

# Polymer Chemistry

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Full Paper

## Towards development of versatile and efficient strategy for fabrication of GO based polymer nanocomposites

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Surface modification of graphene oxide (GO) with polymers is of particular importance for its applications. Although much progress has been made in the surface modification of GO, the surface modification of GO with synthetic polymers in aqueous solution has demonstrated to be problematical. In present work, we reported for the first time a versatile and effective method for surface modification of GO with synthetic polymers in aqueous solution taken advantage of the mussel inspired chemistry. The poly(ethylene glycol) methyl ether methacrylate and itaconic anhydride (IA) monomers were chosen to prepare hydrophilic polymers (poly(IA-co-PEGMA)) via free radical living polymerization. These hydrophilic polymers were further reacted with dopamine through ring-opening reaction between IA and dopamine, which could be high-efficiently attached to the GO surface via mussel inspired chemistry using dopamine as the adhesion component. The successful modification of GO with polymers was confirmed by a series of characterization techniques. The resulting GO-polymer nanocomposites displayed great dispersibility in aqueous and organic solution, making them promising for various applications. As compared with previous methods, the biomimic strategy described in this work could facilitate and effectively immobilize synthetic polymers on GO in aqueous solution at room temperature and air atmosphere. More importantly, this strategy could also be utilized for fabrication of almost any polymer nanocomposites because of the designability and applicability of living polymerization, versatility and strong adhesion of dopamine.

### 1. Introduction

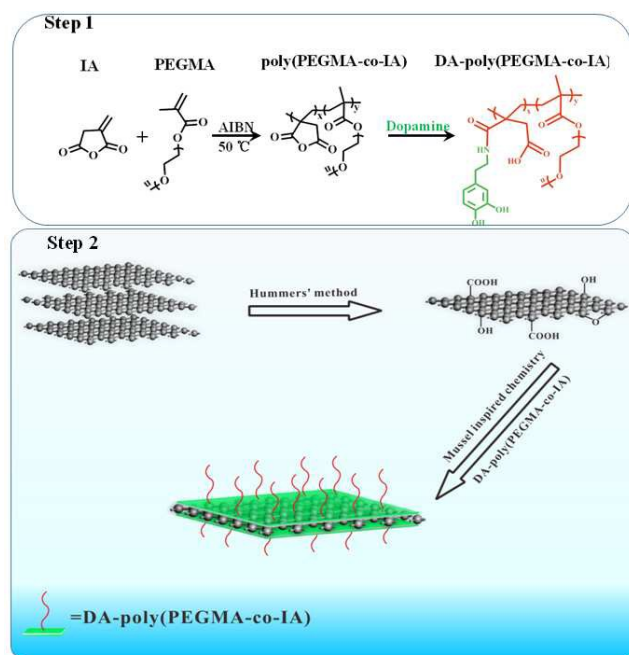
Since the first discovery of graphene by Geim and Novoselov in 2004, the development of graphene-based materials has been the focus of many research fields.<sup>1</sup> The appearance of graphene not only added a new member to carbon family, but also quickly inspired scientists to explore the ascendant properties and applications of graphene. Of course, as a unique two-dimensional hexagonal carbon network, the already discovery of ultrahigh Young's modulus, high-efficiency migration of electron, thermal properties, specific surface area and biocompatibility have prompted graphene become a superstar in science and technique fields.<sup>2-6</sup> Furthermore, as well as other carbon materials such as carbon nanotubes and fullerene, the unique physicochemical properties of graphene make them get extensive applications in many fields such as electronics, medical imaging, drug delivery and tissue engineering.<sup>6-17</sup> To date, oxidation of graphite powder using strong oxidants to obtain graphene oxide (GO) has demonstrated to be a relative popular and low cost route for preparation of graphene using different reducing agents.<sup>18-20</sup> Comparing with graphene, the introduction of hydrophilic functional groups (hydroxyl, carboxyl and epoxy) slightly enhance the dispersibility of GO in water and polar solution, which could keep dispersed in water.<sup>21</sup> On the other hand, the

introduction of these chemical functional groups provide many reactive sites for further surface modification of GO via a series of chemical reaction such as amidation of the carboxylic groups, nucleophilic addition to the epoxy groups. However, because of the existence of strong  $\pi$ - $\pi$  and Vander Waals interactions, single-layer GO is tended to agglomeration and formation of graphite oxide during reduction and removal of the dispersion solvents.<sup>22-26</sup> Therefore, surface modification of GO is necessary to avoid its agglomeration.

