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Full Paper

Biomimic Modification of Graphene Oxide

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Surface modification of graphene oxide has attracted increasing attention in recent years. In this article, a green, facile and efficient method was developed to modify graphene oxide with polymers via combination of mussel inspired chemistry and Michael addition reaction. Graphite powder was first oxidated and exfoliated into single layer of slices through a modified Hummers method, then coated with polydopamine, which was formed via self polymerization of dopamine in alkaline solution. Next, the intermediate (GO-PDA) was grafted by polyacrylic acid, which was synthesized via reversible addition-fragmentation chain transfer polymerization, through Michael addition reaction. The resulting products were characterized by Fourier transform infrared spectroscopy, thermal gravimetric analysis, transmission electron microscopy and X-ray photoelectron spectrometry. The characterization results indicated the success of adhesion and graft of PDA and polyacrylic acid, respectively. The resulting products also exihibited sensitivity to pH. Apart from the polymer demonstrated in this work, many other polymers may be also grafted onto graphene oxide through the strategy when different monomers were adopted. Furthermore, this strategy can be also extended to surface modification of many other materials for the versatility of mussel inspired chemistry. It is therefore recommended that the novel strategy developed in this work should be a general strategy for fabrication of various functional nanocomposites, which can exihibit better performance for different applications.

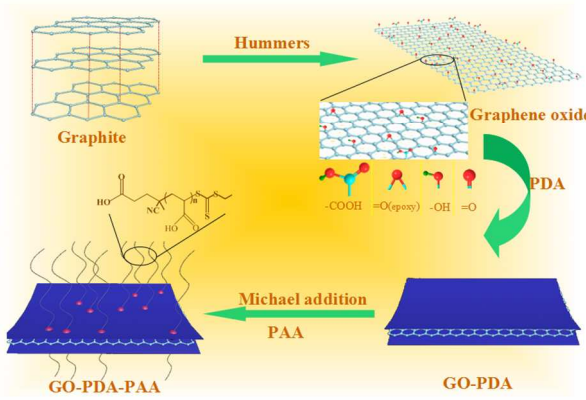
1. Introduction

Graphene, one of the most popular carbon nanomaterials, has attracted irresistible interest over the past decades as its outstanding electrical,[1-4] thermal,[5, 6] catalytic, and mechanical properties.[7, 8] These properties prompt graphene to be potentially used in electrode,[9-12] miniaturized electronic devices,[13-15] nanocomposites,[16, 17] environment,[18] drug delivery and photothermal treatment[19-25] and so on. Among them, the preparation of graphene based polymer nanocomposites is one of the most interesting research fields. It has been demonstrated graphene oxide (GO) could integrate with various polymers to form diversified graphene based nanocomposites by means of "graft-onto" or "graft-from".[26] For example, *Lee* and coworkers first reported the "graft-from" method to modify GO.[27] Styrene, methyl methacrylate and butyl acrylate can be attached to the surface of GO via atom transfer radical polymerization.[28] Huang et al. employed Br-containing initiating groups to attach onto the edge of GO and then grew poly[poly(ethylene glycol) ethyl ether methacrylate] (PPEGEEMA), poly(N-isopropylacrylamidein) (PNIPAM) and poly(2-hydroxyethyl acrylate) in situ via single-electron-transfer living radical polymerization (SET-LRP).[29-31] In addition, Huang et al. also reported the strategy of "graft-onto" which graft poly(N-(2-hydroxypropyl) methacrylamide) onto the surface of graphene via click chemistry.[32] Garcia-Valdez et al. modified the surface of GO via grafting polystyrene and polyisoprene, respectively.[33] The dispersibility of the modified GO was prominently enhanced. Despite great advance has been made in this field, there are still some drawbacks in these methods. For example, the initiator should be first immobilized on the surface of GO without water for ATRP.[34, 35] In this procedure, the GO will be restacked during the removal of water. Non-covalent strategies could functionalize GO in the present of water, however, the GO based polymer nanocomposites obtained from non-covalent strategies are not stable in some extent.[36] These drawbacks will inevitable influence the properties and performance of graphene based polymer nanocomposites. Therefore, it is of utmost urgency to develop novel strategies to prepare GO based polymer composites.

