

The Preparation Approaches of Polymer/graphene Nanocomposites and their Application Research Progress as Electrochemical Sensors

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Abstract: Graphene, a two-dimensional sheet of sp^2 -hybridized carbon atoms packed into a honeycomb lattice, can be combined with various polymers through different methods and techniques. Polymer/graphene nanocomposites are expected to not only preserve the favorable properties of graphene and polymers, but also greatly enhance the intrinsic properties due to the synergetic effect between them. In this review, the preparation approaches of graphene/polymer nanocomposites, including melt blending, solution blending, in-situ polymerization and in-situ synthesis, were presented comprehensively in order to study the relationship between these approaches and the final characteristics and performances. Each approach had different influences on the final properties of the nanocomposites. The advantages and disadvantages of the preparation methods were discussed respectively. Additionally, the application researches of the polymer/graphene nanocomposites as electrochemical sensors, were introduced in detail. With regard to some important or novel sensors, the mechanisms were proposed for reference. Finally, conclusions were given and the issues waiting to be settled for further development were pointed out. The current review demonstrates that polymer/graphene nanocomposites exhibit superior electrochemical performances and will be applied practically in the field of sensor devices.

Keywords: Graphene, polymer, nanocomposites, performance, electrochemical sensors

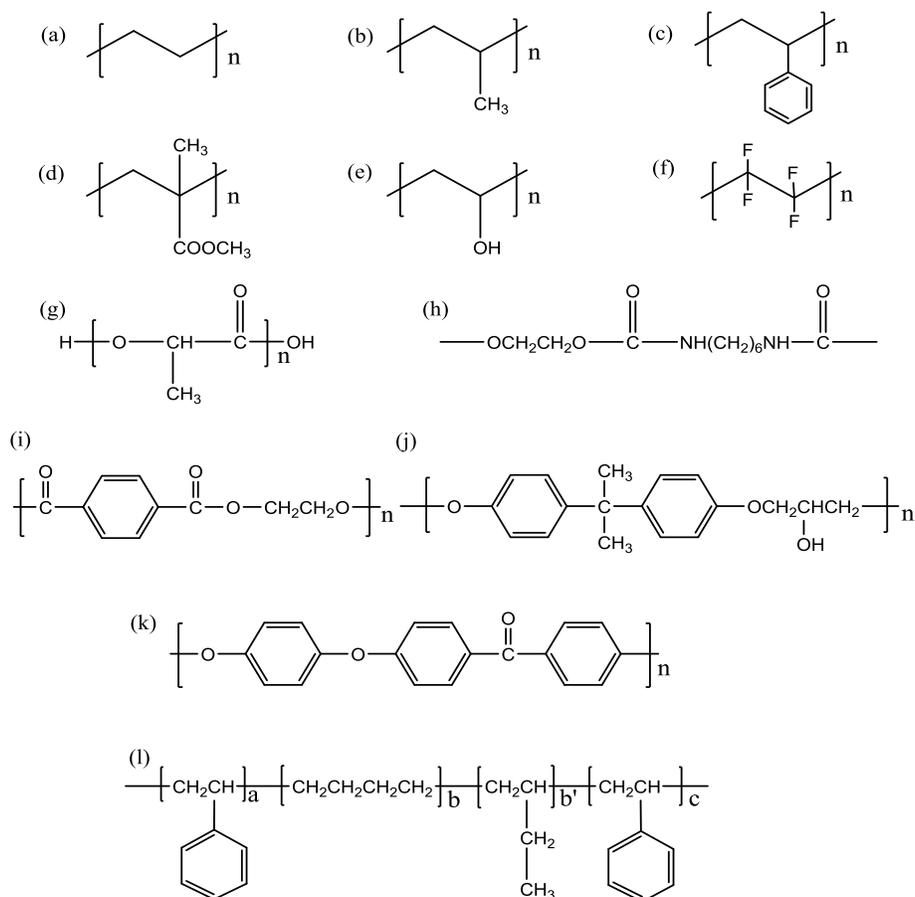
1. INTRODUCTION

During the past decades, a variety of polymer nanocomposites were obtained by adding nanoparticles in polymer matrix. Polymers were endowed with excellent mechanical properties, thermal properties, electronic properties, etc. by nanoparticles because of their nanometer size effect. Moreover, polymer substrates can be kept with good processing property, light weight and favorable stability[1-2]. As everyone knows, graphene is a novel two-dimensional inorganic nano-material developed recently. It has great potential applications in the fields of chemistry, physics, material science, electronics, and so on, since it was first successfully fabricated. Especially, due to its ultrahigh mechanical property, excellent electrical and thermal conductivity, and abundant resources (graphite), graphene shows promise as an ideal nano-material for preparation of polymer nanocomposites. Development of nanocomposites utilising graphene as the nanofiller offers desired properties to the added polymer matrix. Furthermore, incor-

poration of functional groups such as hydroxyl, epoxy, carboxyl, etc. on the surface of graphene enhances the interaction with the polymer matrix. Better interaction between the nanofiller and polymers leads to exfoliation of the nanofiller in the matrix, which indeed significantly improves the physical, mechanical, thermal, electrical, electronic properties of the polymer. Many studies indicate that the performances of polymer/graphene nanocomposites are comparable to or even better than those of the polymer/carbon nanotubes (CNT) composites. Therefore, the fabrication of new polymer/graphene nanocomposites with novel performances and how to make them into practical applications have become the hottest topics in the research fields of the nanocomposites[3-15].

Much research work has proved that polymer/graphene nanocomposites exhibit superior comprehensive performances. The nanocomposites are promising to be applied in many fields of materials and devices, such as sensors, conductive materials, electromagnetic shielding materials, photocatalytic materials, supercapacitors, aerogel and drug carrier[16-29]. To today, there have been several reviews about polymer/graphene nanocomposites,

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Scheme 1. the structure of the relevant polymers projected in this review. (a) polyethylene[66-69], (b) polypropylene[40, 123], (c) polystyrene[42,124], (d) poly(methyl methacrylate)[62-65], (e) poly(vinyl alcohol)[91,125], (f) polytetrafluoroethylene[50-53], (g) poly(lactic acid)[90], (h) polyurethane[79-82], (i) poly(ethylene terephthalate)[41,126], (j) epoxy resin[87-89], (k) poly(ether ether ketone)[43], (l) styrene-ethylene/butylene-styrene triblock copolymer[44].

due to the significance and urgency of the researches on them[30-36]. For instance, the recent research findings on the development of polymeric nanocomposites utilising pure and functionalised graphene were explored by Saravanan, et al.[32]. They focused on the method of synthesis of graphene and functionalised graphene, followed by their characterisation methods and inferences, and also summarised the routes for the preparation of graphene and modified graphene-based polymer nanocomposites. Additionally, the possibilities to tune interfacial interactions between graphene and polymers through graphene surface functionalization were introduced by Vikas Mittal[30]. Various types of modification of graphene oxide and graphene for the preparation of polymer-based nanocomposites were reviewed by Shah, Rahim, et al.[31]. The different methods of manufacturing graphene based composites and their electrical, mechanical and thermal properties were discussed by Deepak Verma, et al.[33].

In this review, the preparation approaches of graphene/polymer nanocomposites, including melt blending, solution blending, in-situ polymerization and in-situ synthesis, were introduced comprehensively. The relationship between these approaches and the final characteristics and performances of the nanocomposites were dis-

cussed deeply. Moreover, the application research progress of the polymer/graphene nanocomposites as electrochemical sensors, was presented in detail. The mechanisms of some important or novel sensors were proposed for reference. Finally, the challenges for further development were presented. The current review demonstrates that the nanocomposites exhibit superior electrochemical performances and will be applied practically and broadly in the future.

2. APPROACHES OF PREPARATION

The surface of graphene is inert and the interfacial force between polymer matrix and graphene is weak because it does not contain any active groups, though graphene exhibits excellent mechanical, electrical and physical properties. Additionally, graphene are modified through oxidization to turn into graphene oxide (GO), which contains some oxygen containing groups. Due to the large number of hydrophilic groups on the surface of graphene oxide, most of the hydrophobic polymers are incompatible with it. Therefore, for the fabrication of polymer/graphene nanocomposites, the homogeneous incorporation of graphene into polymer matrix and optimizing the interfacial interactions between them are still obstacles to be re-

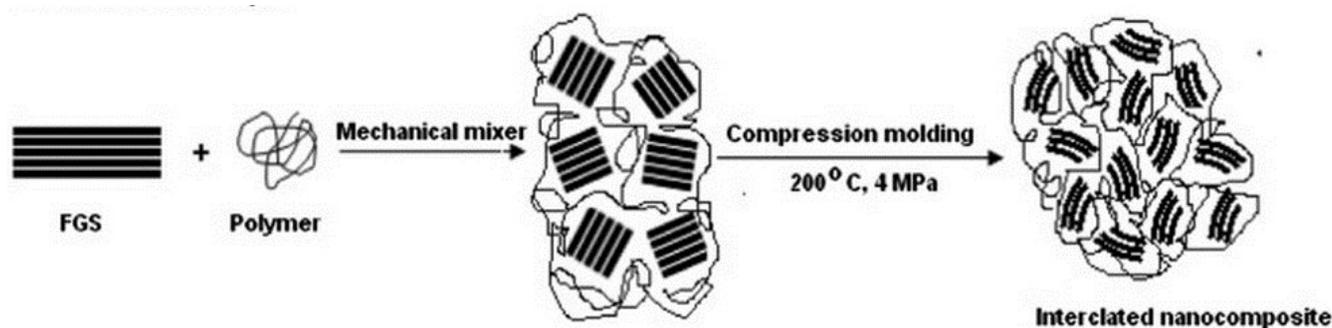


Figure 1. The mechanism of FGS incorporation into polymer for melt blend technique[37].