Over the past decade, great research effort has been made in surface modification of GO.<sup>27-35</sup> Among them, surface modification of GO with synthetic polymers through different polymerization methods has demonstrated to be the most effective strategies.<sup>36-39</sup> For example, Huang *et al* reported that the immobilization of poly(ethylene glycol) ethyl ether methacrylate chains on the GO surface via surface initiating single electron transform living radical polymerization (SET-LRP). They demonstrated that tris(hydroxymethyl) aminomethane (Tris) was introduced to the surface of GO through ring-open reaction with epoxy groups to increase the quantity of hydroxyl and subsequently reacted with 2-bromo-2-methylpropionyl bromide to obtain Br-containing SET-LRP initiator.<sup>40, 41</sup> Recently, a novel reversible addition fragmentation

chain transfer (RAFT) agent was synthesized using GO as substrate for in situ growing of poly(N-vinylcarbazole) (PVK) chains directly from the GO surface. The resulting PVK-GO composite materials exhibited better dispersion in organic medium.<sup>42</sup> However, these polymerization strategies should be first immobilization of initiators on the surface of GO. And these polymerization procedures can only occurred in the absent of oxygen and water at relative high temperature. Some of them are required using metal catalysts. Therefore, the development of novel strategies for surface modification of GO with synthetic polymers, that could occur in aqueous solution, air atmosphere, at room temperature, and need not involving in the metal catalysts is of great importance.

Mussel inspired chemistry was firstly put forward by Lee in 2007, which was demonstrated to be a robust and versatile surface modification strategy to any materials regardless of their shape, size and structure.<sup>43-46</sup> It has been proven that a high content of 3,4-dihydroxy-L-phenylalanine (DOPA) and lysine (Lys) existed in marine mussel adhesive protein (Mefp-5) play an important role in direct contact with substrates. Respectively, the dopamine (DA) was certified to have similar function with Mefp-5, which could spontaneously form a film in the alkaline solution and strongly attached on the various material surface.<sup>47-63</sup> More importantly, the amine and hydroxyl groups would introduce onto the material surface, which have great significance for importing other molecules via a series of chemical reactions. In this contribution, we reported for the first time that GO can be facily and efficiently functionalized with synthetic polymers through a biomimic strategy. The experimental process could be summarized in **Scheme 1**. The resulting GO-polymer hybrid materials were characterized by different instruments include Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), thermogravimetric analyzer (TGA) and X-ray photoelectron spectroscopy (XPS). The biocompatibility and drug delivery applications of GO-poly(DA-IA-PEGMA) were also examined.



**Scheme 1** Schematic illustration for the preparation of DA-poly(PEGMA-co-IA) modified GO via mussel inspired chemistry. Step 1 showed the synthesis of poly(PEGMA-co-IA) by free radical living polymerization, which was subsequently reacted with DA to get DA-poly(PEGMA-co-IA). Step 2 illustrated that attachment of DA-poly(PEGMA-co-IA) onto GO via mussel inspired chemistry.

## 2. Experiment

### 2.1 Materials and Characterization

All chemicals were of analytical grade and were used as received without any further purification. All aqueous solutions were prepared with distilled water. Purified natural graphene powders were suffered from Sinopharm chemical reagents. Dopamine hydrochloride (MW: 189.64 Da, > 98%) were supplied from company of Sangon Biotech, Tris hydroxyl methyl aminomethan (Tris), poly(ethylene glycol ) methyl ether methacrylate (PEGMA, MW: 950 Da, 98%), itaconic anhydride (IA, MW: 112.19 Da, 96%), 2,2-Azodiisobutyronitrile (AIBN, MW: 164.21 Da, 98%) were purchased from Aladdin (Shanghai, China), anhydrous ethyl acetate and methanol were offered by Heowns (Tianjin, China). <sup>1</sup>H NMR spectra was recorded on Bruker Avance-400 spectrometer with D<sub>2</sub>O as the solvent. The synthetic polymers and materials were characterized by FT-IR using KBr pellets, The FT-IR spectra were supplied from Nicolet5700 (Thermo Nicolet corporation). TEM images were recorded on a Hitachi 7650B microscope operated at 80 kV, the TEM specimens were got by putting a drop of the nanoparticle ethanol suspension on a carbon-coated copper grid. TGA was conducted on a TA instrument Q50 with a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. Samples weighing between 10 and 20 mg were heated from 25 to 600 °C in N<sub>2</sub> flow (60 mL min<sup>-1</sup>). Each sample was ultrasonicated for 30 min prior to analysis. The XPS spectra were performed on a VGESCALAB 220-IXL spectrometer using an Al K $\alpha$  X-ray source (1486.6 eV). The energy scale was internally calibrated by referencing to the binding energy (E<sub>b</sub>) of the C1s peak of a carbon contaminant at 284.6 eV.

