

EFFECTS OF SURFACE MODIFICATION AND CROSS-LINKED GRAPHENE OXIDE WITH ETHYLENEDIAMINE ON ELECTRICAL PROPERTIES OF REDUCED GRAPHENE OXIDE FILMS

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Keywords: Graphene oxide, cross-linked, Electrical conductivity, surface modification

ABSTRACT

Cross-linked graphene oxide (GO) films, with simultaneous reduction and surface functionalization, were fabricated through filtration using a pressure-assisted self-assembly technique. Cross-linking between graphene sheets was realized by chemical reaction between ethylenediamine monomers and oxygen functional groups on GO surface in solution. The effect of cross-linking on the electrical properties of functionalized graphene oxide films was investigated. Ethylamine was used to produce uncross-linked graphene films, whose structures and properties were compared to those of graphene films cross-linked with ethylenediamine. The surface modification of GO with ethylamine or ethylenediamine took place under mild conditions with nitrogen protection. The removal of epoxide, carboxyl and hydroxyl groups from GO by ethylamine or ethylenediamine was confirmed by Fourier transform infrared and X-ray photoelectron spectroscopy (XPS). XPS results also demonstrated that both ethylamine and ethylenediamine were chemically bonded to GO. Results show that, after surface modification, the electrical conductivity of GO film modified with ethylenediamine is greatly improved, meanwhile an improvement as high as four orders of magnitude for the unmodified GO film. After annealing at 800°C for 2 hours, the sheet resistance of reduced graphene oxide films modified with ethylenediamine decreased to 1.07 Ω, much lower than that of reduced graphene oxide films (10.63 Ω).

1 INTRODUCTION

Due to its superior mechanical properties, excellent thermal and electrical conductivity, graphene has attracted much attention in the fields of drug delivery, electronic devices, and polymer composites.^[1-3] To expand its use in above applications, large-scale production of graphene is required. The most economic and effective method for the large-scale production of graphene is chemical oxidation of graphite, conversing graphite oxide to graphene oxide (GO), then reducing GO to graphene.^[4,5]

GO has numerous oxygen-containing functional groups: hydroxyl and carboxyl groups are located around the edges, whereas carbonyl and epoxide groups are in the center, resulting in intrinsic insulation of GO for the break of sp² structure. Therefore, the reduction of GO is essential for

obtaining highly conductive graphene, which could be achieved by thermal annealing, chemical reduction or electrochemical reduction^[6-9]. To avoid agglomeration of reduced graphene oxide while using strong reducing methods, chemical functionalization of GO followed by reduction is one potential way to overcome agglomeration. However, the electrical conductivity of functionalized graphene oxide is significantly lower than that of pristine graphene. This is attributed to oxygen functional groups on GO surface, increasing defect concentration, and an increase of contact resistance between graphene sheets.^[10-13]

In order to decrease the contact resistance between adjacent GO sheets, conjugated polymers were used to form cross-linking between carbon nanotubes or graphene sheets, obtaining highly conductive carbon nanomaterials.^[14,15] However, long aliphatic chain of the conjugated polymers might hinder the surface modification and need to be functionalized before using. Moreover, a majority of conjugated polymers are insoluble in most solvent.

Ethylenediamine possesses short carbon chains which may not hinder the conductivity, but may achieve surface modification and cross-linked graphene sheets.^[16-19] Two amine functional groups on both side of the ethylenediamine might connect adjacent graphene oxide sheets by the formation of covalent bonds, which enhance electron transport channels, thus decreasing contact resistance between graphene oxide sheets. In this work, we report an effective and easy-processing method for functionalization and reduction of GO using ethylamine (EA) and ethylenediamine (EDA). Moreover, cross-linked graphene sheets were formed by the reaction between diamine groups of EDA and oxygen-containing groups of GO. The as-prepared functional graphene sheets were characterized by a variety of complementary methods to confirm the structure and properties. The electrical conductivity of these films before and after thermal annealing was also investigated.

2 MATERIALS AND METHODS

2.1 Materials

The GO dispersions used in the experiment were purchased from C6G6, with size of GO ranging from 10 to 30 μm . Ethylamine (EA) and ethylenediamine (EDA) were purchased from Chemical Reagent Company Sinopharm and used for reduction and surface modification. 55% hydroiodic (HI) acid was obtained from Sigma-Aldridge Chemical Reagent Co., Ltd.

2.2 Preparing GO and its surface modification films

First, the concentration of GO dispersions was diluted to 500 ppm with deionized water and the GO solution was dispersed through ultra-sonication about 0.5 h. Next, ethylamine or ethylenediamine was dissolved in the suspension to form a 0.1 M solution. Then, the above suspension was refluxed in a three-neck flask with mechanical stirring for 10 h at 85 °C, under protection of nitrogen. Then, the resulted suspension was filtrated with a mixed cellulose ester membrane with an average pore size of 5 μm , washed with deionized water for several times. Finally, GO and its surface modified films were left to dry at room temperature for 24 h, and further dried at 60 °C for more than 48 h. As a result, we can obtain graphene oxide film modified with ethylenediamine (GO-EDA) and ethylamine (GO-EA).