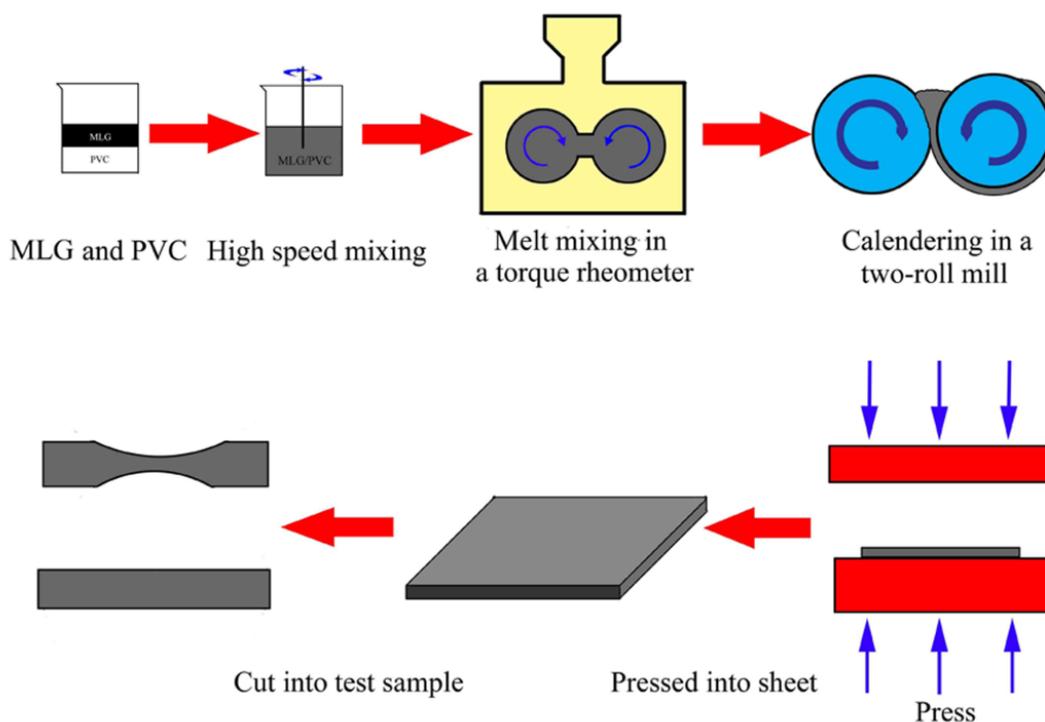


Figure 2. Fabrication schematics (a) of the MLG/PVC composites[45].

solved in both academia and industry. It is the critical step to scatter graphene well-dispersedly in polymer matrix. Good dispersion state can ensure that the contact interface between polymer matrix and graphene is maximized. Both benign dispersion and strong interfacial forces are extraordinarily beneficial to the overall performances of the nanocomposites. Scientists have made a lot of effort on dispersing modified or unmodified graphene and graphene oxide in polymer matrix evenly and achieved some results[22-24,29]. The structure of the typical polymers which are utilized as the matrix of polymer/graphene nanocomposites is shown as scheme 1.

Many researches realized the preparation of graphene and functionalized graphene with employing some novel methods, and successfully fabricated high-performance polymer/graphene nanocomposites.13,15 So far, there are mainly four preparation routes for fabrication of polymer/graphene nanocomposites: (1) melt

blending; (2) solution blending; (3) in-situ polymerization; (4) in-situ synthesis.

2.1. Melt blending

Compared with other methods, melt blending is more attractive for the preparation of commercial products because it is convenient and environmentally friendly without using organic solvents. For this method, researchers can mix polymer and graphene directly in twin screw extruder, and then adjust the parameters of extruder screw, including temperature, screw speed and blending time. The mechanism of foliated graphene nanosheets (FGS) incorporation into polymer for melt blend technique is shown as Figure 1[37]. Polymers, such as polyurethane, polypropylene, poly(ethylene terephthalate), polystyrene, poly(ether ether ketone), styrene-ethylene/ butylene-styrene triblock copolymer[38-44], were report-

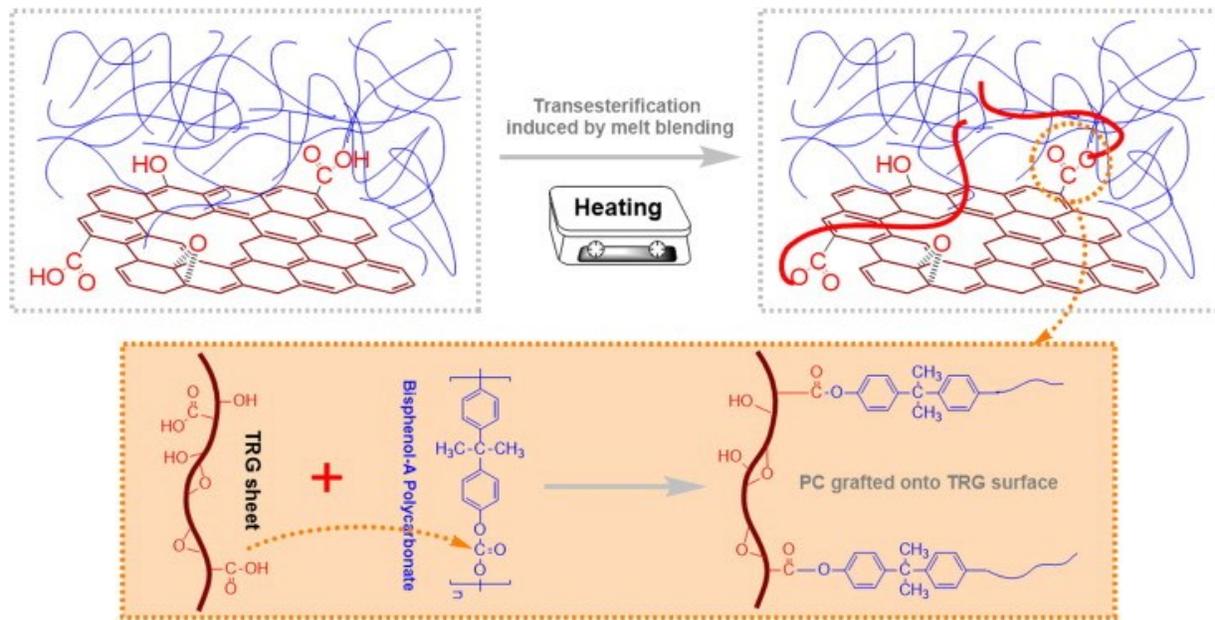


Figure 3. Schematic diagrams of the transesterification between the carbonate groups in PC chains and the carboxyl groups on TRG sheets at high temperature during melt blending[49].

ed to blend with graphene to obtain the nanocomposites by this method.

For instance, in order to improve toughness of rigid poly(vinyl chloride) (PVC), Wang et al. prepared multilayer graphene (MLG) filled PVC composites through conventional melt-mixing methods by taking advantages of high flexibility of graphene[45]. The fabrication procedure is shown as Figure 2. The weighed PVC powders, MLG, stabilizers, and lubricants were mixed in advance at room temperature using a high-speed mixer. Thereafter, the obtained mixtures were molten at 165°C and mixed well for 5 min in a torque rheometer. The obtained MLG-PVC blends were transferred into a two-roll mill, and further mixed at 170°C and squeezed into thin sheets. Then, these thin sheets were stacked together, transferred into a hot-press machine, and pressed into flat MLG/PVC composite sheets. It is found that a small amount of MLG loadings (0.36 wt%) could greatly increase toughness and impact strength of the MLG/PVC composites.

Besides, graphene-reinforced polymer matrix composites (G-PMCs) were produced with good distribution and particle-matrix interaction of bi/trilayer graphene in poly ether ether ketone (2Gn-PEEK and 5Gn-PEEK) through a high shear melt-processing method by Arya, et al.[43]. Poly(lactic acid) (PLA) composites reinforced with two types of graphene nanoplatelets varying in lateral size, small (GNP-S) and large (GNP-L), were produced via melt compounding by Gao et al.[46], in order to investigate the influence of particle size on mechanical, electrical and thermal properties of PLA nanocomposites. Polypropylene (PP) nanocomposites reinforced with graphene nanoplatelets (GNPs) were prepared via melt extrusion by Zhang et al.[47]. It indicates that the high shear stress exfoliate the GNPs effectively to a thinner layer and then enhance the electrical, thermal, and mechanical properties.

Futhermore, modified graphene is also used to reinforce polymer

blends via melt blending and some valuable results have been gained. For instance, nitrogen-doped graphene (NG) was introduced into immiscible poly(butylene succinate)/polylactide (PBS/PLA) blends by melt compounding.⁴⁸ When the NG concentration increased to 1.0 wt%, the NG filled PBS/PLA nanocomposites exhibited an obvious improvement in the storage modulus and loss modulus in comparison with the pristine PBS/PLA blend. The tensile strength, tensile modulus and elongation at break of the blends could be enhanced by the low concentration of NG. It indicates the main reason for such improvements is the strong interfacial interactions between the NG and the polymer matrices.

However, the adverse of this approach is that the density of graphene is very small and difficult in feeding and leads to poor dispersion of graphene in polymer matrix, making mechanical properties and other performances to decrease. Therefore, some modified methods have been presented to solve this problem. For example, the polycarbonate(PC)/graphene nanocomposites containing 3.0 wt% thermally reduced graphene (TRG) were firstly prepared by solution mixing and subsequent melt-mixing.⁴⁹ The occurrence of transesterification between the carbonate groups in PC and TRG is one possible mechanism for the enhanced interfacial interaction. The proposed schematic diagrams of the formed chemical bonding between PC and TRG, where the carboxyl groups on TRG sheets react with the carbonate groups of PC through transesterification during melt blending, was shown in Figure 3.

In general, without using solvents, melt blending method is not only environmentally friendly, but also simple and economic. It has been widely used for the synthesis of polymer nanocomposites. However, the high temperature required to achieve a homogenous mix can lead to occasional degradation of the polymer, thus, requiring care during the compounding process.