Dopamine is a key component for mussel inspired chemistry which can self-polymerize to form adhensive polymers polydopamine (PDA).[37, 38] In recently, dopamine has been widely used for surface modification of various material surfaces for its universal and strong adhesion.[39-41] The surface synechiae of PDA is so general that it can adhere to almost all of the solid surface without pre-treatment.[40, 42, 43] In addition, PDA can provide a reactive platform for further immobilization of polymers or small organic molecules bearing thiol or amino groups through Michael addition or Schiff base reaction.[44-46] For example, Zhao *et al.* prepared BSA-g-pRGO via PDA adhesion and bovine serum albumin (BSA) graft to improve the dispersibility and biocompatibility.[47-49] Our pervious work also demonstrated that

carbon nanotube (CNTs) can be functionalized with mercapto sulfonic acid sodium (MPS) and N-dodecyl mercaptan (NDM) via combination of mussel inspired chemistry and Michael addition reaction.[50, 51] More recently, the surface modification of carbon nanotubes with synthetic polymers via combination of mussel inspired chemistry and SET-LRP has also been demonstrated by our group.[52, 53] RAFT polymerization was ever reported to modify chitosan and proteins.[54, 55] In addition, Bing-Joe Hwang et al. functionalized graphene using RAFT polymerization and click chemistry.[56] However, surface modification of GO with synthetic polymers through Michael addition and RAFT polymerization is rarely reported.

In this contribution, we report a facile and efficient mean to prepare functional GO modified by PDA and poly(acrylic acid) (PAA). In the method, GO, derived from graphite powder, was first functionalized with PDA and then grafted by PAA, which was prepared from RAFT polymerization (**Scheme 1**). Different characterization techniques have confirmed that GO-PDA-PAA can be facilely prepared through the bioinspired strategy. The resulting GO-PDA-PAA display high water dispersity and stability, as well as pH responsive property.



Scheme.1 Schematic representation for the preparation of GO-PDA-PAA. Step 1, Graphite was first oxidated and exfoliated into a single layer of slices through a modified Hummers. Step 2, GO coated with polydopamine, in Tris solution through mussel adhesion. Step 3, the intermediate, GO-PDA, was grafted with PAA through Michael addition reaction.

2. Experimental

2.1 Materials and characterization

All of the chemicals were directly used without further purification. Graphite powder was purchased from Amdnano science and technology Co., Ltd (Shanghai, China). Dopamine hydrochloride was purchased from Sangon Biotech. Co., Ltd (Shanghai, China). 2, 2-azobis(2-methylpropionitrile) (AIBN) and the monomer acrylic acid were purchased from Aladdin (Shanghai, China). Tris-(hydroxymethyl) aminomethane (Tris) is obtained from Sinopharm Chemical Reagent Co., Ltd. Chain transfer agaent (CTA) was synthesized according to our previous report.[57] The other chemical agents were all of commercially available and analytical grade. The water involved tin the experiment was deionized water (D.I. water).

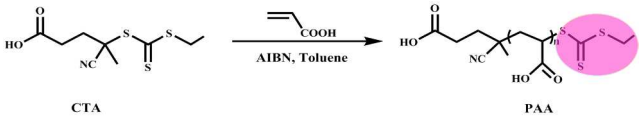
^{1}H NMR spectrum was recorded on Bruker Avance-400 spectrometer with D_2O as the solvent. The Fourier transform infrared (FT-IR) spectra were gained in a transmission mode on a Nicolet 5700 spectrometer (Waltham, MA, USA). Thermal gravimetric analysis (TGA) was tested on a TA instrument Q50 with a heating rate of 20 °C min^{-1} using crucibles of aluminum under N_2 atmosphere. The X-ray photoelectron spectra (XPS) were measured on a VGESCALAB 220-IXL spectrometer using an A1 Ka X-ray source (1486.6 eV). Transmission electron microscopy (TEM) images were recorded on a Hitachi 7650B microscope operated at 80 kV; the TEM specimens were made by placing a drop nanoparticle ethanol suspension on a carbon-coated copper grid.