### 2.2 synthesis of single-layer GO sheets

A modified Hummers' method was adopted to prepare single-layer GO sheets using graphite powders as raw materials. The mixture of graphite powders (1 g), NaNO<sub>3</sub> (0.5 g) and H<sub>2</sub>SO<sub>4</sub> (46 mL) were poured into a conical flask in ice-water bath. When temperature arrived 0 °C, the KMnO<sub>4</sub> (3 g) was added into conical flask and stirring at surrounding temperature for 15 min and subsequently 92 mL water was added into the mixture. Afterward, above experimental device was moved to oil bath and stirred at 98 °C for 15 min. After cooling to room temperature, 140 mL of water and 3 mL of H<sub>2</sub>O<sub>2</sub> (30%) were added under ultrasonic treatment for 30 min, centrifuging and washing with HCl solution (3%). The resulting product could be received by dialysis with deionized water to dislodge acid and other ions.

### 2.3 Synthesis of poly(IA-co-PEGMA)

The purified poly(IA-co-PEGMA) could be successfully prepared via living free radical polymerization based on IA and PEGMA monomers. Preparing procedure could be summarized as follows. The mixture of PEGMA (4 mM, 380 mg) and IA (1 mM, 120 mg) were dissolved in anhydrous ethyl acetate solution (20 mL) at 80 °C for 10 min. When the mixture were completely

dissolved, AIBN (2 mM, 330 mg) in 10 mL anhydrous ethyl acetate solution were quickly injected into reactive bottle and stirring at 80 °C for 24 h. The system was maintained under N<sub>2</sub> atmosphere all the time. After the reaction, the crude product was purified by dialysis against anhydrous ethyl acetate solution for 24 h. The resulting product was dried in vacuum oven at 40 °C overnight.

#### 2.4 Preparation of DA-poly(IA-co-PEGMA)

Preparation of DA-poly(IA-co-PEGMA) was attributed to the ring-open reaction between amine and anhydride in anhydrous methanol and ethyl acetate solution.<sup>64, 65</sup> The procedure could be clearly described. The previously obtained poly(IA-co-PEGMA) (200 mg) was dissolved in anhydrous ethyl acetate (10 mL) and mix with DA (100 mg) in anhydrous methanol (20 mL). The system kept stirring at 40 °C for 6 h. the final purified DA-copolymer could be received through dialysis treatment with fresh water for 24 h and dried in vacuum oven at 40 °C one night.

#### 2.5 Preparation of GO-poly(DA-IA-PEGMA)

The promising GO-polymer hybrid materials were prepared via mussel inspired chemistry. The GO powders (100 mg), DA-poly(IA-co-PEGMA) (200 mg) was blended in 60 mL Tris solution (pH = 8.5, 1.21 mg/mL) and ultrasonic treatment for 10 min. the reaction system merely stirring at room temperature for 8 h without any other treatments. The absolute GO-polymer hybrid materials could be obtained via centrifugation-washing three times to remove residual polymers.

#### 2.6 Drug loading and release properties of GO-poly(DA-IA-PEGMA)

The loading and release of cis-platinum using GO-poly(DA-IA-PEGMA) was measured UV-Vis spectrometer with adsorbance peak at 710 nm. The detailed information can be found in the supporting information.

#### 2.7 Biocompatibility evaluation of GO-poly(DA-IA-PEGMA)

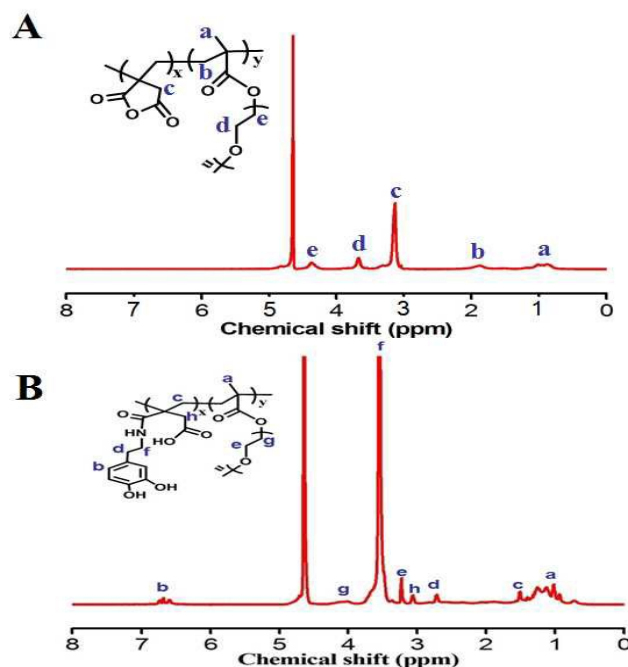
The biocompatibility evaluation was conducted based on our previous report.<sup>66, 67</sup> The detailed information can be found in the supporting information.

