the specific capacitance of the MoS₂/PPy composite achieved 553.7 F g^{-1} at the condition of 1 A g^{-1} , which was nearly two-folds larger than the pure MoS₂ (235 F g^{-1}). When the discharge current density was increased to a high value of 10 A g^{-1} , the specific capacitance was maintained at 90% compared to the result of 1 A g^{-1} . Xiao et al. [104] reported a significant enhancement of capacitance

by using the poly(ethylene oxide) (PEO)/MoS₂ composites. The mixture of Li_xMoS₂ and PEO was dissolved in deionized water and sonicated together and then it was centrifuged to obtain the composites. From the experiment, with a loading of 5 wt% PEO, the dielectric capacity of the composite was 2-folds of the neat MoS₂, showing a similar improvement as previously reported.

3.3. MOF/Polymer Composites. MOFs are classes of porous materials with a special crystalline structure, generally composed of metal-containing nodes and constructed by organic linkers [108]. There are four typical categories of MOFs, including 0D for clusters, 1D for chains, 2D for layers, and 3D for frameworks [109]. 2D MOF is one type of the novel ultrathin nanosheets with a large number of cavities exposed on the surface, whose typical thickness is less than 10 nm [33]. The extended π -conjugation inside the MOFs nanosheets [110] ensures the highest electrical conductivity among other categories of MOFs reported [111, 112]. It makes 2D MOFs suitable for the next-generation electronic devices.

During the last two decades, various preparation methods have been well established and, therefore, a large number of MOFs have been synthesized with different morphology [113, 114]. In addition to the synthesis and application of pure MOFs, researchers also paid attention to the MOFs-based composites with polymer matrices. The porous structure of the 2D MOFs can be used for gas separation and storage [33]. Moreover, the good flexibility of the 2D MOFs give them chances to fabricate the advanced flexible gas separation and storage devices. Conventional preparation methods of MOFs-based polymers include two categories: (1) MOFs are formed on the template of polymers [112]; (2) polymers are added into presynthesized MOFs with polymerization [115]. Calvez et al. [116] reported a convenient way to synthesize MOFs-based polymer composites in one step. The experiment

followed the idea of precipitation polymerization, and High Internal Phase Emulsion (HIPE) served as monomer to form a polyHIPE with macroporous structure. By this method, a suitable polymer was chosen to have a good dispersity in MOF precursor solution, leading to porous MOFs-polyHIPE composites. Based on the porous structure of the composites, it is interesting to use MOFs as a filler to form a polymer membrane for the gas separation. For example, Rodenas et al. [33] demonstrated a significant improvement of the selectivity in CH_4/CO_2 separation by incorporating MOF (CuBDC) nano-sheets within polyimide. The selectivity of CH_4 to CO_2 had been increased to 80% by using the *ms*-CuBDC/PI membrane (Figure 5), and this value was 60% for pure PI membrane. The more interesting finding in this work was that when the upstream pressure increased, the selectivity also showed a slight increase for *ms*-CuBDC/PI membrane, while the other composite membranes or the pure PI membrane presented an opposite change in selectivity. Bachman et al. [117] chose a better polyimide (6FDA-DAM) to incorporate MOFs $\text{N}_2(\text{dobdc})$ to form polymer membrane, resulting in an enhanced selectivity and permeability for ethylene/ethane. With a loading of 25 wt% $\text{N}_2(\text{dobdc})$ nanocrystals, the selectivity for ($\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$) of the membrane was around 5 at atmospheric pressure, which was two-folds of the separation value by using the neat polymer 6FDA-DAM. Meanwhile, the composite membrane showed great resistance in plasticization (~ 20 bar for plasticization pressure).

4. Applications of the 2D Materials/Polymer Composites in Energy Storage

Conventional fossil fuels sources, such as petroleum oil and coal, are nonrenewable and environmentally unfriendly. The conversion of renewable energies, such as solar energy and wind energy, into electric power has become a hot research topic. Meanwhile, the demands for the storage of these converted energies with high efficiency have increased, namely to improve both power density and energy density of the devices. To solve this problem, storing energy into electrochemical devices is one of the main strategies. The 2D materials have been widely used in electrochemical devices and demonstrated good performances. There are two main reasons: first, the restacked 2D materials provide a large inter-layer spacing, making it easy for the insertion and extraction of ions, such as the Li^+ , K^+ , and OH^- ; secondly, there are more opportunities for the ions binding to the active sites of the 2D materials due to their high theoretical specific surface area. For example, graphene is one of the most popular 2D materials, showing a unique structure with high specific surface area and electrical conductivity. Therefore, graphene and its derivatives perform an important role in the application of energy storage systems. Besides the research on pure 2D materials, 2D material-based polymer composites have also been used in energy storage applications. In the following section, we will discuss the use of polymer-based composites in popular energy storage systems, such as lithium-sulfur batteries (LSBs), and supercapacitors. First, we will review the 2D-based polymer composites as separators for the battery applications.

