Stimuli-Responsive Polymer Covalent Functionalization of Graphene Oxide by Ce(IV)-Induced Redox Polymerization

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ABSTRACT: Stimuli-responsive polymers, poly(acrylic acid) and poly(N-isopropylacrylamide), were covalently grafted onto the surface of graphene oxide through a facile redox polymerization initiated by cerium ammonium nitrate in aqueous solution at mild temperature. Thermogravimetric and element analyses show that the graft ratio of polymers increased with the increase of feeding amount of monomers. Atomic force microscopy reveals that the size and morphology of graphene oxide are well retained after the redox polymerization, with the exception of being covered by a homogeneous layer of polymer. The covalently grafted poly(acrylic acid) and poly(N-isopropylacrylamide) afforded pH and thermal responsivity to graphene oxide, and the assemble—disassemble behaviors of polymer-grafted graphene oxide in aqueous solution could be controlled by varying the pH or temperature of the solution, which provided a favorable strategy to handle the aqueous solution of graphene oxide.

1. INTRODUCTION

Graphene oxide (GO), as a novel 2D nanomaterial with one-atom thickness,† has gained increasing attention owing to its outstanding physical and chemical properties2–6 and its promising applications in nanoelectronic devices,7–9 nanocomposites,10–15 and nanomedicines16–18 as well. Generally, GO is an intermediate product in the process of preparing graphene by chemical oxidation—exfoliation of graphite powders.18 The strong oxidation treatment would generate many oxygen-containing groups,19,20 such as carboxyl groups and hydroxyl groups, which would not only improve the solubility of GO but also afford targets for further chemical functionalization of GO.21–23 Chemical functionalization is an effective way to endow graphene with new features and resolve the reaggregation of graphene,24 which greatly hindered the application of graphene.25

To date, many methods for chemical functionalization of GO have been reported, and these approaches could be divided into “graft onto” and “graft from” strategies.12,26–28 To “graft onto” strategy, polymer chains could be covalently linked to graphene by esterification or amidation reactions. However, this strategy requires the polymer chains must contain hydroxyl or amino groups, which greatly confined the kinds of grafted polymer.25,29,30 In contrast, via “graft from” strategy, various vinyl monomers could be used, and various methods, such as atom transfer radical polymerization (ATRP),31–33 reversible addition-fragmentation chain transfer polymerization (RAFT),34,35 ring-opening polymerization36 and SET-LRP (single-electron-transfer living radical polymerization)37 have been employed to prepare polymer chemically functionalized GO. However, most of the methods mentioned above need rigorous reaction conditions and tedious post-treatment. It is greatly required and still a challenging work to explore a facile and safe method to prepare polymer grafted GO.

In previous work, we have reported a convenient method to prepare polymer-functionalized multiwalled carbon nanotubes through redox polymerization initiated by cerium ammonium nitrate.38 Herein, this method was expanded to prepare poly(acrylic acid) (PAA) and poly(N-isopropylacrylamide) (PNIPAM) functionalized GO (Figure 1). This reaction could be carried out in aqueous solution and mild temperature. The graft ratio of PAA and PNIPAM could be controlled by varying the feeding amount of monomers. Because of the covalent functionalization of pH-responsive PAA39–41 and thermal-responsive PNIPAM,42,43 the solubility of obtained PAA grafted GO (GO-PAA) and PNIPAM grafted GO (GO-PNIPAM) in water are obviously pH- and thermal-responsive, respectively. Thus, the assemble—disassemble behaviors of GO-PAA and GO-PNIPAM could be controlled by environmental stimuli (pH or thermal), which is favorable to the handling characteristics of GO.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Graphite, with an average particle diameter of 4 mm and a purity ≥99.95%, was purchased from Qingdao Tianhe...
Graphite Co. Ltd. Potassium persulfate (K$_2$S$_2$O$_8$), potassium permanganate (KMnO$_4$), and phosphorus pentoxide (P$_2$O$_5$) were purchased from Sinopharm Chemical Reagent Co. Ltd. Concentrated sulfuric acid (H$_2$SO$_4$), hydrochloric acid (HCl), hydrogen peroxide (H$_2$O$_2$), and acrylic acid (AA) were purchased from Shanghai Chemical Reagent Co. Ltd. N-Isopropylacrylamide (NIPAM, purity >97%) and ammonium ceric nitrate (CAN, purity >99.99%) were purchased from Sigma-Aldrich. All the reagents were used as received.