### 3 Result and discussion

A novel methodology was developed to fabricate GO/polymer hybrid materials via mussel inspired chemistry and free radical living polymerization. The functional GO with hydrophilic polymer have great dispersibility in water and some organic solvents. As shown **Scheme 1**, the fabrication approach for the high-dispersity and compatibility GO-poly(DA-IA-PEGMA) composites was described. As we can see from step 1, the hydrophilic copolymers (poly(IA-co-PEGMA)) were successfully synthesized using IA and PEGMA as the monomers and AIBN as initiator via free radical living polymerization. And then the DA was facily linked with the IA of poly(IA-co-PEGMA) via ring open reaction with DA at room temperature. And then the GO sheets were prepared via a modified Hummers' method and subsequently linked with hydrophilic polymers via mussel inspired chemistry (Step 2 in **Scheme 1**).

The successful preparation of poly(PEGMA-co-IA) and DA-

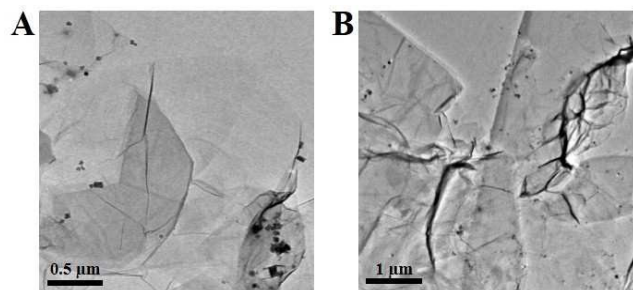
poly(PEGMA-co-IA) copolymers was confirmed by <sup>1</sup>H NMR spectra. As shown in **Fig. 1**, the structure of poly(PEGMA-co-IA) and DA-(PEGMA-co-IA) copolymers could be decided by <sup>1</sup>H NMR (D<sub>2</sub>O) spectra. The results of <sup>1</sup>H NMR spectra described as following. According to the **Fig. 1A**, the peaks at  $\delta = 0.9\text{--}1.2$  ppm (-CH<sub>3</sub>),  $\delta = 1.8\text{--}2.0$  ppm (-CH<sub>2</sub>-CH<sub>2</sub>-),  $\delta = 3.15$  ppm (-CO-CH<sub>2</sub>),  $\delta = 3.67$  ppm (O-CH<sub>2</sub>) and  $\delta = 4.37$  ppm (-COO-CH<sub>2</sub>) could demonstrated that successful preparation of poly(PEGMA-co-IA) via free radical living polymerization. Furthermore, **Fig. 1B** also shows that DA-poly(PEGMA-co-IA) was successfully synthesized. Different peaks belonged to DA-poly(PEGMA-co-IA) polymers could be summarized as follows:  $\delta = 1.13$  ppm (-CH<sub>3</sub>),  $\delta = 1.50$  ppm (-CH<sub>2</sub>-CH<sub>2</sub>-),  $\delta = 2.71$  ppm (Ph-CH<sub>2</sub>),  $\delta = 3.06$  ppm (-CO-CH<sub>2</sub>),  $\delta = 3.32$  ppm (-O-CH<sub>2</sub>),  $\delta = 3.54$  ppm (NH-CH<sub>2</sub>),  $\delta = 4.02$  ppm (-COO-CH<sub>2</sub>) and  $\delta = 6.68$  ppm (C<sub>6</sub>H<sub>5</sub>-).



**Fig 1** <sup>1</sup>H NMR spectra of (A) poly(PEGMA-co-IA) and (B) DA-poly(IA-co-PEGMA) using D<sub>2</sub>O as solvent.

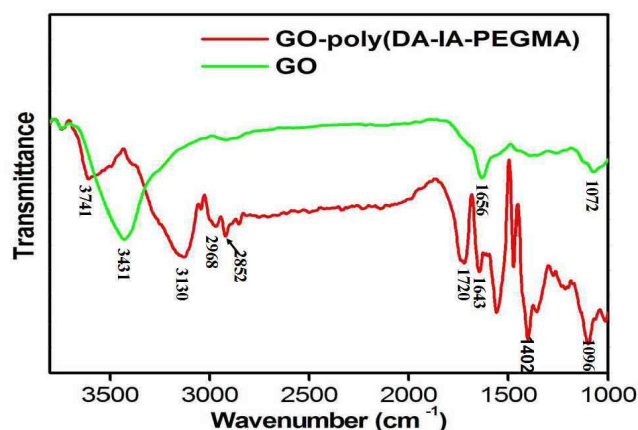
The morphology and size of GO and GO-poly(DA-IA-PEGMA) could be clearly observed by TEM images (**Fig. 2**). A paper-like morphology was exhibited in samples of GO, demonstrating the successful preparation of GO nanosheets based on the graphite powders via modified Hummers' approach. As shown in **Fig. 2A**, the distinct thin stratified structure of GO could be observed, which provide direct evidence that GO sheets possess great advantage of large high surface areas. As we can see from **Fig. 2B**, the enlarged TEM image of GO-poly(DA-IA-PEGMA) reveals that GO surface was coated with many nanowhiskers. However, comparing with pristine GO without modifying with polymers which owned extreme smooth surface, the surface of functionalized GO with hydrophilic polymers by mussel inspired chemistry is obviously different to pristine GO, which could be attributed to the perfect connection of polymers with GO surface using DA as the adhesion agent. The methodology described in this work is foolproof and effective. Not only modifying GO,

more importantly, it should be a universal method for surface modification of any materials due to the strong and versatile adhesion of DA.