Then, the application of supercapacitors with 2D-based polymer composites acting as electrode materials will be summarized. For each aspect, the main development in 2D materials history and the challenges will be discussed.

4.1. Li-S Battery Separators. LIBs are widely used in our daily lives, such as cell-phones, laptops, and electric cars, due to its high energy density, rechargeability, and good safety. In the commercially used LIBs, LiCoO_2 , graphite and polymer membrane (PVDF or PP) have been used as a cathode, anode and the separator, respectively. The energy density for this LIB was $150\text{--}190 \text{ W h kg}^{-1}$, while the result could be obtained up to $\sim 240 \text{ W h kg}^{-1}$ for commercial LIBs [118, 119]. In recent years, the idea of using lithium batteries for vehicle applications has got much research attention because this type of battery system in vehicles will reduce the use of fossil fuels and resultantly air pollution will also be decreased. However, for vehicle applications, higher energy density ($600\text{--}1300 \text{ W h kg}^{-1}$) should be provided [120]. Therefore, many advanced battery systems have been proposed and studied, such as Li-air batteries and Li-S batteries.

As one of the most promising systems, the Li-S battery was calculated to have a theoretical energy density of $\sim 2600 \text{ W h kg}^{-1}$ [121], which was 10-folds of the LiCoO_2 cathode battery. However, the shuttle effect of sulfur is one fatal restriction for the real use of Li-S battery. The formed polysulfide (Li_2S) during cycling would be dissolved in the electrolyte and would go through the separator, leading to a sharp decrease in capacity and poor performance of cycle life of the Li-S cells. More severely, the Li-S battery will “die”. Therefore, it is necessary to use a suitable separator to prevent the transfer of the polysulfide and ensure the normal diffusion of other important ions. Although porous polymer membranes are widely used for LIBs’s separator such as PVDF and PP, these are not suitable candidates for the LSB system. For example, PP is considered to be a poor membrane material due to its large pore size ($\sim 100 \text{ nm}$), which is not adequate for preventing the transportation of polysulfide. To overcome this problem, Zhou et al. [122] introduced a method by directly coating graphene on the surface of PP separator and the polymer composite membrane played a role in the current collector (Figure 6). The area on the separator coated by graphene provided a useful place to store the polysulfide dissolved in the electrolyte, retarding polysulfide diffusion and therefore increasing the cycle life of Li-S cells. Zhuang et al. [123] reported a novel ternary-layered structure of the separator by integrating nafion, PP, and GO together. The reason for using GO was that there were many functional groups on the surface of GO, such as carboxyl and hydroxyl group, which exhibited a strong repulsion to the polysulfide anions due to the electrostatic interaction. The decay of capacitance showed a significant reduction to 0.18% per cycle, while the reduction per cycle for pure PP separator was 0.34%.

4.2. Supercapacitor Electrodes. The supercapacitor is another type of novel energy storage device with a higher power density ($\sim 1000 \text{ W kg}^{-1}$) and excellent cycling stability but lower energy density than traditional batteries [124]. Based on large power density, supercapacitors have attracted much attention