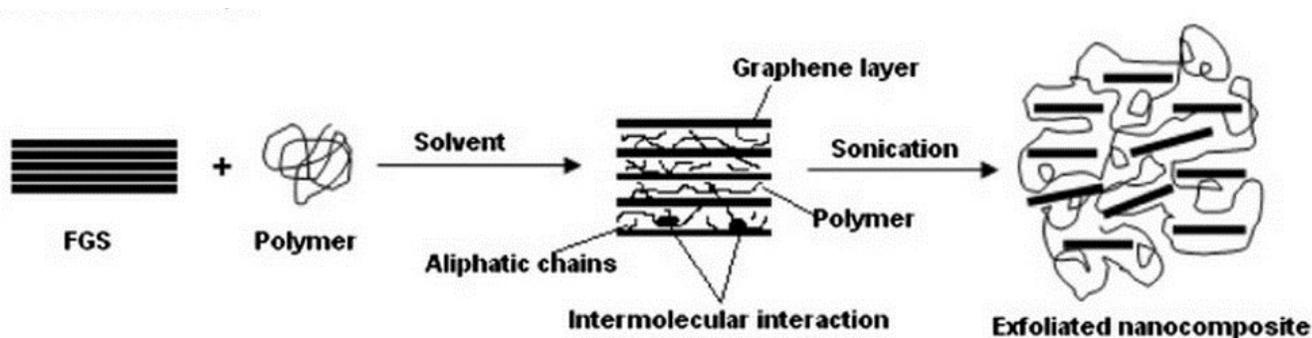


Figure 4. The mechanism of FGS incorporation into polymer for solution blend technique[37].

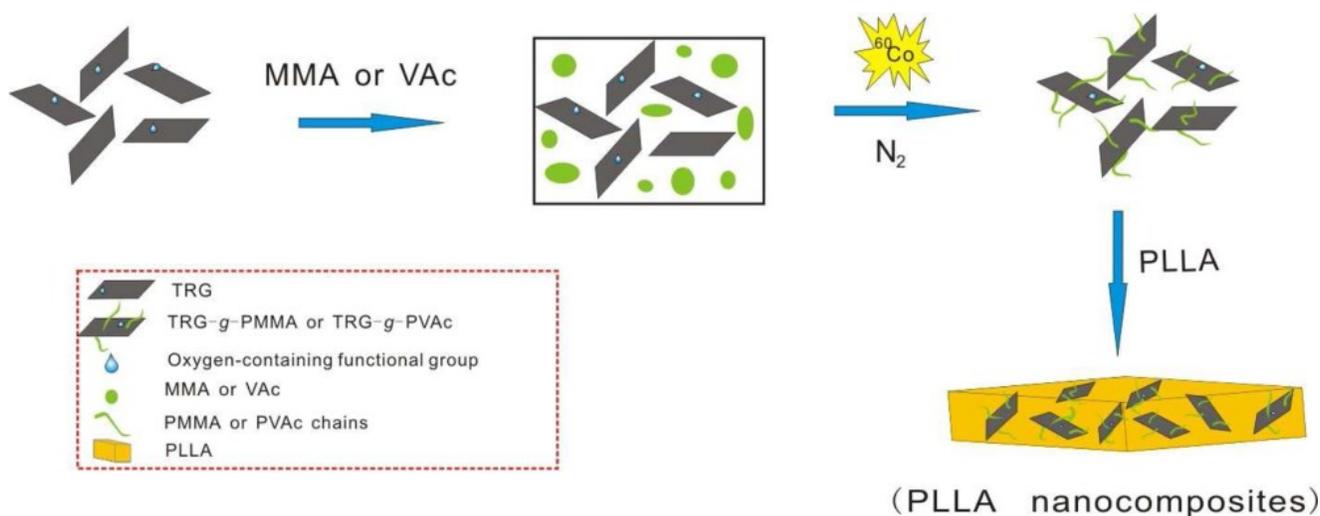


Figure 5. The process of preparation of TRG-g-PMMA and TRG-g-PVAc and their PLLA composites[70].

2.2. Solution blending

Solution blending is the most extensive method for preparation of polymer/graphene nanocomposites, especially in laboratory. For this method, the chemically or thermally reduced graphene oxide, which has many oxygen containing groups not being removed completely, are often used in the preparation. They can be well dispersed in organic solvents due to the presence of these groups. There are three steps in solution blending. Firstly, disperse reduced graphene oxide in a suitable organic solvent under sonication. Secondly, mix polymer in the solvent and make it dissolved. Thirdly, remove the solvent. A variety of nanocomposites, such as polytetrafluoroethylene composites[50-53], polystyrene composites[54-58], polyurethane composites[59-61], poly(methyl methacrylate) composites[62-65], polyethylene composites[66-69], were reported via solution blending method. This method is effective for the preparation of most of the nanocomposites, and is very suitable for the researches in the laboratory. Thus, it can be predicted that many new polymer/graphene nanocomposites will be obtained via this method in the future. The mechanism of foliated graphene sheets (FGS) incorporation into polymer for solution blend technique is shown as Figure 4[37].

PLLA/functionalized-TRG composites were prepared via this method by Chen et al.[70]. In the work, thermally reduced graphene oxide (TRG), which have lots of defections on the surface, was prepared firstly. Then a facial strategy of γ -ray irradiation was employed to functionalize TRG in monomers of polymethyl methacrylate (PMMA) and polyvinyl acetate (PVAc) for strong interaction between TRG and hydrophobic polymer. Finally, PLLA/functionalized-TRG composites were obtained via solution blending. The scheme of γ -ray radiation induced functionalization of TRG to prepare TRG-g-PMMA, TRG-g-PVAc and preparation of the PLLA nanocomposites is shown in Figure 5. It indicates the elongation at break of PLLA nanocomposites is enhanced without reducing the tensile strength and modulus, showing the improvement of PLLA toughness by introducing the TRG grafted with PMMA or PVAc chains.

Fluorescent polymer films, containing of a matrix of bio-polymer and graphene quantum dots (GQDs), were fabricated by Javanbakht et al (shown as Figure 6)[71]. In the preparation, crude native corn starch and glycerol was added to different volume of prepared graphene quantum dots (GQDs) stock solution. Complete gelatinization occurs at 80 °C with continues stirring about 30 min.

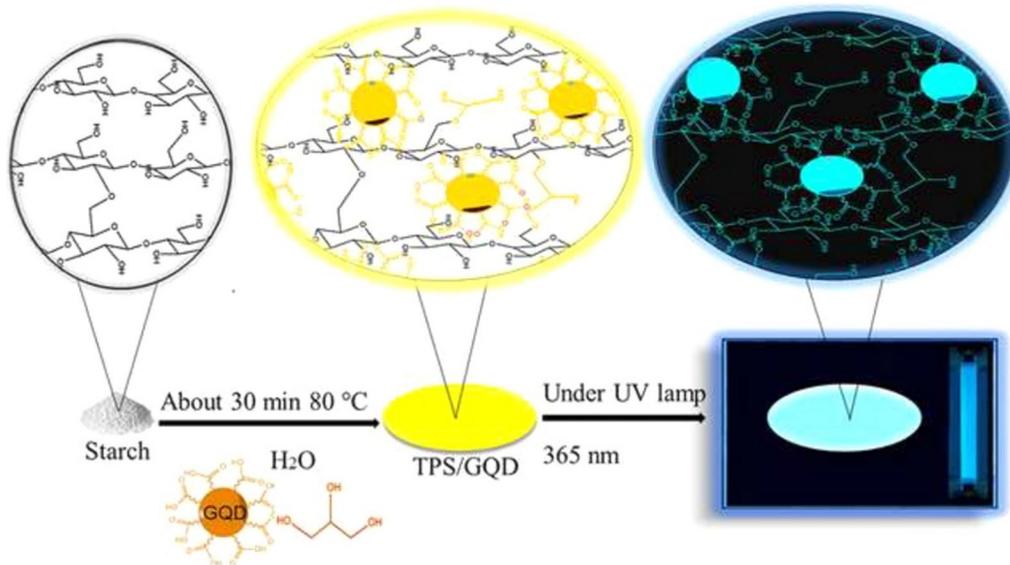


Figure 6. The process of preparation of fluorescent TPS/GQDs films[71].

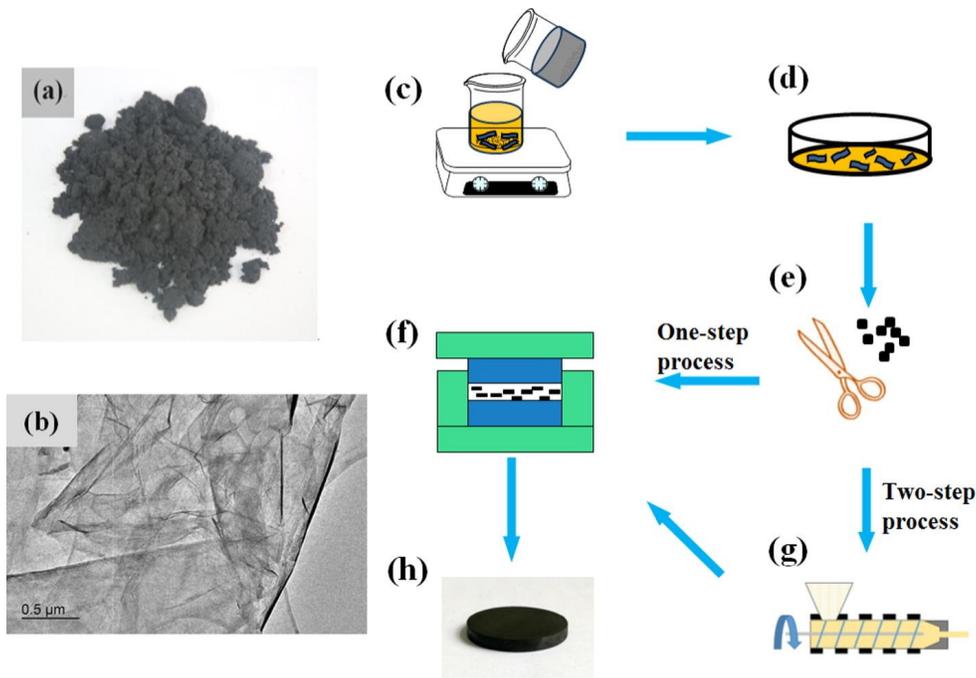


Figure 7. (a) Digital image (b) TEM image (c-h) showing the sample preparation methods applied in this work[72].