2.2 Preparations of GO and GO-PDA

GO was produced from graphite powder through a modified Hummers method. The detailed process is as follows. First, 1 g graphite powder and 0.5 g $NaNO_3$ are put into a 500 mL conical flask, and blend well. And then, 46 mL concentrated sulfuric acid (H_2SO_4) was added in ice bath. After that, 6 g $KMnO_4$ was slowly lowered with stirring. Then 92 mL deionized water was cautiously added dropwise with stirring. The temperature was kept at 98 °C for 15 min under agitation. In the next, 10 mL H_2O_2, 100 mL H_2O was added in processor. Later, the solution was maintained 30 min at room temperature by ultrasonic. The generated mixture were centrifuged and washed with HCl for three times. At last, dialyse in D.I water for 2 days, collect, and keep in solution for further use. The GO-PDA was synthesized using GO and dopamine hydrochloride. 100 mg GO and 100 mg dopamine hydrochloride was dispersed in 100 mL Tris buffer (pH = 8.5). The mixture is agitated for 6 h on a magnetic stirrer at room temperature. And then, GO-PDA was obtained via repeated washing and centrifuging with D.I. water until the decanted solution is clear.

2.3 Preparation of PAA

PAA was prepared through RAFT polymerization in toluene under N_2 using AIBN as initiator (Scheme. 2). Acrylic acid (525 mg), AIBN (6 mg), CTA (19 mg), toluene (5 mL) were added into a Schlenk tube with a magnetic stir rotor and eliminated air by nitrogen flow for 20 min. Next, the handled solution was put into an oil bath maintained at 70 °C for 24 h. Subsequently, the purified poly(acrylic acid) (PAA) was achieved by the processing unit of petroleum ether precipitation after dissolving in ethanol. In the last, the obtained materials were dried under vacuum.



Scheme. 2 Schematic procedure to fabricate PAA through RAFT polymerization.

2.4 Preparations of GO-PDA-PAA

GO-PDA-PAA was gained in a quite simple way. 40 mg GO-PDA and 80 mg PAA were added to 25 mL NaOH aqueous solution (pH = 10) and then stirred for 12 h at room temperature. As CTA-terminated PAA can be hydrolyzed in alkaline solution to generate thiol at the end of PAA, GO-PDA will occur Michael

addition with it.[58, 59] The GO-PDA-PAA was obtained via centrifuging to remove the unreacted polymers. The resulting GO-PDA-PAA was set down and then dried in vacuum at 35 °C.

3. Results and discussion

In this study, a green, practical and effective method was developed to prepare profitably dispersive and stable GO-PDA-PAA. GO was synthesized by a modified Hummers method where chose graphite powder as raw materials and $NaNO_3$, H_2SO_4, H_2O_2, $KMnO_4$ as oxidant. Then, Tris solution (pH = 8.5) followed by putting appropriate dopamine and GO. Next, PAA synthesized from RAFT polymerization and GO-PDA was mixed in NaOH aqueous solution (pH = 10). The CTA of PAA can be hydrolyzed in alkaline solution and generated thiol terminated PAA, which can be introduced onto the GO-PDA via Michael addition reaction (**Scheme a**).[58, 59] The PAA synthesized from RAFT polymerization was first characterized by ^{1}H NMR spectroscopy using D_2O as the solvent. ^{1}H NMR spectrum of PAA was observed as shown in **Fig. S1**. The peaks a, c, d and e were attributed to RAFT carbon proton, and the peaks b was assigned to the repeating unit of PAA. All the evidence proved the successful polymerization of PAA. However, we could not calculate the molecular weight of PAA based on the ^{1}H NMR spectrum as the signals of b and c were so close that they overlapped. The molecular weight and conversion ratio of PAA was also determined using UV-Vis spectroscopy. According to the absorption values of CTA and PAA at 302 nm and the law of Lambert-Beer, the molecular weight of PAA is 6565 Da (Fig. S2). And therefore the coversion ratio of PAA from RAFT polymerization is 91.1%. TEM was used to characterize the surface structure and morphology of GO, GO-PDA and GO-PDA-PAA. It can be seen a typical wrinkled thin sheet in **Fig. 1a**, which was consistent with the feature structure of GO. Nevertheless, the GO sheets were obviously thicken after PDA coating and surface grafting with PAA. The difference thickness of GO and modified GO indicated that PDA and PAA were indeed coated on GO through mussel inspired chemistry and Michael addition reaction. On the other hand, small particles were found in the sample of GO-PDA-PAA although the GO-PDA-PAA was thoroughly purified to remove the free PDA and PAA, implying the PAA immobilized on the surface of GO sheets are rather stable.