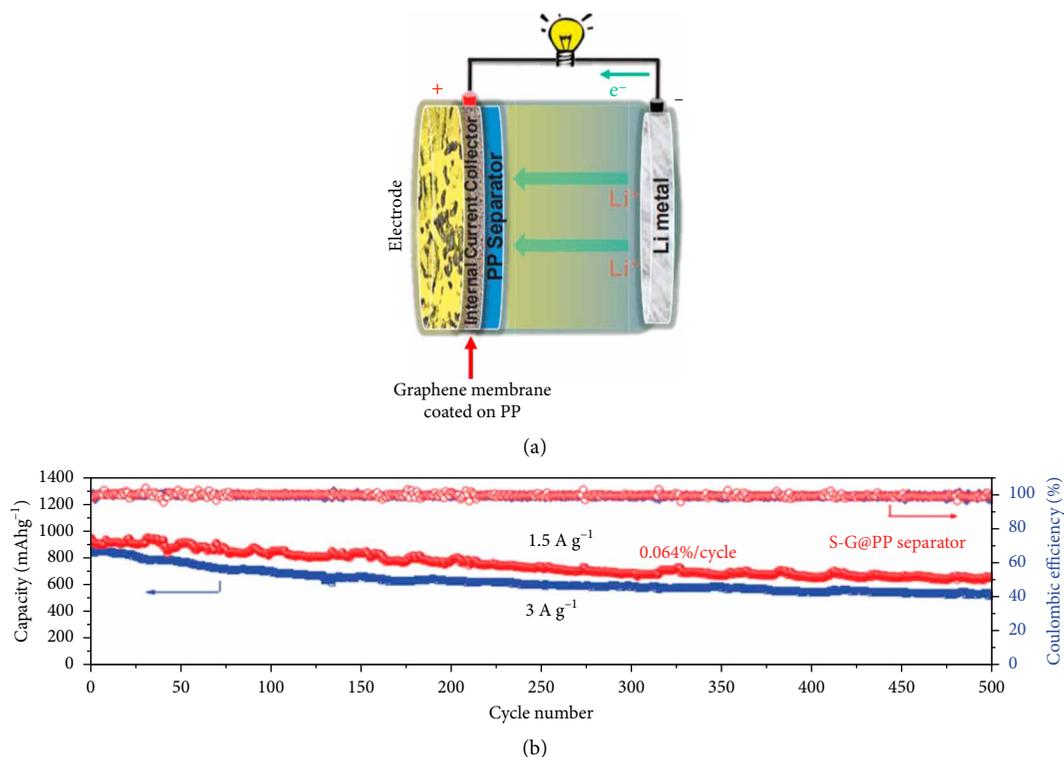


FIGURE 6: (a) Schematic illustration of electrode configuration with PP and graphene composite. (b) Cycle stability of graphene/PP separator at current density of 1.5 and 3 $A g^{-1}$. Adapted from [122].

in various commercial applications, such as transportation and elevators. Supercapacitors can be divided into two categories based on different charge storage mechanisms, i.e., electric double-layer capacitor (EDLC), where the charge is absorbed on the surface, and pseudocapacitors with redox reaction occurs on the surface to store charges [124]. Generally, both mechanisms will contribute to the capacitance of the electrode material. For the materials with high pseudocapacitance, they need good conductive material to improve the stability and good charge transfer at the electrolyte/electrode interface [125]. Various conducting polymer materials have been used in supercapacitors such as polyaniline (PANI) [54, 126], PAN [127] and PVA, which showed good pseudocapacitance [128–130]. However, relatively poor cycling stability of these polymers restricts the application. Therefore, carbon materials such as CNTs have been first introduced to overcome this problem due to their excellent stability [131]. Later, graphene-based fillers, with remarkable electrical conductivity and excellent mechanical properties, were considered as fillers for these polymers to use in supercapacitor electrode [43]. Wang et al. [126] prepared graphene/PANI composite via in situ anodic electropolymerization. The capacitance of the composite reached 233 $F g^{-1}$ generated by polyaniline films, while the electric double layer capacitance was much lower than the previous capacitance, mainly ascribed to the stacking of graphene nanosheets. However, the strong π - π interaction between graphene layers makes them easily restacked, leading to the poor performance of the electrode. To avoid this problem, graphene filler has been replaced by GO, which acts as another doped material for a polymer. Zhang et al. [54] prepared the

GO/PANI composite by in situ polymerization, and the specific capacitance and conductivity for different GOs loading were discussed. With a loading of 10 wt% of GO, the conductivity of the composite achieved 231.3 S/m^{-1} , which was 20 times larger than the pure PANi. When increasing the loading of GO from 10 to 50 and 80 wt%, a significant drop in conductivity (from 231.3 to 0.4 S/m^{-1}) can be seen. Also, after doping GO into PANi, the specific capacitance decreased at the current density of 0.1 $A g^{-1}$. To improve the capacitance, graphenes have been organized into three-dimensional (3D) porous structures with a high specific surface area [132]. The 3D graphene can greatly enhance the charge storage and pseudocapacitance of PANi. Tai et al. [133] prepared self-assembled 3D graphene/PANI composite hydrogel with the strategy of in situ polymerization. The specific capacitance of the composite reached 334 $F g^{-1}$, which was 3-folds of the neat PANi. Kulkarni et al. [134] prepared 3D graphene by CVD on the template Ni and aniline monomer was added by the oxidative chemical polymerization to form 3D graphene/PANI composite. The experiment showed much higher supercapacitive performance of $\sim 1002 F g^{-1}$ (Figure 7), with the discharge current density of 1 $mA cm^{-2}$. All these experiments demonstrated the important role of the 2D materials to improve the electrical conductivity and capacitance of the polymer matrix.