Then the materials were spread into polystyrene Petri dish and dried in an oven at 50 °C for one day. The maximum photoluminescence intensity of materials has been obtained at 50 wt% of GQD content. These materials have great potential to use in flexible electronic displays, light emitting diodes, and other optoelectronics applications. The surface modified graphene (DA-G) was mixed into polyethylene to prepare modified graphene-based polymer composite by solution mixing techniques[56-66]. It indicates that the tensile strength of the composite increase with 3 wt.% of

DA-G loading and is 46% higher than that of neat LDPE. A sharp increase in electrical conductivity of the composite is observed at 3 wt.% of DA-G content.

Significantly, there was a research that compared solution blending method with two-step process (solution blending and subsequent melt blending) by Bai, et al.⁷² In the work, graphene platelets (GNPs) in expansive form were firstly prepared through a solvent-exfoliated method. Figure 7a and b shows the images of GNP powder which were obtained through the common digital camera and

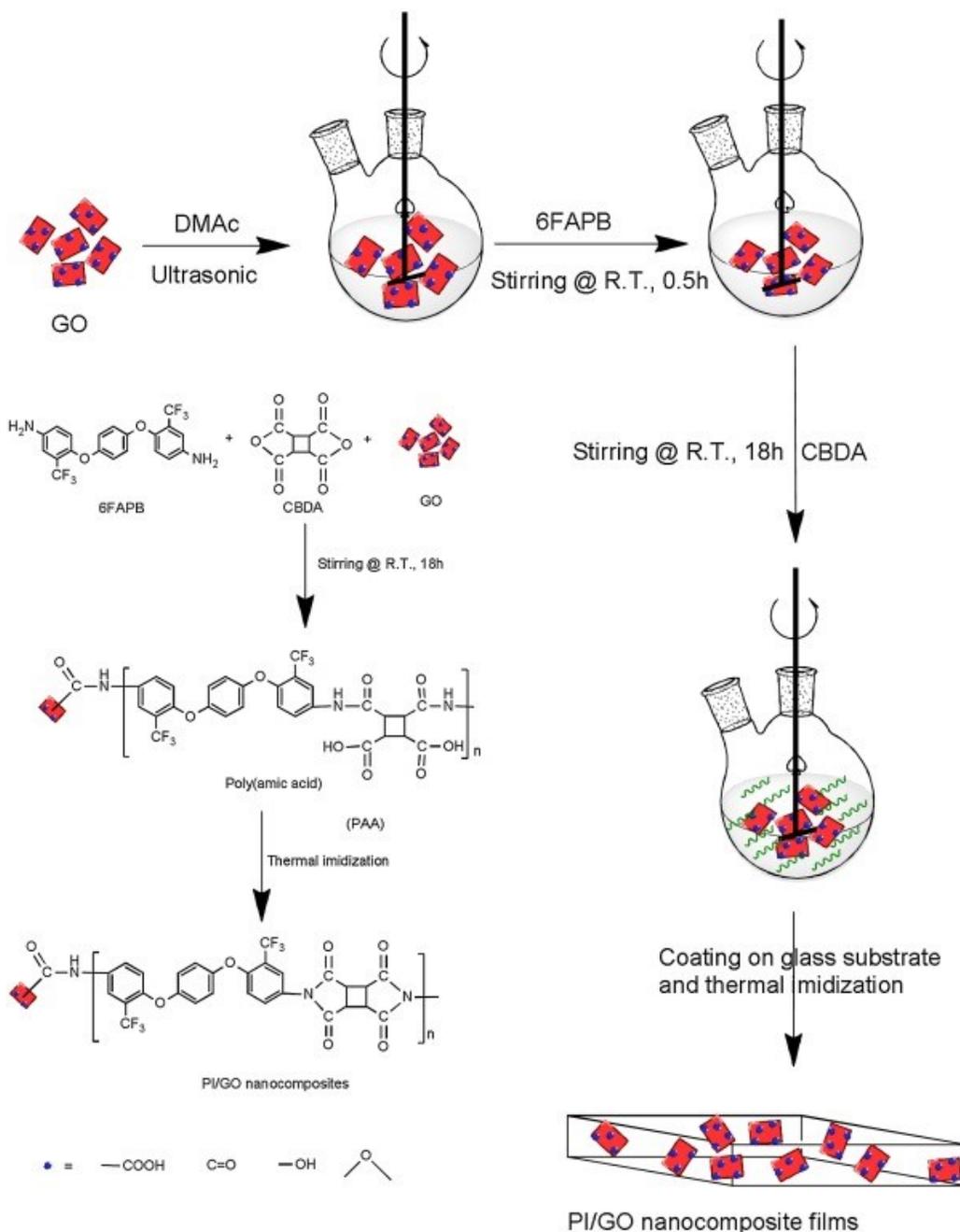


Figure 8. Schematic diagram for preparing alicyclic PI-based nanocomposite films with different GO loadings[92].

transmission electron microscope (TEM). Then the GNPs were introduced into polystyrene (PS) to prepare the composites through solution blending (PS/GNP-S) and two-step process (PS/GNP-SM) respectively, as shown in Figure 8(c-h). The dispersion states and microstructures of GNPs in the composites were comparatively investigated. The results demonstrates that the PS/GNP-S composites exhibits relatively poor dispersion of GNP particles but relatively high ability to form the percolated GNP network compared with the PS/GNP-SM composites. Conductive properties measurements show that the PS/GNP-S samples exhibits relatively low

volume resistivity.

However, it is worthy of attention that the organic solvents are commonly adsorbed between graphene layers for this method. The remained solvents have adverse effects on the performances of the nanocomposites. Some polar and nonpolar solvents of the adsorption between the graphene layers were studied systematically by Barroso-Bujans, et al.⁷³ It indicates that all tested solvents are inserted into the graphene layers and the solvents are difficult to be removed completely even at high temperatures. This is a shortcoming of solvent blending method. Moreover, it is not environmental-

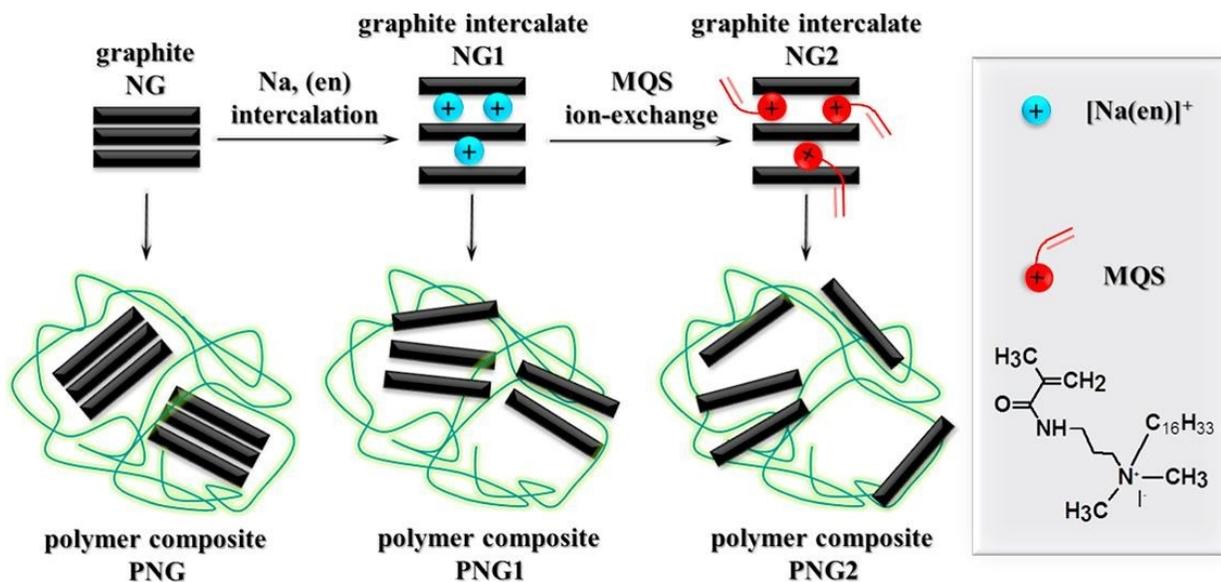


Figure 9. General scheme of the preparation of the natural graphite (NG) intercalation compounds (NG1, NG2) and the related polymer composites (PNG, PNG1, PNG2)[93].

ly friendly because much of organic solvent need to be used in the preparation process.

2.3. In-situ polymerization

In this method, sometimes with a suitable solvent, graphene is added into the monomer or prepolymer, and then the monomer is made to polymerize, or the prepolymer is made to cure into polymer. Because the surface of the chemically or thermally reduced graphene oxide contains some functional groups, graphene can be directly connected to the polymer. The groups can also be used as the reaction point of graphene for further modification, such as being covalently grafted on polymer chains by atom transfer radical polymerization (ATRP)[74-78]. The advantage of in-situ polymerization is that there forms a strong interfacial interaction between polymer and graphene. It is not only advantageous to the load transfer but also can make graphene dispersed evenly in the polymer matrix. All the same, the viscosity of the system will usually increase for the polymerization, which brings some troubles to the subsequent processing and material forming. There were many reports of polymer/graphene nanocomposites prepared by in-situ polymerization. The polymers which were used as the matrices included polyurethane[79-82], polystyrene[83,84], poly(methyl methacrylate)[85,86], epoxy resin[87,89], poly(lactic acid)[90], poly(vinyl alcohol)[91], etc.