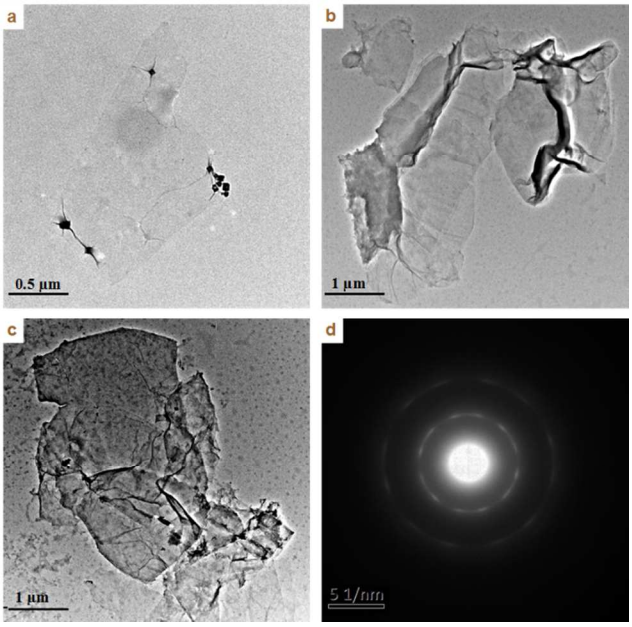


Fig. 1 (a) A TEM image of GO observed at low magnification; (b) a TEM image of GO-PDA revealing the PDA wrapper upon GO surface; (c) a TEM image of GO-PDA-PAA; (d) diffraction patterns of GO-PDA-PAA in a region as shown. As evidenced by the TEM images, more thicker GO based sheets can be observed in the sample of GO-PDA and GO-PDA-PAA, suggesting that PDA and PAA were successfully grafted on GO.

FT-IR spectroscopy was used to characterize the functional groups on the samples of GO, GO-PDA and GO-PDA-PAA. As shown in **Fig. 2**, GO showed multiple characteristic peaks confirmed with functional groups. For example, strong peaks at 1060, 1250 and 1365 cm^{-1} can be assigned to C-O, C-O-C and C-OH. Meanwhile, the peak at 1720 cm^{-1} was C=O in carboxylic acid and carbonyl moieties. Besides, the peak near 3450 cm^{-1} was hydroxyl groups and water. After being wrapped with PDA, a series of peaks located between 1800 and 1200 cm^{-1} was observed, that can be assigned to the aromatic rings of PDA. Furthermore, strong peaks were observed between 3438 and 3552 cm^{-1} in the sample of GO-PDA, that can be attributed to the stretching vibration of -OH or N-H groups. The difference of FT-IR spectra between GO and GO-PDA suggested PDA was coated on the GO sheets successfully. Finally, as compared with GO and GO-PDA, the characteristic peaks refer to C-H stretching vibration of acrylate units was observed between 2800-2940 cm^{-1}, evidencing that PAA was grafted onto GO-PDA through Michael addition reaction. Moreover, the C-S stretching vibration at 720-600 cm^{-1} was also found in the sample of GO and GO-PDA-PAA. It provided further evidence that PAA was conjugated with GO-PDA successfully.