**Fig. 2** Representative TEM images of GO (A) and GO-poly(PEGMA-co-IA) (B). As compared with the **Fig. 2A**, the thickness of GO sheets were increased after GO was coated with poly(PEGMA-co-IA) (**Fig. 2B**), indicating that the copolymers were attached on the surface of GO using DA as the adhesion agent. These results could provide evidence that polymers were linked to the GO surface via mussel inspired chemistry.

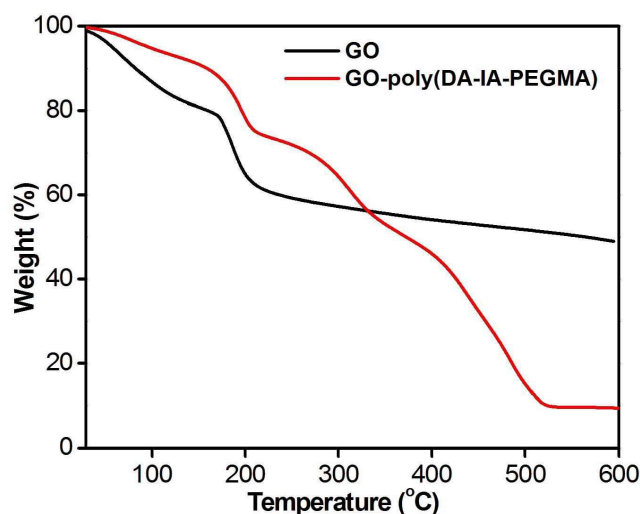
FT-IR spectra were further performed to evaluate the chemical structure information and functional groups on GO and GO-poly(DA-IA-PEGMA). The spectrum of GO was shown in **Fig. 3**, the peaks located at  $1072\text{ cm}^{-1}$  could be attributed to the stretching vibration of epoxy group. Respectively, the vibrational bands at about  $3431$  and  $1656\text{ cm}^{-1}$  could be ascribed to the hydroxy and carbonyl stretching vibration. These results demonstrated that thin GO sheets were prepared successfully via modified Hummers' method. **Fig. 3** also showed FT-IR spectrum of GO-poly(DA-IA-PEGMA). The peaks at  $2968$  and  $2852\text{ cm}^{-1}$  were due to the fundamental stretching vibration of  $-\text{CH}_3$  and  $-\text{CH}_2$ , which were not found in the the unmodified GO. Additionally, a new peak at  $3130\text{ cm}^{-1}$  could be ascribed to the ring stretching from a benzene ring, demonstrating the presence of DA in the samples of GO-poly(DA-IA-PEGMA). Respectively, the peaks appeared at  $3741$ ,  $1720$  and  $1096\text{ cm}^{-1}$  were severally attributed to the stretching vibration of N-H, C=O and C-O-C. Based on the FT-IR results, we concluded that DA-poly(PEGMA-co-IA) was successfully attached on the GO surface via mussel inspired chemistry.



**Fig 3** The FT-IR spectra of GO (green line), GO-poly(DA-IA-PEGMA) (red line). A series of characteristic FT-IR peaks at  $3130$ ,  $2968$ ,  $1720$ ,  $1096\text{ cm}^{-1}$  were observed in the sample of GO-poly(DA-IA-PEGMA).

These peaks can be attributed to the signals of  $\text{CH}_2$ ,  $\text{CH}_3$ , C-O and C=O in PEGMA. These results clearly demonstrated that these copolymers have been successfully immobilized on GO through mussel inspired chemistry.