5. Summary and Outlook

In this review, we have summarized the recent progress of 2D materials-based polymer composites and their applications in

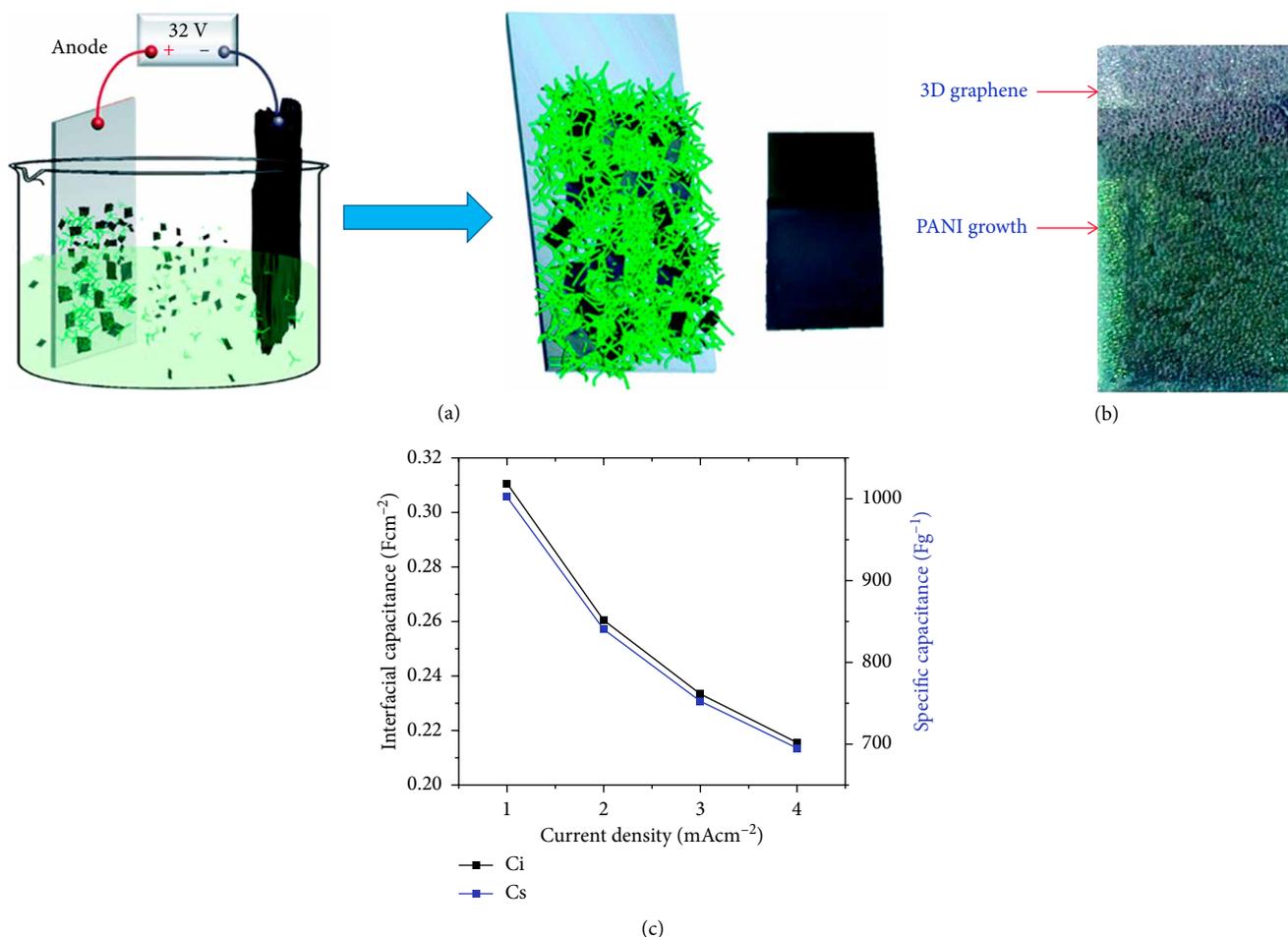


FIGURE 7: (a) Schematic illustration of the electrophoretic deposition preparation of MoS_2/PANI hybrid supercapacitor electrode. Adapted from [135]. (b) Optical image of 3D graphene/PANI supercapacitor electrode. Adapted from [134]. (c) Specific capacitance of 3D graphene/PANI is related to the current density. Adapted from [134].