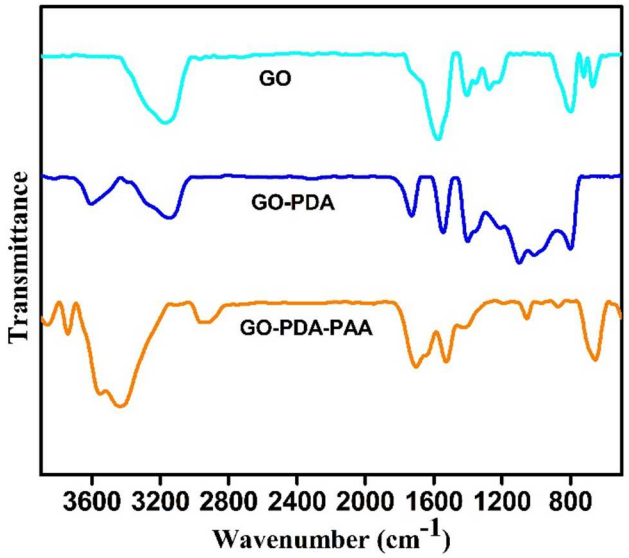


Fig. 2 FT-IR spectra of GO, GO-PDA, GO-PDA-PAA, respectively. GO showed multiple characteristic peaks with peaks at 1060, 1250, 1365 and 3450 cm^{-1}, suggesting that the functional groups such as hydroxyl, carboxyl and epoxy groups were existed in the sample of GO. As compared with the GO and GO-PDA, GO-PDA-PAA showed obvious peaks located between 2800 to 2950 cm^{-1}, which can be assigned to the stretching vibration of C-H bond of CH_2 and CH_3. The FT-IR results clearly demonstrated that the GO sheets can be successfully modified by PDA and PAA through the biomimic strategy.

GO, GO-PDA, GO-PDA-PAA were further characterized by XPS, which provides information on the type and number of four given atoms carbon (C), nitrogen (N), oxygen (O) and sulfur (S), were detected in all the samples (**Fig. S3**). The wide spectra of XPS suggested that C and O are the main compositions of all the samples. Very intersting, a few percentages of N and S were also observed from the XPS spectrum in GO. The two elements are likely incorporated into GO during oxidation of graphite powder by concentrated sulfuric acid and $NaNO_3$. Detailed XPS spectra (C1s, N1s, O1s and S2p) of GO, GO-PDA and GO-PDA-PAA were displayed in **Fig. 3**. It can ben seen that the C1s spectra of GO samples were mainly located at 284-290 eV (**Fig. 3a**). And the C1s spectrum can be further divided into three peaks at 284.78, 286.68 and 288.28 eV corresponding to C-C, C-O, C=O, respectively (**Fig. S4a**). In C1s spectrum of GO-PDA, the peak at 285.68 eV, associated with C-N was observed (**Fig. S4b**). Besides, the N1s spectrum was shown in Fig. 3b. It can be seen that the peaks of N1s of GO were mainly located at 399.88 ev, which can be attributed to the pyridinic-N. It implied that nitrogen was incorporated into GO via bonding with the carbon atom with six-membered rings at the edge of graphene layer. After surface modification with PDA, binding energy peak located at 402 eV assigned to the amino group of dopamine was observed, suggesting that PDA has coated on GO surface. On the other hand, the higher binding energy at 403.3 eV was also emerged, that can be likely attributed to the formation of N contained heterocyclic during self polymerization of dopamine. Furthermore, the intensity of N1s peak in GO-PDA was also little stonger than that of GO, also indicating the successful coating of GO with PDA. However, much weaker intensity of N1s peak was observed in GO-PDA-PAA, suggesting the PAA can be further conjugated with GO-PDA through Michael addition reaction. The O1s peaks located between 530 and 535 eV were observed in all the samples (**Fig. 3c**). It can be seen that the major peak of GO and GO-PDA is located at 532.5-532.8 eV, that indicated the present of C-O-C and C-OH in GO and GO-PDA. However, the binding energy peak was shifted to 532 eV, suggesting that C=O group is the major components in GO-PDA-PAA. The O1s results further confirmed that the successful modification of GO with PAA through combination of mussel inspired chemsitry and Michael addition reaction. Moreover, a obvious peak at 168.88 eV corresponding to the binding energy of S2p of GO. However, The intensity of S2p peak was significantly decreased in the sample of GO-PDA, indicating the successful coating of GO with PDA. No obvious enhancement of S2p intensity was observed in the sample of GO-PDA-PAA although the present of S element in the CTA of RAFT derived PAA (**Fig. 3d**).