A series of alicyclic polyimide/graphene oxide (PI/GO) nanocomposites were successfully fabricated via this method[92]. The typical process for the preparation of alicyclic PI-based nanocomposites consists of in-situ polymerization and the thermal imidization, as shown in Figure 8. Here, the $-\text{COOH}$ group on the GO surface can react with NH_2 group of 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene(6FAPB) to produce amide structure during the in-situ polymerization and thermal imidization process. The optical properties of the pure alicyclic PI and corresponding PI-based nanocomposite films showed that the addition of GO

reduced the transparency of PI films in the range of 200–800 nm obviously. With the increase of GO loading, the mechanical and thermal properties of alicyclic PI-based nanocomposites were enhanced.

A novel method for the preparation of polymer nanocomposites containing in situ exfoliated graphene nanoplatelets was reported by Poláková et al.[93]. First, graphite particles were modified by sodium and ethylenediamine (en), yielding first-stage graphite intercalation compounds (GICs) containing $[\text{Na(en)}]^+$ complex between carbon sheets. After subsequent ion-exchange reaction of the intercalated complex with quaternary ammonium salt bearing methacrylamide group, GICs possessing polymerizable double bond were obtained. GICs derived from natural graphite were further employed in the synthesis of polymer nanocomposites. General scheme of the GICs preparation as well as the synthesis of their related polymer composites is shown in Figure 9. Besides, a simple yet effective and scalable one-step method was reported to prepare graphene-based 3D covalent networks (G3DCNs) with tunable interlayer distance via controlled polymerization of benzidines with graphene oxide at different reaction temperatures under catalyst- and template-free conditions. The reduced form of G3DCNs can be used as electrodes in supercapacitors and reveals a high specific capacitance. The scheme of the reaction as well as of the chemical structures of the three obtained G3DCNs is shown in Figure 10[94].

In general, the graphene is dispersed in monomer at first. On initiation of the reaction, the monomer present in and out of the interlayers polymerizes to generate nanocomposites. However, a control of the polymerization in and out of the graphene layers is required in order to achieve high extents of exfoliation. Besides, the research of the nanocomposites fabricated via in-situ polymerization should not be limited in the final morphology, structure and performances. It should be taken into account that the effect of graphene on the polymerization or the cure reaction. There need

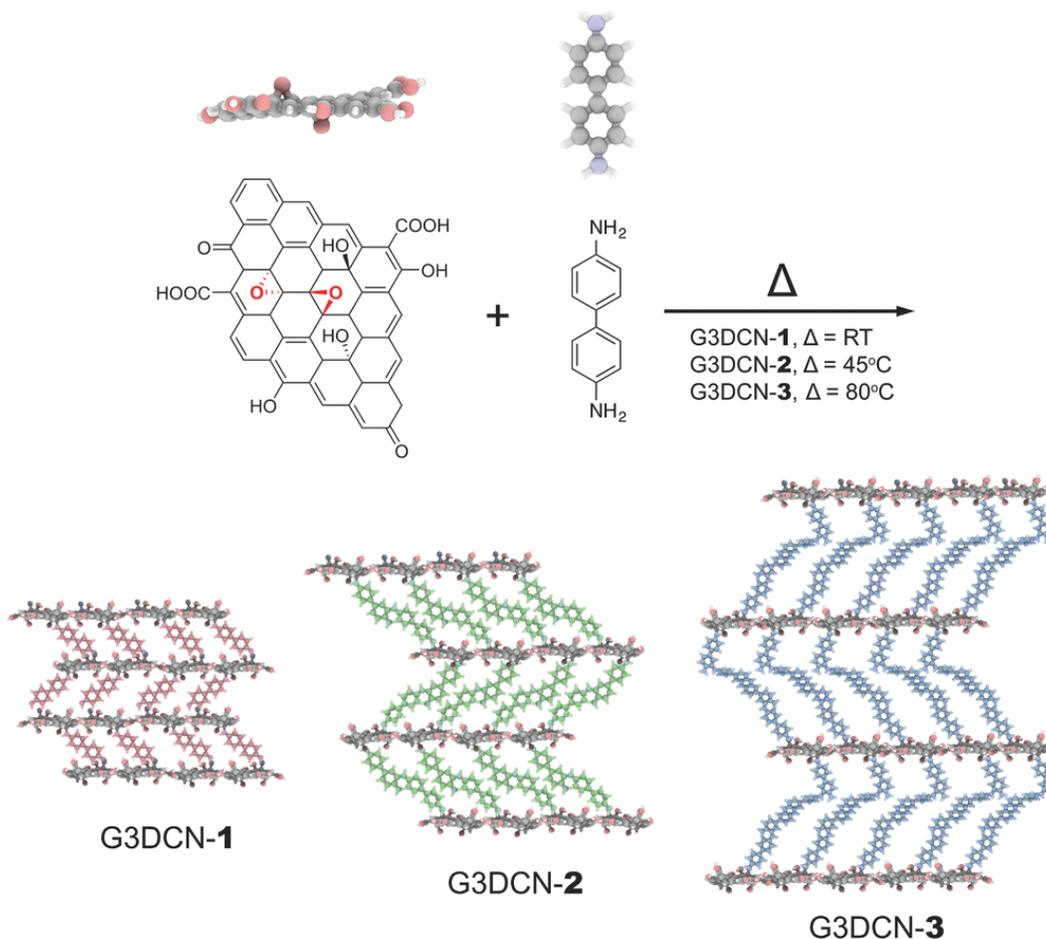


Figure 10. Reaction scheme and simplified representation of G3DCNs. G3DCNs with tunable interlayer distance obtained via controlled polymerization of benzidines with graphene oxide at different reaction temperatures. G3DCN-1 is obtained at room temperature; benzidine units are stitched between GO layers. Upon increase of temperature to 45 or 80 °C, PBZ-based oligomers, with different degree of polymerization, are covalently connecting GO layers, yielding G3DCN-2 and G3DCN-3, respectively[94].

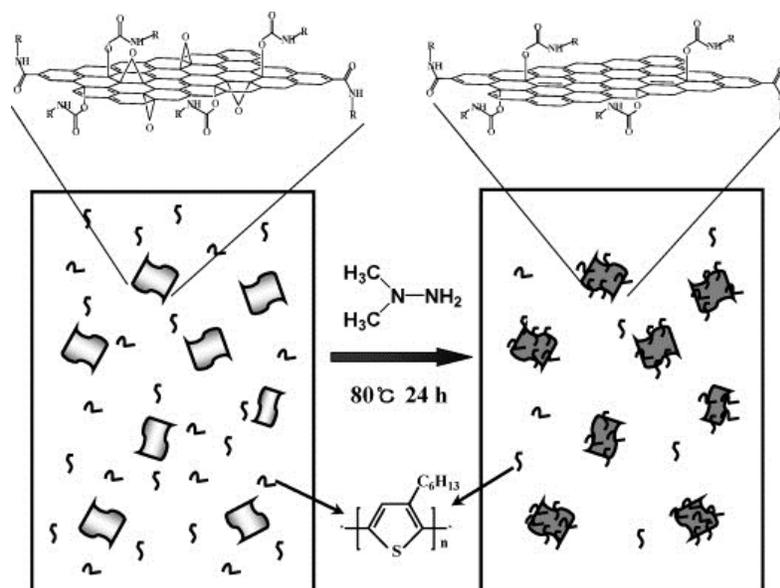


Figure 11. Schematic illustration of in situ reduction of modified graphite oxide sheets in the presence of P3HT[95].

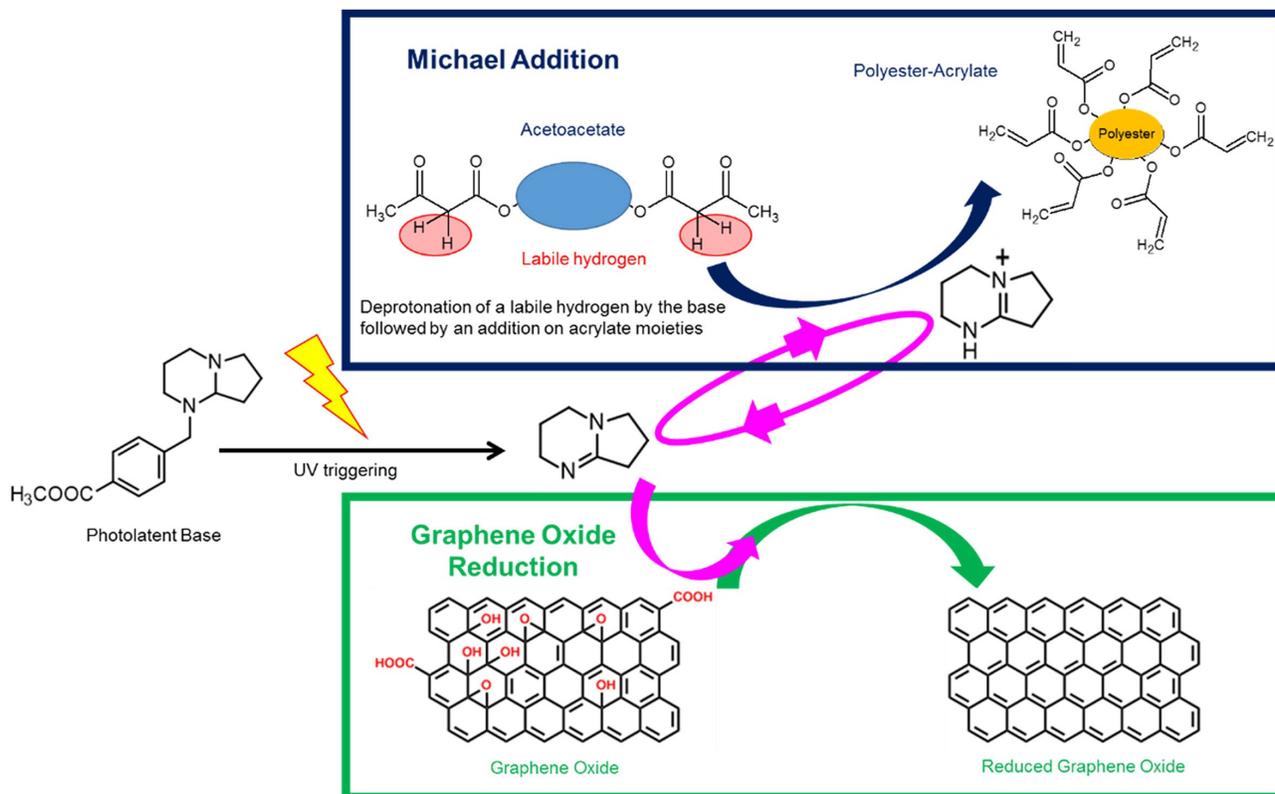


Figure 12. Schematic representation of the Michael addition reaction between acetoacetate and acrylic double bonds catalyzed by the photolabile base concomitant with the reduction of graphene oxide[98].

more researches on how the addition of graphene would change the polymer structure and molecular weight for the polymerization.