2.3 Thermal annealing of films

The as-prepared films were pre-reduced with HI at 100 °C for 1 h to remove most of the oxygen-containing functional groups, and dried at 60 °C for more than 7 days at vacuum to remove

solvent thoroughly. Then the films were further annealing step by step with a heating rate of 5 °C min⁻¹ in a tubular furnace under protection of argon flow and then cooled down slowly to room temperature. After annealing at 800 °C, we can obtain thermally reduced graphene oxide films (rGO), thermally reduced graphene oxide film modified with ethylenediamine (rGO-EDA) and thermally reduced graphene oxide film modified with ethylamine (rGO-EA).

2.4 Electrical conductivity measurements

The measurement of electrical conductivity of films was carried out on a Keithley 2450 Source Meter under small currents in order to avoid significant self-heating. The sample dimensions were 10 mm × 10 mm × 3 μm, and measured by a four-probe method. The sheet resistance (R_s , Ω/sq) of the films was obtained from current-voltage curves.

2.5 Characterizations

Scanning electron microscopy (SEM) images were taken on a Hitachi S4800 field emission system. X-ray photoelectron spectroscopy (XPS) was performed with a PHI 5000C ESCA System operated at 14.0 kV. X-ray diffraction (XRD) data were collected with a X'Pert Pro (PANalytical) diffractometer using monochromatic Cu Kα1 radiation ($\lambda=1.5406 \text{ \AA}$) at 40 KV. Fourier transform infrared (FTIR) spectra were recorded over a wavenumber range of 4000-400 cm⁻¹ using a Nicolet 10 spectrometer. Thermal degradation behavior was studied on a thermo-gravimetric analyzer (TGA, Mettler toledo Instruments), at a ramp rate of 10 °C min⁻¹ under nitrogen atmosphere.

3 RESULTS AND DISCUSSION

3.1 FTIR analysis

A first indication of the reduction of GO is the color change of GO solution from brownish yellow to black after the mixture of GO and amine monomers was heated to 85 °C and reacted for several minutes. The FTIR spectra of the GO film, shown in Figure 1(a), exhibit absorption peaks that refer to hydroxyl (OH), carboxyl (C=O), aromatic (C=C), and epoxy (C-O-C) at wavenumbers of 3430, 1726, 1625, and 1103 cm⁻¹, respectively. After the reaction with amine monomers, the characteristics absorption bands of OH, C=O, and C-O-C of GO decreased obviously (both for reaction with EDA or EA), indicating the reduction of GO simultaneously. Furthermore, a new absorption peak was observed at the wavenumber of 1577 cm⁻¹, corresponding to in-plane vibration of amine N-H, and another new peak at 1215 cm⁻¹ (C-N stretching vibration). These results confirm that amine monomers could react with the oxygen-containing functional groups of GO, generating C-N covalent bonds through the condensation reaction between amine and hydroxyl and the nucleophilic addition reaction of the amine and the epoxide groups. Because the hydroxyl groups of GO participate in the condensation reaction, their absorption peak at the wavenumber of 3430 cm⁻¹ almost disappeared.

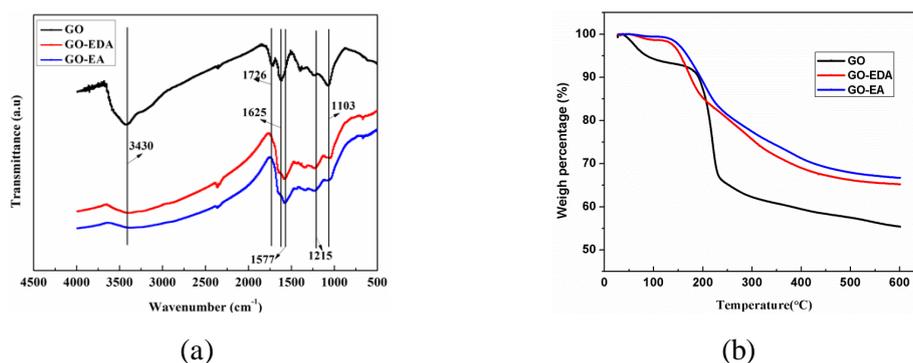


Fig. 1 FTIR spectra (a) and TGA curves (b) of unmodified GO, GO-EDA, and GO-EA

3.2 Thermal stability analysis

As could be seen in Figure 1(b), the functionalization and reduction of GO with EDA improves the thermal stability of GO. For GO, there is a weight loss of 5.3 wt% around 100 °C because of the removal of physically-absorbed water, and the weight loss of 37.8 wt% around 300 °C is mainly ascribed to the decomposition of labile oxygen-containing functional groups, yielding H₂O, CO and CO₂. The final mass loss is 44.5 wt% at 600 °C because of the loss of more stable oxygen functionalities. Comparing with unmodified GO, the thermal stability of GO-EA and GO-EDA above 230 °C is enhanced owing to the reduction of GO. By comparison, the weight losses of GO-EDA materials at 300 °C and 600 °C are 22.6 and 33.2 wt%, respectively. The TGA results clearly demonstrate that GO-EDA materials possess higher thermal stability than GO. As could also be seen in Figure 1(b), GO-EA materials possess better thermal stability than that of GO-EDA, due to the attachment of more ethylenediamine on the surface of GO compared to ethylamine. The TGA data are well verified with XPS results as shown in Table 1.