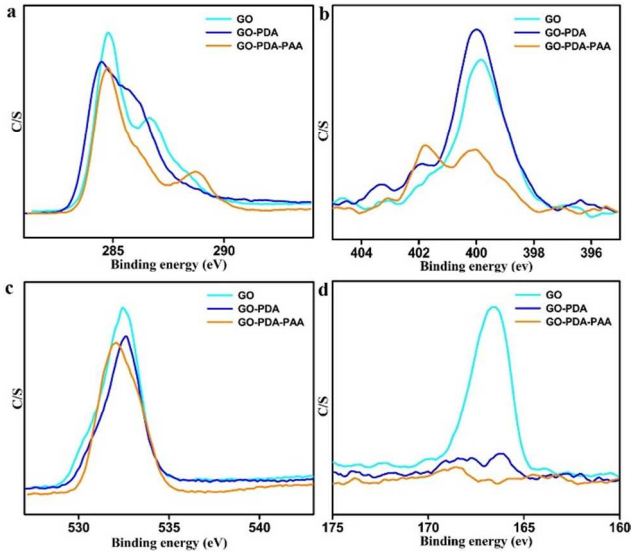


Fig. 3 High-resolution XPS spectra of GO, GO-PDA, GO-PDA-PAA. (a) The C1s region, (b) N1s region, (c) O1s region and (D) the S2p region.

In addition, the weight percentage of the elements (C, N, O, S) in GO, GO-PDA and GO-PDA-PAA was calculated based on the area of C1s, N1s, O1s and S2p. As shown in **Table 1**, there were four elements, C, N, O and S contained in GO, and each weight percentage was 67.8%, 2.74%, 27.22% and 2.01%, respectively. The appearance of N and S can be attributed to the process of Hummers modification. As H_2SO_4 and $NaNO_3$, graphene powder had probably generated GO which contained N and S beyond the removal ability of washing with water.[60] However, the weight percentage of C, N, O and S in GO-PDA changed to 69.58%, 2.92%, 26.92% and 0.46%, respectively. The increased content of N was attributed to the attachment of PDA on the GO surface. Meanwhile, the percentage of S in GO-PDA decreased after adhesion of PDA. This proved the mussel inspired chemistry had triumphantly coated on the surface of GO. But the appearance of S in GO-PDA also showed the film of PDA on the GO's surface was not thick enough. Then, the weight percentage of C1s, N1s and O1s in GO-PDA-PAA changed to 69.21%, 1.63%, and 28.72%. On the other hand, 0.44% S was also observed in GO-PDA-PAA. Based on the molecular weight of PAA determined by UV-Vis spectroscopy, the percentage of S in PAA, which can incorporate with GO-PDA is about 0.48%. The possible

explanation is that the low content of S in PAA and the limited detection depth of XPS measurement. Based on the molecular weight of PAA determined by UV-Vis spectroscopy, the S content is about 0.48%, which is much close to the S content of GO-PDA. The further decrease of S content to 0.44% may be due to the limited detection depth of XPS and the S content of PAA is much lower than that of GO.