2.2. Preparation of GO. GO was prepared by the modified Hummers method. Typically, 15 g of K$_2$S$_2$O$_8$ and 15 g of P$_2$O$_5$ were added into 30 mL of 98% H$_2$SO$_4$ with stirring in an ice/water bath. Then, the mixture was heated to 80 °C, followed by slowly adding 30 g of graphite powder. After reaction for 10 h, the suspension was cooled to room temperature and diluted to 2 L by deionized water. The precipitates were filtered and dried to obtain the preoxidized graphite. The preoxidized graphite powder (5 g) was added into 115 mL of 98% H$_2$SO$_4$ with stirring in an ice/water bath, and then 15 g of KMnO$_4$ was slowly added. After reaction at 35 °C for 2 h, 700 mL of deionized water containing 12.5 mL of 30% H$_2$O$_2$ was slowly added. The precipitates were washed with dilute hydrochloric acid, followed by distilled water to remove the acid. To obtain GO, one hour’s ultrasonic exfoliation (bath sonicator, 60 kHz) was conducted. After purification by repeated centrifugation/washing with deionized water and one-week dialysis to remove residual salts and acids, the obtained GO was dried in vacuum at 50 °C for 24 h. The yield of GO is about 74.6%.

2.3. Preparation of Stimuli-Responsive Polymer-Functionalized GO. In a typical procedure, 30 mg of GO powder were added into 45 mL of deionized water, and then the mixture was ultrasonicated for 1 h to obtain a homogeneous GO dispersion. After adding 1.0 g of AA and purging with N$_2$ for 30 min, CAN/H$_2$O (0.1 g/5 mL) was injected into the mixture to initiate the polymerization. The reaction was carried out at 50 °C under N$_2$ atmosphere for 8 h. Subsequently, the suspension was centrifugated and washed 5 times to remove the residual salts and monomers and then dried in a vacuum oven at 50 °C, to give poly(acrylic acid) functionalized GO (GO-PAA). Poly(N-isopropylacrylamide) functionalized GO (GO-PNIPAM) was prepared by the similar procedure.

2.4. Characterization. Thermogravimetric analysis (TGA) measurements were carried out on a Perkin-Elmer Pyris-1 series thermal analysis system under nitrogen atmosphere at a scan rate of 20 °C/min. FT-IR spectra were recorded on a Nicolet Magna 550 spectrometer using KBr pellets. Atomic force microscopy (AFM) images were obtained on a NanoScope IV in tapping mode. Samples for AFM measurements were prepared by spin-coating an aqueous solution of GO, GO-PAA, or GO-PNIPAM onto freshly cleaved mica. Element analysis measurements were carried out on a Vario EL3 elemental analyzer.

3. RESULTS AND DISCUSSIONS

Ce$^{4+}$—alcohol redox pair is an effective initiator for radical polymerization of a variety of water-soluble vinyl monomers. By utilization of the hydroxyl groups on GO, together with Ce$^{4+}$, an efficient redox polymerization system could be established. Two monomers with good water solubility, AA and NIPAM, were initiated to polymerize by this system in aqueous solution at 50 °C. As shown in Table 1, a series of PAA- and PNIPAM-functionalized GO were prepared with different feeding amount of monomer.

As shown in the AFM images of Figure 2, the surface of the as-prepared GO is clear and smooth. The thickness of GO is about 0.42 nm, demonstrating that the GO is single layer. After grafting with PAA and PNIPAM, the size and morphology of GO are well retained. The surfaces of GO-PAA-3 and GO-PNIPAM-3 are uniformly covered by a layer of PAA and PNIPAM, respectively, and much rougher than that of GO. The thickness of GO-PAA-3 and GO-PNIPAM-3 evidently increased to 1.64 and 2.84 nm,

![Figure 1. Schematic synthetic route of polymer-grafted GO.](https://example.com/figure1)

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Monomer weight (g)</th>
<th>Graft ratio of polymer (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-PAA-1</td>
<td>1.0</td>
<td>21.41</td>
</tr>
<tr>
<td>GO-PAA-2</td>
<td>2.0</td>
<td>37.33</td>
</tr>
<tr>
<td>GO-PAA-3</td>
<td>3.0</td>
<td>45.49</td>
</tr>
<tr>
<td>GO-PNIPAM-1</td>
<td>1.0</td>
<td>16.82</td>
</tr>
<tr>
<td>GO-PNIPAM-2</td>
<td>2.0</td>
<td>35.32</td>
</tr>
<tr>
<td>GO-PNIPAM-3</td>
<td>3.0</td>
<td>40.77</td>
</tr>
</tbody>
</table>

*a* The feed ratio of GO/CAN/H$_2$O is kept at 30 mg/0.1 g/50 g in all the recipes. *b* The graft ratio of polymer was determined by TGA.
respectively. These results indicated that both of the PAA and PNIPAM were successfully grafted onto the surface of GO.

The FTIR spectra of GO, GO-PAA-3, and GO-PNIPAM-3 are given in Figure 3. To that of GO, it could be clearly seen a broad peak centered at 3412 cm\(^{-1}\), which is the characteristic vibration of hydroxyl group, and two peaks at 1735 cm\(^{-1}\) and 1055 cm\(^{-1}\), assigned to the absorption of C\(=\)O stretch and the C\(—\)O stretch of epoxy groups, respectively. After grafting with PAA, two new peaks appeared at 2920 and 2860 cm\(^{-1}\), due to the C\(—\)H bond.