2.4. In-situ synthesis of graphene

In the technique of in-situ synthesis, the graphene is synthesized in the presence of the polymer matrix. It is opposite to other usual routes of nanocomposite and is not wide for the preparation of polymer/graphene composites, compared to the methods introduced above, because the synthesis process of graphene may lead to adverse effect on the polymer matrix. There have been researches done to explore the feasibility of this strategy, and some positive results have been achieved. For instance, poly(3-hexylthiophene)/GO (P3HT/GO) nanocomposite has been successfully obtained via the methods of in situ reduction of isocyanate-treated graphite oxide in the presence of P3HT[95]. The resulting nanocomposite materials exhibit good dispersity in chloroform and show high storage stability. The schematic illustration of in situ reduction of modified graphite oxide sheets in the presence of P3HT is shown in Figure 11. In detail, P3HT is loaded into a vial equipped with a magnetic stir bar and 1,2-dichlorobenzene (DCB) is then added under nitrogen to form P3HT solution. Graphite oxide dispersion is next dropping added followed by addition of dimethylhydrazine. The mixture was allowed to react for 24 h at 80 °C. The final product was filtrated and dried under vacuum at 40 °C to obtain the nanocomposite.

The preparation of poly (vinyl alcohol) (PVA)/graphene nano-

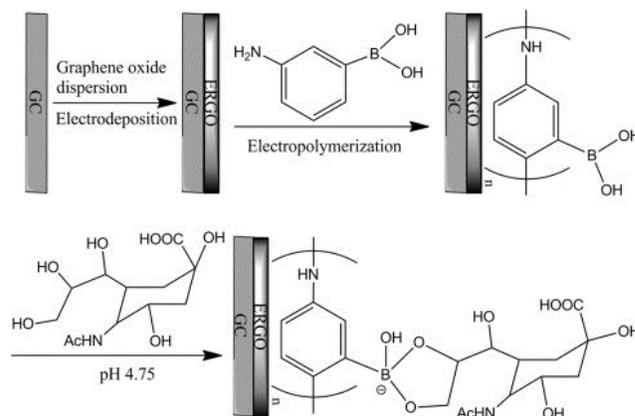


Figure 13. Schematic illustration of modification procedure of the GC electrode and the sensing mechanism of SA[100].

composites is realized via this method by Zhou et al.[96]. There are two simple steps: the synthesis of PVA/graphite oxide (GO) nanocomposites film and immersion of such a film in the reducing agent aqueous solution. This method prohibits the agglomeration of GO during direct reduction in PVA/GO aqueous solution, and opens a new way to scale up the production of graphene nanocomposites using a simple reducing agent. In the work of Wang et al.[97],

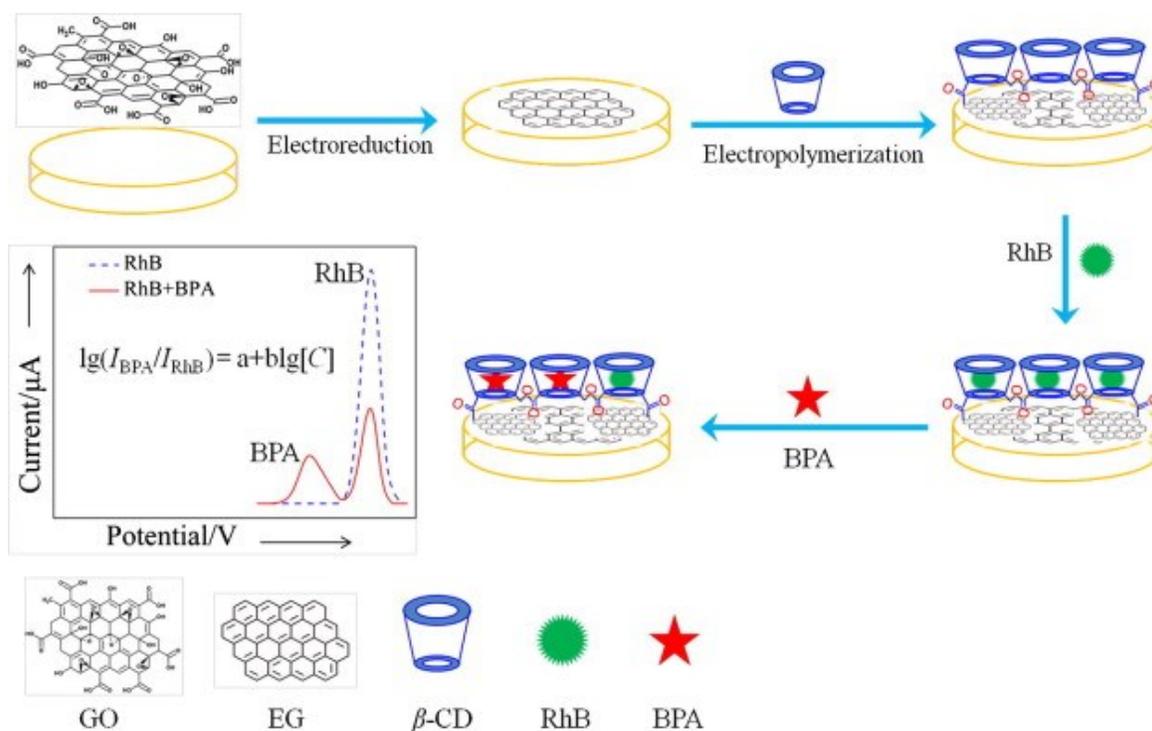


Figure 14. Schematic illustration of the ratiometric electrochemical sensor for BPA detection[101].

poly(lactic acid)/poly(butylene succinate)/reduced graphene oxide (PLA/PBS/RGO) nanocomposites were first prepared by the in situ thermal reduction of graphene oxide (GO) during the processing, and the influence of RGO on the morphology, thermal, and mechanical properties of biodegradable PLA/PBS blends were investigated.

Furthermore, it is innovative that in-situ polymerization and in-situ synthesis of graphene were combined by Gigotab et al.[98]. In the work, the photolabile base ((1,5-diazabicyclo [4.3.0]non-5-ene) DBN) is used for the first time as photocatalyst for the curing of a formulation, which undergoes crosslinking by Michael addition reaction between acetoacetate and acrylate groups together with the reduction of graphene oxide. The schematic representation of the process is reported in Figure 12.

3. APPLICATION OF THE NANOCOMPOSITES AS ELECTROCHEMICAL SENSORS

Many nanocomposites of polymer and carbon nanotube were studied in order to develop and utilize its excellent mechanical properties, or to introduce some new properties to polymer matrix, such as electrical and optical properties. Compared to carbon nanotubes, it is more feasible for the nanocomposite system based on the structure and function of graphene. It is because that graphene has the larger specific surface area, more strong interface binding force and more excellent physical properties than carbon nanotubes. Therefore, polymer/graphene nanocomposites have a broad application in many realms, such as sensors, conductive materials, electromagnetic shielding materials, photocatalytic materials, supercapacitors[16-24].

Graphene can be used for the preparation of electrochemical sensors with high sensitivity, good selectivity, quick response and wide detection range, due to its unique electronic structure, physical and chemical properties. It provides a rich place of the adsorption and reaction for the detected substance because of a large number of boundary points, structural defects and functional groups on it. Meanwhile, various of graphene derivatives with abundant composition and structure are continually fabricated to further regulate the performances. However, graphene cannot satisfy all testing requirements. It is necessary to combine graphene with polymers or other functional materials to improve some desired physical properties when it is applied as electrochemical sensors[99].

A novel potentiometric approach was described for probing sialic acid (SA) using a poly(anilineboronic acid)/graphene modified glassy carbon (GC) electrode by Zhou et al.[100]. The proposed electrode was prepared by electrodeposition of reduced graphene oxide (ERGO) at a GC electrode and then coated with a poly(anilineboronic acid) (PABA) film by electropolymerization of its monomer. Figure 13 shows the fabrication procedure of PABA/ERGO/GC electrode and the sensing mechanism of SA. Principle of SA detection at the PABA/ERGO/GC electrode is ascribed to a reversible and covalent boronic acid-diol binding which is sensitive to the electrochemical potential of the prepared sensor. The graphene layer introduced on the electrode surface is shown to dramatically improve the sensitivity of the sensor response.