TGA was utilized to evaluate the contents of polymer grafted onto the GO surface. As shown in **Fig. 4**, a small weight loss of GO and GO-polymers is respectively about  $13.24\%$  and  $5.3\%$  upon heating below  $100\text{ }^\circ\text{C}$  in all samples, which could be ascribed to the evaporation of free water. For the pristine GO, the weight loss was about  $51.04\%$  when the temperature arrived to the  $600\text{ }^\circ\text{C}$ . The major weight loss occurred at around  $200\text{ }^\circ\text{C}$  because of the thermal decomposition of the labile oxygen-containing groups, which also evidenced the preparation of GO sheets with a number of functional groups such as epoxy, hydroxy and carboxyl. These groups have great meaning for the surface modification of GO sheets. As compared with GO, the weight loss of GO-poly(DA-IA-PEGMA) was become more complex. Three weight loss sections were found in the TGA curve of GO-poly(DA-IA-PEGMA), the first weight loss section was occurred at the temperature below  $200\text{ }^\circ\text{C}$ . The second and third sections were began from about  $200$  and  $330\text{ }^\circ\text{C}$ . These weight weight loss can be ascribed to the degradation of polymers attached on GO. For the TGA curve of GO-poly(DA-IA-PEGMA), the weight loss arrived to about  $90.56\%$  when the temperature raised to  $600\text{ }^\circ\text{C}$ . Comparing to the weight loss of pristine GO, the polymer segments coated on the GO surface could be calculated about  $47.46\%$ . These results demonstrated that copolymer could be simply and effectively grafted to the GO surface through mussel inspired chemistry. Moreover, in this work, the described method could be used to surface functionalization any materials with different polymers. It is significant meaningful to prepare other polymer nanocomposites.



**Fig. 4** TGA curves of the GO, GO-poly(DA-IA-PEGMA) nanomaterials at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  in  $\text{N}_2$  atmosphere.

The XPS spectrum of GO and GO/polymer were shown in **Fig. 5**. As shown in **Fig. 5**, the survey spectra ranging from  $0$  to  $1200\text{ eV}$  were appeared to describe the different elements existed in GO samples. Three different elements (C, N, O and S) were appeared in the GO samples. The single peaks at  $285$ ,  $400$ ,  $533$  and  $167\text{ eV}$  were corresponding to  $\text{C}1s$ ,  $\text{N}1s$ ,  $\text{O}1s$  and  $\text{S}2p$ , respectively. The high-resolution XPS curves of  $\text{C}1s$ ,  $\text{N}1s$ ,  $\text{O}1s$  and  $\text{S}2p$  were shown in **Fig. S1**. As we can see from  $\text{C}1s$  spectra, there were

several different but similar binding energy peaks of carbon showed overlap between 284 and 289 eV. The C1s spectrum of GO clearly suggested different carbon bonds, corresponding to the carbon atom existed in diverse functional groups. That is, C-C bonds (254.5 eV), C-O bonds (284.5 eV), C=O bonds (288.5 eV) and C (epoxy, 286.17 eV). After surface immobilized with copolymers, the binding energy of C=O enlarged to 288.6 eV, which could be ascribed to the introduction of polymers. Furthermore, as seen from Fig. S1B, the peak at 400.04 eV could be contributed to the N1s, which demonstrated that DA-poly(PEGMA-co-IA) was attached to the GO surface via mussel inspired chemistry. The O1s XPS spectra of GO samples were shown in Fig. S1C. It can be clearly observed the binding energy of O1s of GO-poly(DA-IA-PEGMA) located at 533 eV. In addition, the element S was likely incorporated into GO when the graphite powder was oxidized by H<sub>2</sub>SO<sub>4</sub>. After functionalized with copolymers via mussel inspired chemistry, the S content was obviously decreased which provided the powerful evidence of poly(IA-co-PEGMA) was conjugated on the surface of GO successfully (Fig. S1D). As compared with pristine GO, the intensity of N1s and O1s belonged to functional GO sheets with copolymers was significantly improved. Therefore, according to the results of XPS spectra, the method described in this work is successful modification of GO sheets. Furthermore, the percentages of C, N, O and S in GO and GO-poly(DA-IA-PEGMA) was calculated based on the XPS spectra. As listed in Table. S1, the contents of C, N, O and S in GO is 68.23%, 27.38%, 2.27% and 1.95%, respectively. After modified with copolymers, the percentages of C, N, O and S in GO was changed to 73.35%, 25.12%, 1.08% and 0.5%, respectively. Due to the absent of S in the copolymers, the decrease of S content in the sample of GO-poly(DA-IA-PEGMA) clearly confirmed that the copolymers have successfully combined with GO through the strong adhesion of DA. On the other hand, the decrease of N and O contents in GO-poly(DA-IA-PEGMA) is likely due to the relative low contents of N and O in copolymers. Therefore, the XPS results further indicated that we could effectively prepare synthetic polymers modified GO nanocomposites.