In the situation of grafting with PNIPAM, the characteristic bands appeared at 2970 and 2930 cm\(^{-1}\), due to the C\(—\)H bond, and at 1640 cm\(^{-1}\), due to the C\(=\)O vibration of amide group. These results indicate a successful polymerization of AA and NIPAM on the surface of GO.

Figure 4 shows the TGA results of GO, GO-PAAs, and GO-PNIPAMs. It could be seen that GO gives a main weight loss at 150—300 °C, due to the thermal decomposition of oxygen containing groups. GO-PAAs and GO-PNIPAMs give two distinct weight loss steps at 150—300 °C caused by the thermal decomposition of remaining oxygen-containing groups and carboxyl groups in PAA and 300—550 °C caused by the thermal decomposition of polymer backbones. Considering that the oxygen containing groups participated in the redox polymerization of monomers, we used the weight loss at 300—550 °C to calculate the graft ratio of polymers, and the data were summarized in Table 1.
The content of PAA and PNIPAM in GO polymers increased with the increase of feeding amount of monomers and could reach up to 45.49 and 40.77 wt %, corresponding to GO-PAA-3 and GO-PNIPAM-3, respectively. To confirm this calculating method, elemental analysis was performed to evaluate the graft ratio of PNIPAM on GO. As shown in Table 2, the graft ratios of PNIPAM evaluated by element analysis were consistent with that determined by TGA, which indicated that the weight loss at 300–550 °C was mainly derived from the thermal decomposition of polymer backbones.

As it could be seen from Figure 5, GO-PAA-3 (2 mg) in aqueous solution (5 mL) gives a homogeneous stable brown solution upon standing for three hours. When an aqueous HCl solution (2 M) was added into the above solution, the resulted mixture (pH = 3, 4, and 5) becomes phase separated, which proceeds smoothly and finally leaves a precipitation of GO-PAA-3 after three hours. The speed of precipitation increased with the decrease of solution pH. On the other hand, when the pH value increased to 6.0 or higher upon addition of ammonia solution and sonication for several minutes, the brown precipitates dissolved to give a homogeneous solution. The high critical soluble pH value for GO-PAA-3 was evaluated to be 6.0, upon examination of a series of solutions at different pH values, which is higher than that of PAA-functionalized multiwalled carbon nanotubes, reported in our previous work.38 The pH-driven aggregation and dissolution of GO-PAA are reversible and can be repeated for many times. Therefore, PAA chains capable of a protonation–deprotonation cycle, while anchored on the surface of GO, make it possible for the GO-PAA-3 to respond reversibly to the change of the pH value.

The thermal behavior of GO-PNIPAM-3 in an aqueous solution was investigated. In a typical experiment, 2 mg of GO-PNIPAM-3 was added to 5 mL of water at 25 °C, and the resulting solution was heated up to 35 °C and then cooled down to 25 °C. We found that GO-PNIPAM-3 at 25 °C forms a stable homogeneous brown solution. Of note, when the solution was heated at 35 °C, GO-PNIPAM-3 aggregates too quickly and precipitates completely from the solution in a few minutes. When the mixture was cooled at 25 °C and ultrasonicated for several minutes, a homogeneous brown solution recovered again. Since an aqueous solution of GO at the same concentration does not show any precipitation while heating at 35 °C, PNIPAM segments on the surface of GO-PNIPAM-3 take account for the above thermal responsibility. The low critical soluble temperature (LCST) of GO-PNIPAM-3 was evaluated to be 32 °C upon examination of a series of solutions at different temperature, which is similar to that of ordinary PNIPAM. However, compared with PNIPAM, which forms particles at LCST, the thermal response of GO-PNIPAM-3...
is much too drastic to give even a precipitation. While heated to the LCST, PNIPAM segments most likely shrink to form hydrophobic aggregates on the surface of GO-PNIPAM-3. Therefore, once they lose their hydrophilic protection, GO will further aggregate and eventually precipitate from the aqueous solution. See Figure 6.

4. CONCLUSIONS

Stimuli-responsive polymers, PAA and PNIPAM, were successfully grafted on the surface of GO by a facile redox polymerization. The oxygen containing groups on GO, upon reaction with Ce⁴⁺, could form redox centers and efficiently initiate the polymerization of AA and NIPAM. The grafting density of PAA and PNIPAM could be controlled and increased with the increase of the feeding amount of monomers. Because of the covalent graft of pH-responsive PAA and thermal-responsive PNIPAM, the assemble–disassemble behaviors of GO-PAs and GO-PNIPAMs in aqueous solutions could be controlled by varying the pH and temperature of the solutions, respectively. Furthermore, this method provided a convenient way to prepare polymers covalently grafted GO by utilizing various water-soluble vinyl monomers.

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