Table 1 Element contains (%) of GO nanocomposites based on XPS analysis

Samples	C	N	O	S
GO	67.9	2.74	27.35	2.01
GO-PDA	69.68	2.92	26.94	0.46
GO-PDA-PAA	69.21	1.63	28.72	0.44

The mass percentage of PDA and polymers reacted on GO was measured by thermal gravity analysis (TGA). As shown in **Fig. 4**, the weight loss below 100 °C was 13.26 wt%, 8.16 wt% and 1.01 wt%, implying the moisture content of GO, GO-PDA and GO-PDA-PAA, respectively. The second acute weight loss of GO, attributing to the dissociation of epoxide and/or hydroxyl groups on GO, was appeared in the range of 170 to 220 °C, where the weight loss was about 18 wt%. And then the weight loss of GO became rather slow, and the total weight loss of GO was 19.84% between the temperature 220 to 600 °C. Therefore the toal weight loss of GO was 37.84 wt% except water. The DTA data of GO was displayed in **Fig. 4b**. Well consistent with the TGA curve of GO, a sharp endothermic peak at about 200 °C with a broad endothermic peak from 220 to 600 °C was observed in the sample of GO. As compared with GO, the weight loss in the second unstable stage of GO-PDA was just only 9%, suggesting PDA affinity was effective in enhancing the thermal stability of GO. The major weight loss of GO-PDA-PAA started from 300 °C and lasted until to 600 °C where the quality was no longer changes. The total weight loss of GO-PDA-PAA was up to 67.06 wt% from the temperature from 100 to 600 °C. Apart from a small endothermic peak at around 160 °C, no specific endothermic peak was observed from the DTA curves of GO-PDA and GO-PDA-PAA (**Fig. 4C** and **Fig. 4D**). The lack of sharp endothermic peak clearly suggested that PDA was coated on GO sheets via mussel inspired chemistry. Furthermore, the obvious weight loss of GO-PDA-PAA also indentified that PAA was conjugated on GO-PDA via Michael addition reaction. Taken together, the TGA curves and DTA curves of GO samples further confirmed that GO can be facilely modified by PDA and PAA through combination of mussel inspired chemistry and Michael addition reaction.

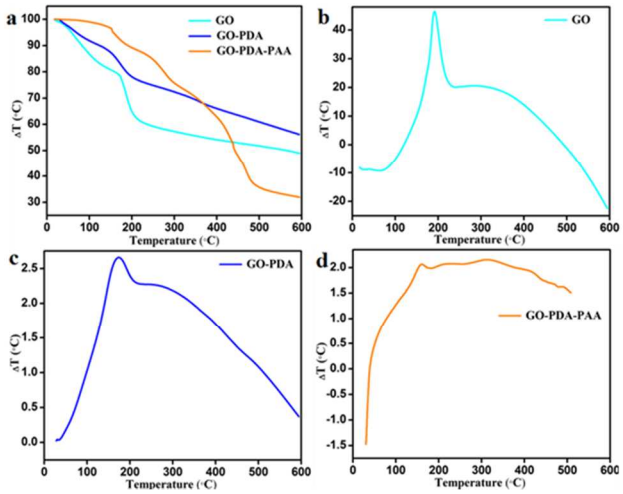


Fig. 4 TGA and DTA curves of GO, GO-PDA, GO-PDA-PAA respectively.

The dispersion of the resulting PAA modified GO-PDA has also been investigated. As **Fig. 5a** shown, GO--PDA-PAA had better dispersion than GO in aqueous solution. In **Fig. 5b**, the influence of pH on dispersion was inspected. However, it seem to have a low tolerance for pH because the color depth of solution gradually faded and the sedimentation on the very bottom gradually increased as the pH changed. When pH = 5, the dispersion of GO-PDA-PAA was obviously bad. The GO-PDA-PAA was deposited at the bottom of bottle within 1 h. However, the situation was immediately changed better as adjusting pH to 7 and maintain despersion within 12 h. This may be explained that the electrostatic repulsion, arisen from electro negativity of oxygenic functional groups, weakened ruling out the other possibility of the two stabilization mechanisms, steric hindrance. Furthermore, the dispersibility of GO-PDA-PAA as a function of time was also investigated. As shown in **Fig. 5c**, GO-PDA-PAA can be well dispersed in water more than 12 h, and gradually deposited within 20 h. The above results suggested that the GO-PDA-PAA can effectively improve the dispersibility of GO. And it also showed good responsiveness toward pH.