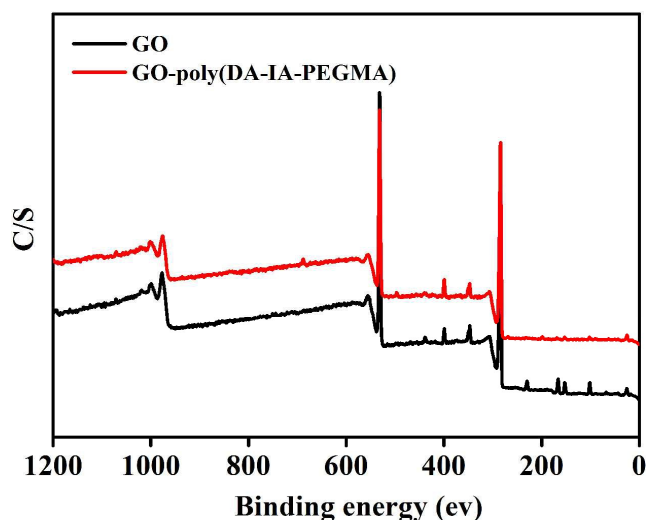


Fig 5 The Survey scan spectrum of the GO and GO-poly(DA-IA-PEGMA) which the spectral region from 0 to 1200 eV.

The great dispersibility of as-prepared GO/polymer in water and

different organic solvents is displayed in Fig. 6. It can be seen that GO can be dispersed in water more than 1 h but deposited within 5 h (bottle 1 in Fig. 6). As compared with GO, the water dispersibility was improved in some extent after GO was modified with hydrophilic polymer via mussel inspired chemistry. No obvious deposition can be found in the sample of GO-poly(DA-IA-PEGMA) at the time point of 12 h. Even the time was upto 24 h, well dispersed suspension can also maintained in GO-poly(DA-IA-PEGMA). The obvious dispersion difference between GO and GO-poly(DA-IA-PEGMA) also indicated that synthetic polymers were immobilized on the surface of GO successfully. On the other hand, the GO-poly(DA-IA-PEGMA) also displayed well dispersibility in some organic solvents such as DMF and DMSO. The significantly improved dispersibility of GO-poly(DA-IA-PEGMA) can be attributed to the PEGMA was attached onto GO surface. On the other hand, PEG is a biocompatible polymers which have been widely used for biomedical applications.<sup>68, 69</sup> It has been demonstrated that the surface modification of nanomaterials with PEG could not only improve the dispersibility and pharmacokinetic behavior, but also enhance their biocompatibility.<sup>70</sup> Therefore, the GO-poly(DA-IA-PEGMA) should be of great research interest for advancing the biomedical applications of GO.

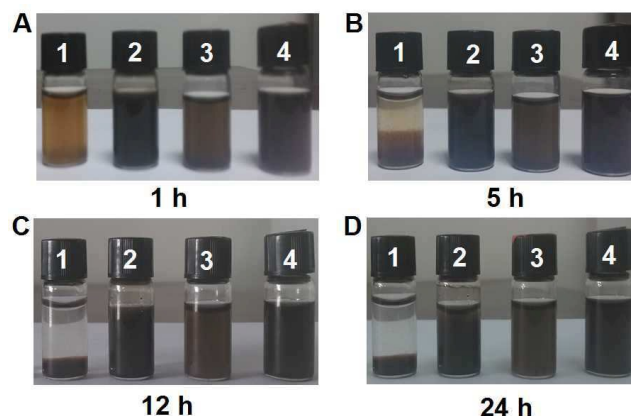


Fig. 6 Representative images of GO and GO-poly(DA-IA-PEGMA) dispersed in water and organic solution at different time. (1) GO in water, (2-4) GO-poly(DA-IA-PEGMA) dispersed in water, DMF and DMSO, respectively.

The property of controlled release is extremely important for the drug-delivery system. As is well-known, pH-responsive drug release has become an important and efficient controlled-release method. As an excellent drug-delivery carbon material, GO possess some unique properties such as stable structure with nano-size, high surface areas and low toxicity. Drug-delivery material based on GO usually enter into the body via endocytosis of cells and complete in endosomes and lysosomes, where the pH is lower than 6.0. Therefore, it is interest that drug-delivery materials have a fast drug release behavior in the acidic environment. To evaluate the potential application of the GO-poly(DA-IA-PEGMA), the loading and release of cis-platinum using GO-poly(DA-IA-PEGMA) was determined. Due to a large number of Carboxyl groups were generated during the ring opening reaction between IA and DA, the GO-poly(DA-IA-PEGMA) can effectively carry cis-platinum through coordinated

interaction. Our results suggested that about 4.68 mg of cis-platinum was loaded on 15.7 mg of GO-poly(DA-IA-PEGMA). Furthermore, the pH responsive release of cis-platinum from GO-poly(DA-IA-PEGMA)@Pt was also examined at the pH values 5.5 and 7.4. As shown in the Fig. 7, which illustrated that cumulative cis-platinum release from the GO-poly(DA-IA-PEGMA)@Pt in the PBS solution of pH 7.4 and 5.5 at 37 °C in the different time points. The GO-poly(DA-IA-PEGMA)@Pt composite materials exhibited greater drug-release behavior in the pH 5.5 than pH 7.4, this unique pH-responsive release properties is very effective for reducing the side effects when the GO-poly(DA-IA-PEGMA)@Pt was in a circulation period in the blood (pH 7.4), while release a higher concentration of cis-platinum into lysosomes. Furthermore, the biocompatibility of GO-poly(DA-IA-PEGMA) to HeLa cells and A549 cells was also evaluated using CCK-8 assay. As shown in Fig. S3, the GO-poly(DA-IA-PEGMA) showed negative toxicity to both HeLa cells and A549 cells. Even at high concentrations (100  $\mu\text{g mL}^{-1}$ ), the cell viability values of GO-poly(DA-IA-PEGMA) are still above 90%. Taken advantage of the pH responsive release behavior and excellent biocompatibility, GO-poly(DA-IA-PEGMA) materials prepared in this work are expected to be ideal drug vehicles for drug delivery applications.