energy storage systems. Firstly, we have introduced the broad applications of the polymer materials in our daily lives and the advantages of 2D materials as a filler to improve their properties. Then, methods to prepare the 2D materials-based polymer composites and their properties enhancement have been discussed. The graphene and its derivatives were used as examples to review the fabrication methods, such as solution mixing, melt intercalation, and in situ polymerization. Other 2D materials such as h-BN, MoS_2 and MOF were introduced into the polymers, and their influence on properties enhancement in the polymer composites has also been discussed. Finally, the applications of 2D materials-based polymer composites in Li-S batteries and supercapacitors have been summarized. The conducting 2D-based polymer composites provide a large surface area with many active sites, leading to an excellent performance for the electrochemical reaction on the supercapacitor. For battery separator applications, both the 2D materials and polymer have porous structure, which prevents the transportation of other ions except Li^+ through the separators, increasing the coulombic efficiency of the batteries.

Although the enormous potential of the 2D materials-based polymer composites have been demonstrated in various fields, there are still many challenges in their practical

applications. First, the mass production of various 2D materials is the main bottleneck in their practical applications. Although the high quality of graphene can be obtained by the scotch tape method, however, the extremely low quantity limits its practical use. Many works have been focused on the mass production of graphene for industrial applications. Currently, the problem of mass production of graphene has been solved, and many commercial applications of graphene-based polymer composites have been reported. However, for the other 2D materials-based polymer composites, the mass production of 2D materials is still the main challenge needed to be solved. To overcome this issue, one should focus on developing highly efficient exfoliation methods, which can exfoliate the layered materials in large scale. Then, how to balance the relationship between quality and quantity also remains a big problem. For example, h-BN-based polymer composites can be produced via ball milling with large quantities, while the size is relatively small due to the fierce collisions between the balls during the exfoliation process. Once the mass production of various 2D materials comes true, it will not be too long to see the 2D-based polymer composites affect our daily life.

Secondly, further exploration of multiple 2D materials-based polymer composites should be done. It is obvious to

find that most of the studies focus on the use of a single 2D material in polymer composites, while there are merely few reports who investigated the polymer composites by adding more than one 2D materials together. In principle, each 2D material has its unique properties but with several drawbacks. For example, graphene has high electrical conductivity and large theoretical specific area, which prefers to be used as a conductive filler for the energy storage device. However, it has been reported that the graphene-based polymer composites exhibit very low energy density. To overcome this problem, the idea of mixing graphene with other 2D materials was proposed [136]. For example, 2D oxide nanosheets with suitable capacitance could be added into polymer composites with graphene together, and the energy density of the resulting 2D polymer composites will be improved and they can be integrated to electrodes because of the polymers.

The polymers have penetrated every aspect of our daily life, and their properties enhancement will greatly influence the development of industrial, medicinal, and other various fields. As a recently developed material, 2D materials have a great chance to tune the mechanical, electrical, and thermal properties of polymers even with little amounts of them. We believe the effort spent on the exfoliation of 2D materials and the study of the 2D materials-based composites deserves to be made both for fundamental research and practical applications.

Abbreviations

PP:	Polypropylene
PMMA:	Polymethyl methacrylate
PPy:	polypyrrole
PEI:	Polyetherimide
PI:	polyimide
PEO:	Poly(ethylene oxide)
TPU:	Thermoplastic polyurethane
PVDF:	Poly(vinylidene fluoride)
PVA:	Poly(vinyl alcohol)
PAN:	Poly(acrylonitrile)
PANi:	Polyaniline
PS:	Polystyrene
PET:	Polyethylene terephthalate
h-BN:	Hexagonal boron nitride
CNTs:	Carbon nanotubes
SWCNT:	Single-wall carbon nanotube
MWCNT:	Multi-walled carbon nanotubes
GO:	Graphene oxide
TMDCs:	Transition metal dichalcogenides
MOFs:	Metal-organic frameworks
EG:	Expanded graphite
FGS:	Functionalized graphene sheets.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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