A ratiometric electrochemical sensor has been developed for highly sensitive and selective detection of bisphenol A by Zhang et al.[101]. The strategy, which is shown as Figure 14, is based on the

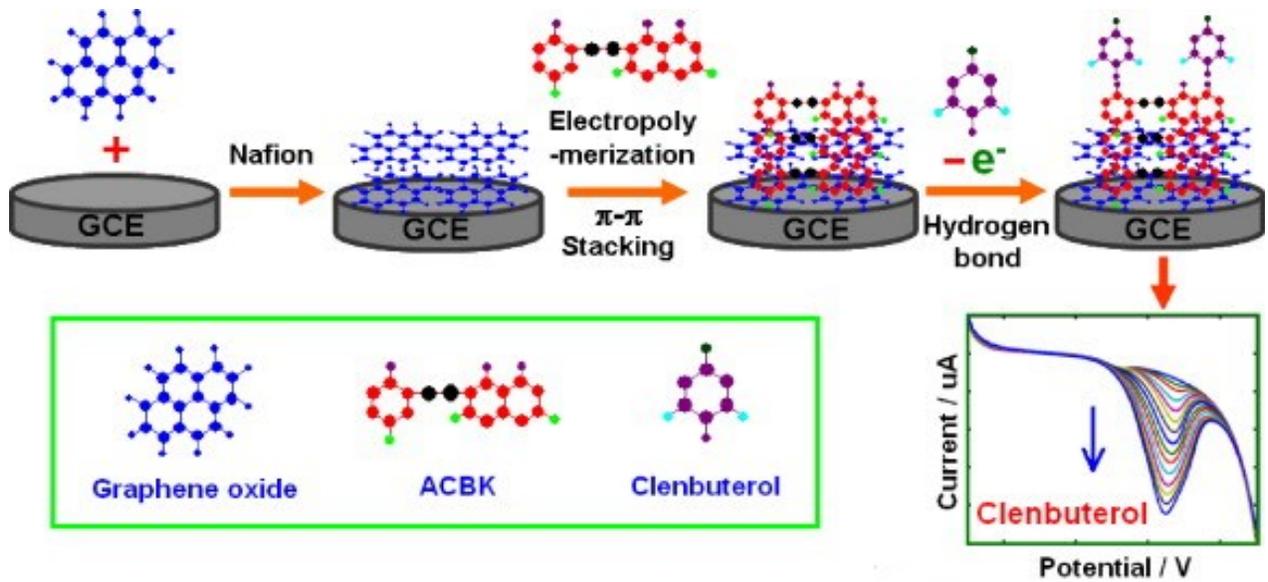


Figure 15. Schematic representation of the fabrication of the poly-ACBK/GO-nafion/GCE, and the possible interaction of clenbuterol at the modified GCE[102].

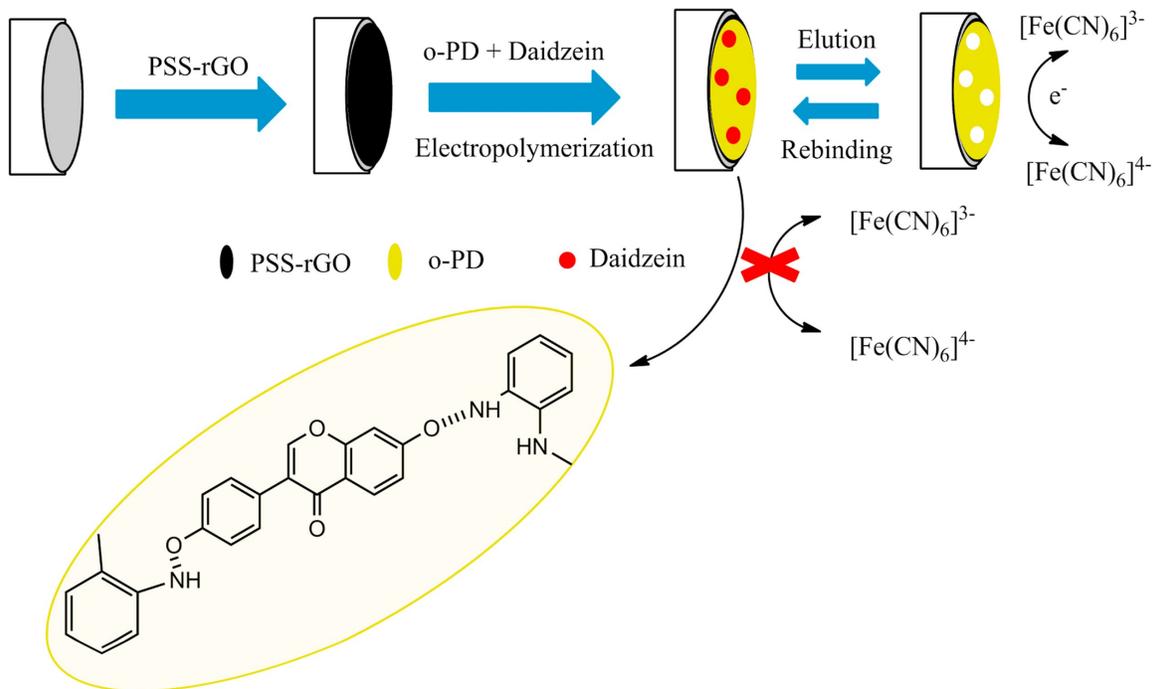


Figure 16. Illustration of the synthesis procedure of molecularly imprinted polymer and the modified electrode construction process[103].

competitive host-guest interaction between poly- β -cyclodextrin/electroreduced graphene (P β -CD/EG) and Rhodamine B (RhB) probe or bisphenol A (BPA) target molecules. RhB can enter into the hydrophobic inner cavity of β -CD and shows an obvious oxidation peak on the P β -CD/EG modified glassy carbon electrode. In the presence of BPA, the RhB molecules are displaced by BPA because the host-guest interaction between β -CD and BPA

is stronger than that between β -CD and RhB. As a result, the oxidation peak current of RhB (I_{RhB}) decreases and the oxidation peak current of BPA (I_{BPA}) increases correspondingly. The logarithmic value of $I_{\text{BPA}}/I_{\text{RhB}}$ is linear with the logarithm of BPA concentration in the range of 1-6000 nM and the detection limit is 52 pM (S/N = 3). This strategy provides a new approach for sensitive detection of BPA, and has promising applications in the detection of

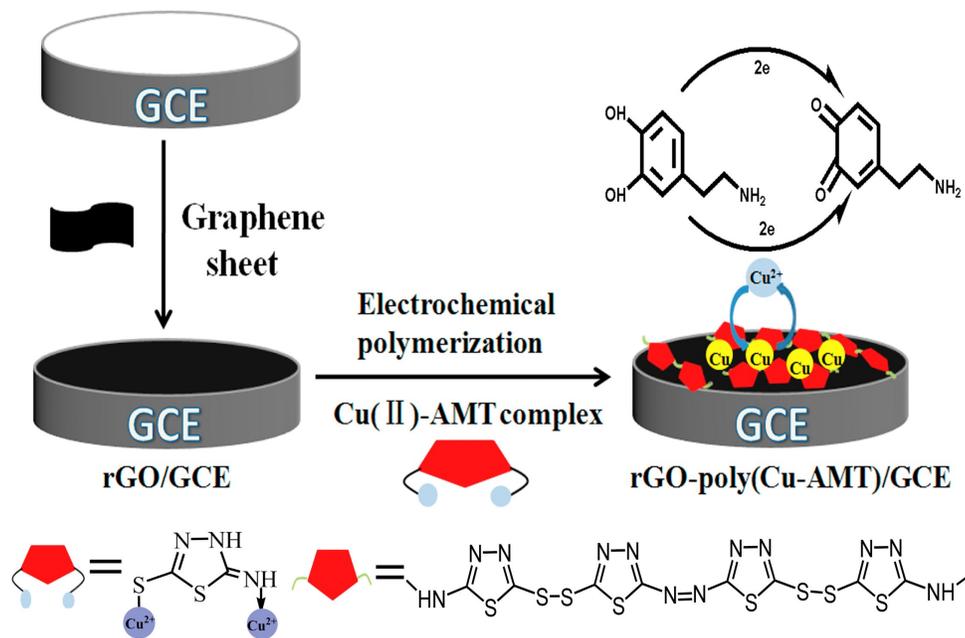


Figure 17. Fabrication process of the biomimetic sensor and the catalytic mechanism for the analysis of dopamine[108].

organic pollutants in real environmental samples.

A novel modified electrode was constructed by the electropolymerization of 4,5-dihydroxy-3-[(2-hydroxy-5-sulfophenyl)azo]-2,7-naphthalenedisulfonic acid trisodium salt (acid chrome blue K (ACBK)) at a graphene oxide (GO)-nafion modified glassy carbon electrode (GCE)[102]. This electrode showed satisfactory reproducibility and stability, and was used successfully for the quantitative analysis of clenbuterol in pork samples. It suggests that the oxidation and reduction of clenbuterol are electro-catalytically enhanced at the poly-ACBK/GO-nafion/GCE. This could be attributed to the large surface areas, π - π conjugated bonds, many potentially active sites and high conductivity for the GO and poly-ACBK films. Moreover, hydrogen bonds could be formed between the polymer and the analytes (Figure 15).

A high sensitive and selective electrochemical sensor for detection of daidzein based on molecular imprinted polymer (MIP) modified electrode was established by Liang, et al.[103]. The sensitive layer was prepared by electropolymerization of *o*-phenylenediamine (*o*-PD) on the surface of Poly(sodium 4-styrenesulfonate) reduced graphene oxide (PSS-rGO) modified glassy carbon electrode (PSS-rGO/GCE) in the presence of daidzein as a template molecule. The negatively charged poly(sodium 4-styrenesulfonate) units and benzene rings of PSS-rGO can attract positive charged *o*-PD and provide π - π stacking effect of *o*-PD and daidzein, which makes the compact imprinted film and more imprinted points. The MIP/PSS-rGO composite could specifically recognize daidzein in aqueous solutions which result in the decrease of peak current of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ at the MIP/PSS-rGO/GCE.