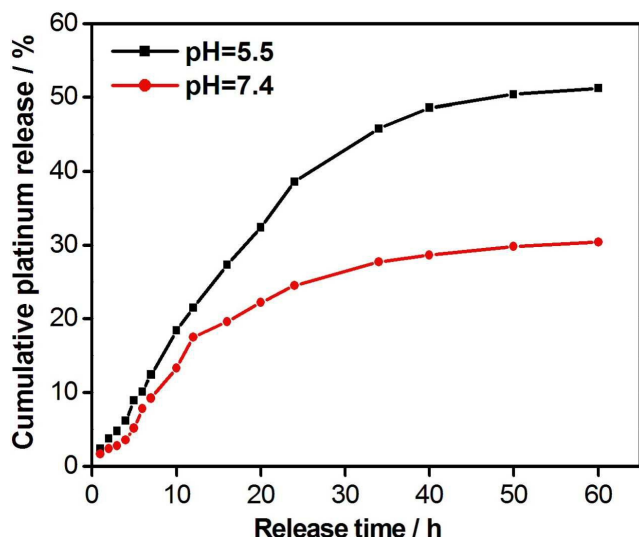


Fig. 7 Cumulative *in vitro* release of cis-platinum from the composite GO-poly(DA-IA-PEGMA)@Pt under the different pH system (PBS of pH= 5.5 and pH= 7.4)

#### 4. Conclusion

In summary, a novel strategy for functionalization of GO surface with hydrophilic polymer was reported to improve the dispersibility in water and several organic solutions. In current work, the DA contained side chain of poly(DA-IA-PEGMA) was prepared via free radical living polymerization using AIBN as initiator and subsequently grafted to the surface of GO via mussel inspired chemistry. A number of characterization techniques was utilized to confirm the successful formation of GO based polymer nanocomposites. The resulting material displayed significantly improved dispersibility in water and some organic solvents. As compared with controlled living polymerization methods, the method described in this work can facilitate and

effectively surface modification of GO with synthetic polymers, that can be reacted using a rather mild conditions, such as in the present of water, room temperature and without requirement of metal catalysts. Apart from PEGMA, many other synthetic polymers can also be utilized for surface modification of GO because of the designability of polymers and versatility of mussel inspired chemistry. It is therefore the strategy described in this work should be a general method for surface modification of GO in aqueous solution, that should be of great importance for promoting and enhancing the further applications of GO based materials such as pH responsive drug delivery applications.

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#### Notes

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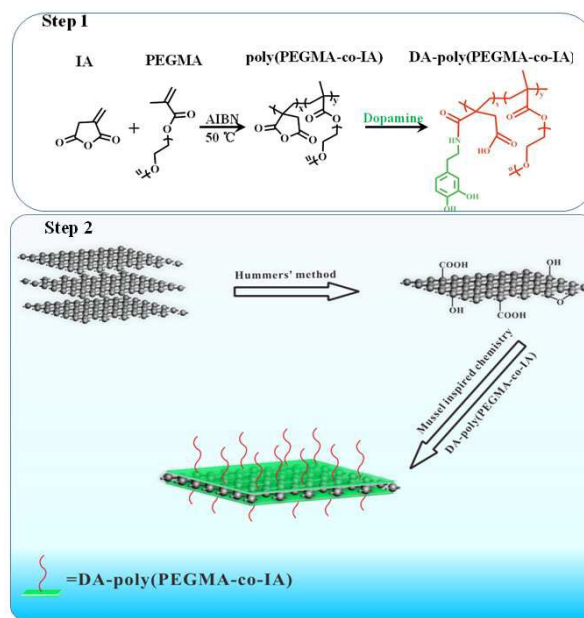
<sup>†</sup> Electronic Supplementary Information (ESI) available: [XPS spectra of C1s, N1s, O1s and S2p, and the elemental contents of GO and GO-poly(DA-IA-PEGMA)]. See DOI: 10.1039/b000000x/

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Graphene oxide was facilely functionalized with synthetic polymers in aqueous solution using dopamine as the adhesion component.