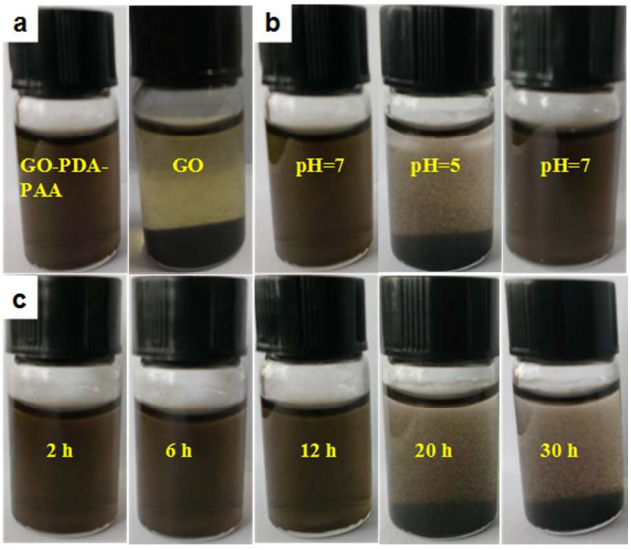


Fig.5 (a) The dispersion of GO-PDA-PAA and GO in aqueous solution for 6 h, (b) The pH responsiveness of GO-PDA-PAA in different pH

values. It can be seen that the GO-PDA-PAA was well dispersed in aqueous solution more than 6 h, however, after the solution pH was adjusted to 5, the GO-PDA-PAA was deposited within in 1 h. Further adjustment of pH to 7, the GO-PDA-PAA can be redispersed in aqueous solution. (c) Dispersion of GO-PDA-PAA in aqueous solution for different deposition time points.

4. Conclusion

In summary, we have developed a green, facile and efficient method to prepare graphene oxide-polymer nanocomposites through a biomimic strategy combining mussel inspired chemistry and Michael addition reaction. The resulting product, GO-PDA-PAA, possessed performance excellence, such as good dispersion in aqueous solution and sensitivity to pH. Both of the two reaction can be occurred under room temperature in aqueous solution and without requiring catalysts and protection inert gases such as N_2 and Ar. More importantly, this strategy may also be extended for preparation of many other polymer nanocomposites because of the universal adhesion of polydopamine and excellent applicability of RAFT polymerization. Therefore, this bioinspired strategy described in this work may be of great research interest for fabrication of many other polymer nanocomposites for different applications.

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Notes

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† Electronic Supplementary Information (ESI) available: [^{1}H NMR spectrum of PAA, survey XPS spectra and XPS C1s peak deconvolution of GO, GO-PDA, GO-PDA-PAA]. See DOI: 10.1039/b000000x/

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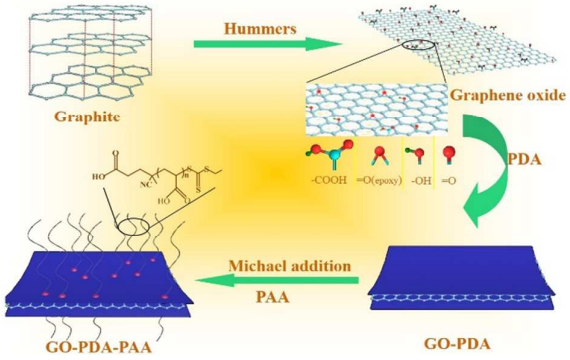

Synthetic polymers modified graphene oxide was prepared via combination of mussel inspired chemistry and Michael addition reaction in aqueous solution