A polymerized film of copper-2-amino-5-mercapto-1,3,4-thiadiazole (Cu(II)-AMT) complex (poly(Cu-AMT)) was success-

fully achieved via a simple and low-cost electrochemical methodology[108]. Subsequently, a noncovalent nanohybrid of poly(Cu-AMT) with reduced graphene oxide (rGO) (rGO-poly(Cu-AMT)) was prepared through π - π stacking interaction as an efficient mimetic enzyme for the ultrasensitive and selective detection of dopamine (DA). Figure 17 represents the fabrication processes of the rGO-poly(Cu-AMT) film and the catalytic mechanism for the analysis of dopamine. The rGO-poly(Cu-AMT) nanocomposites showed considerable mimetic enzyme catalytic activity, which may be attributed to the significant promotion of the electron transfer between the substrate and graphene-based carbon materials, and also the synergistic electrocatalytic effect in mimetic enzyme between rGO sheet and poly(Cu-AMT). The biomimetic sensor enables a reliable and sensitive determination of DA with a linear range of 0.01-40 μ M and a detection limit of 3.48 nM at a signal-to-noise ratio of 3. The sensor in the work shows a broader detection range and lower detection limit than the reported values obtained by other electrochemical sensors[109].

Dai, et al.[110], reported an electrochemical metal ions sensor based on a phytic acid functionalized PPy/GO nanocomposites modified electrode. PPy/GO nanocomposites were simply and rapidly prepared by in situ polymerization with the ferric chloride. Phytic acid was adsorbed on the surface of PPy/GO nanocomposites by electrostatic attraction. Schematic diagram for the synthesis of the PA/PPy/GO nanocomposites and the electrochemical detection of heavy metal ions, is shown as Figure 18. The improvement for sensing of heavy ions on PA/PPy/GO can be attributed to two aspects. Firstly, the high surface area of GO and the excellent electric conductivity of PPy can enhance the electron transfer during the detection processes. Secondly, number of functional groups with large negative charges on PA and GO is beneficial to improving the adsorption capacity of heavy metal ions. In consequence,

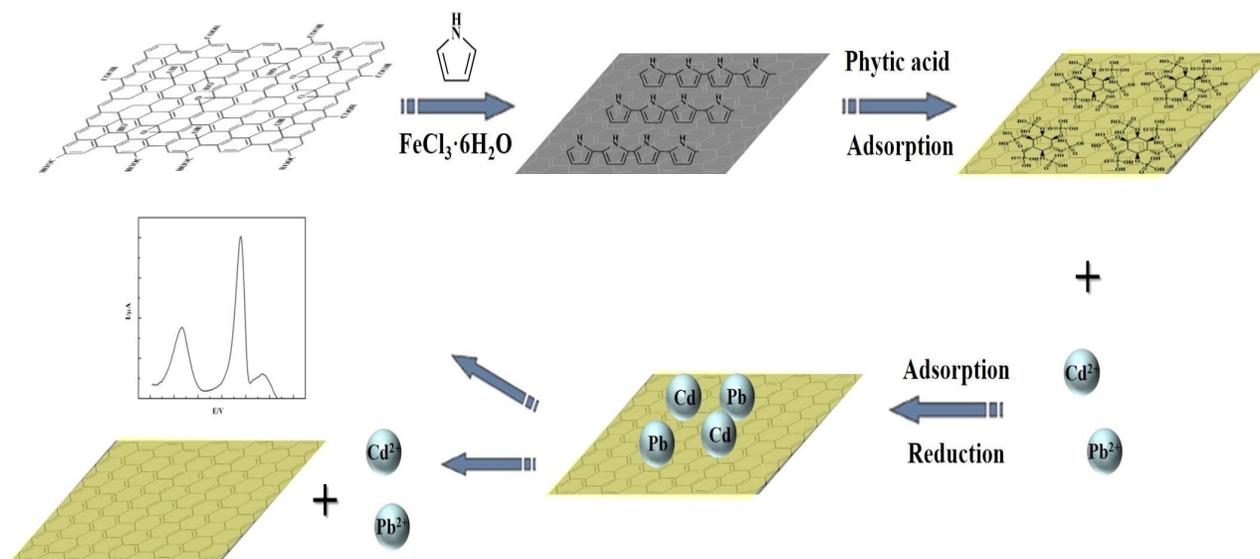


Figure 18. Schematic diagram for the synthesis of the PA/PPy/GO nanocomposites and the electrochemical detection of heavy metal ions[110].

the two aspects synergistic effects can bring about the accumulation of heavy ions and the increase of the detection sensitivity of Cd(II) and Pb(II). With the advent of more functional materials towards analytes, the presented strategy is likely to offer a potential platform for analysis and treatment of trace amount of environmental heavy metals.

A novel molecularly imprinted electrochemical sensor for quercetin (QR) was fabricated via electropolymerization of paraaminobenzoic acid (p-ABA) on a three-dimensional (3D) Pd nanoparticles-porous graphene-carbon nanotubes composite (Pd/pGN-CNTs) modified glassy carbon electrode[111]. The molecularly imprinted poly(p-ABA) exhibits high recognition capacity to the template molecules, 3D graphene-carbon nanotubes (GN-CNTs) hybrids have high surface-to-volume ratio and conductivity which benefits the improvement of sensitivity, and Pd-based nanomaterials have electrocatalysis. Based on the synergistic effect of them, the resulting electrochemical sensor presents high sensitivity and selectivity. It can be applied to the detection of QR in food and medicine samples.

In addition, hybrids of ethylenediamine-modified reduced graphene oxide (RGO) and polythiophene (PTh) were synthesized successfully by in-situ chemical polymerization and loaded on a flexible Poly(ethylene terephthalate) (PET) film to construct a smart sensor[112]. The NO₂-sensing performance of pure PTh- and hybrids-based sensors was examined at room temperature. The results indicated that the hybrid film sensor with 5 wt % RGO exhibited high sensitivity to 10 ppm of NO₂ gas which was nearly 4 times higher than that of pure PTh. The mechanism of sensing performance enhanced by incorporating graphene into PTh is attributed to large specific surface of the hybrid and synergetic effects between the components in a hybrid.

Besides, many novel polymer/graphene composite sensors have been fabricated and researched[113-119]. The expanded graphene-oxide (EGO) encapsulated polyaniline (PA) nanocomposites were

prepared by in-situ chemical oxidative polymerization[120]. The electrical conductivity got increases with temperature, showing semiconducting behaviour, and the conductivity was found to be 101.04 S/m at 413 K. A polyaniline-graphene oxide nanocomposite (PANI/GO/GCE) sensor has been fabricated for quantification of a calcium channel blocker drug levamlodipine (LAMP) by Rajeev, et al.[121]. The sensor showed an excellent performance for detecting LAMP with reproducibility of 2.78% relative standard deviation (RSD).

The proposed method has been successfully applied for LAMP determination in pharmaceutical formulation with a recovery from 99.88% to 101.75%.

Moreover, due to its excellent conductivity and electrocatalytic activity, graphene is an ideal material for the preparation of electrochemical biosensors. For instance, a novel DNA biosensor based on oxidized graphene and polyaniline nanowires (PANIWs) modified glassy carbon electrode was developed[122]. The resulting graphene/PANIw layers exhibits good DPV current response for the complementary DNA sequences. The good electron transfer activity is attributed to the effect of graphene and PANIw. The immobilization of the probe DNA on the surface of electrode is largely improved due to the unique synergetic effect of graphene and PANIw. Under optimum conditions, the biosensor exhibits a fast amperometric response, high sensitivity and good storage stability for monitoring DNA, showing potential application in sensitive and selective DNA detection.

4. CONCLUSIONS

From above, the research work has proved that the emergence of graphene has undoubtedly changed the scope of sensor field due to its outstanding electrochemical properties as well as other unique properties such as large surface area, high electrical conductivity, light weight, and mechanical strength. The recent development of graphene and polymer composites shows very promising features

for sensor applications. Compounded with polymers, graphene would compensate the undesired features of insulating polymers (e.g., insulating nature, low surface area, and low specific capacitance). On the other hand, when graphene makes composites with conducting polymers, it would provide mechanical support for the framework of the polymers and thus greatly improve the durability as well as the conductivity. In addition, the flexible nature of the graphene/polymer composite film makes it possible for flexible, wearable, conformable devices. Despite the innovative ideas and techniques that have been demonstrated for the polymer/graphene sensor device with unique features, the studies of polymer/graphene nanocomposites and their applications in sensors are still in an embryonic stage and there remain a lot of challenges.

First of all, there are still many issues waiting to be settled for further development. For instance, the mechanism of sensing based on the nanomaterials is not very clear, and quantitative calculation is almost impossible till now. Additionally, the novel and effective methods need to be proposed not only for the controllable synthesis and treatment of graphene, but also for the preparation of the nanocomposites. Graphene provides possibilities to tune the surface in order to achieve nanoscale dispersion of platelets in the polymer matrices in order to achieve high aspect ratio of platelets resulting in superior properties. Although the incorporation of surface modified graphene has been reported to enhance filler dispersion and resulting nanocomposite properties, it is necessary to find more suitable way to control morphology and size of graphene in the polymer matrix. Moreover, how to achieve strong interfacial interaction between graphene and polymer matrix need to be further developed.

Besides, further researches for potential applications are also important and must be paid more attention. To today, there is no perfect solution to the cross-sensitivity problem of polymer/graphene nanocomposite sensors at present. For example, when gas concentration is detected, temperature can produce interference to the sensor. Furthermore, repeatability and stability of the graphene sensors are not optimistic. When graphene adsorb chemical molecules, it is difficult to automatically return to the original state, which results in the decrease of sensor sensitivity. There are some ways of desorption, such as heating and UV-light irradiation, but these methods are not suitable for the actual detection environment.

In summary, the development of synthesizing novel nanocomposites with high sensitivity and selectivity is one of the mainstream trends of sensors. Researchers should design more novel electrochemical sensors based on the nanocomposites with superior comprehensive performances and help them to be applied practically in all kinds of realms. All these researches can help us to get a deeper understanding of the polymer/graphene nanocomposites and leads to better application of them in the sensors.

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