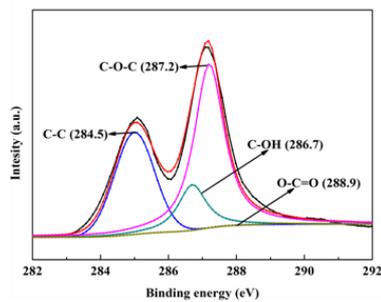
3.3 XPS analysis

XPS was used to characterize the removal of oxygen-containing functional groups and the formation of covalent bonds on the surface of GO after its functionalization with amine monomers as shown in Figure 2. As could be seen in Figure 2(a), there are four different peaks centered at 284.5, 286.7, 287.2, and 288.9 eV, corresponding to C=C in unoxidized graphite carbon skeleton, C-OH in hydroxyl group, C-O-C in epoxide group, and O-C=O in carboxyl group, respectively. Compared with unmodified GO, the peak intensity of C-OH, C-O-C and O-C=O are significantly decreased in GO-EDA and GO-EA. However, the peak intensity of C=C improves obviously in GO-EDA and GO-EA, indicating that GO is reduced to a considerable extent by amine monomers and the majority of the conjugated graphene structure has been restored after the reduction. Meanwhile, the atomic ratio of carbon and oxygen (C/O) improves from 1.9 for GO to 3.07 for GO-EA and 4.17 for GO-EDA. Furthermore, a new characteristic peak related to C-N centered at 285.5 eV appears, implying that amine monomers are covalently bonded to GO surface. Moreover, investigation of the N 1s XPS spectra (shown in Figure 3) in the range from 396 to 410 eV reveals that two more distinct peaks at 397.6 and 400.1 eV, further confirming the formation of C-N bonds owing to the nucleophilic addition of amine monomers with GO.

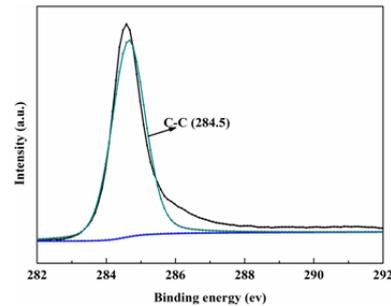
In order to improve the electricity of these films, they were thermally reduced further. After annealing at 800 °C for 2 hours, the peak intensity of oxygen-containing groups was nearly disappeared, but the C=C peak intensity enhanced further. As for nitrogen containing, it decreased from 7.89 to 4.05 for GO-EDA, and from 5.44 to 3.43 for GO-EA, indicating partial pyrolysis of C-N covalent bonds.

Table 1 XPS results of GO, GO-EDA and GO-EA

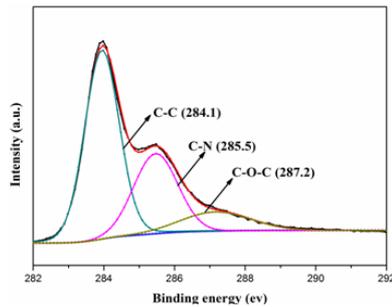
Sample	Carbon (atomic %)	Oxygen (atomic %)	Nitrogen (atomic %)	C/O ratio
GO	65.50	34.50	0	1.90
GO-EDA	74.30	17.81	7.89	4.17
GO-EA	71.34	23.22	5.44	3.07
rGO	96.61	3.39	0	28.50
rGO-EDA	92.88	3.07	4.05	30.25
rGO-EA	93.23	3.34	3.43	27.09



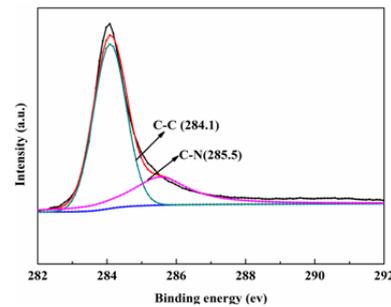
(a) GO



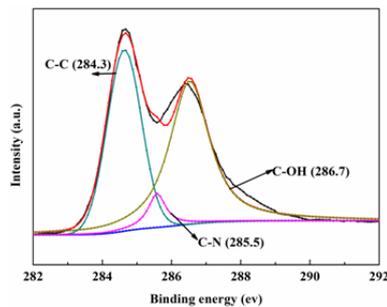
(b) rGO



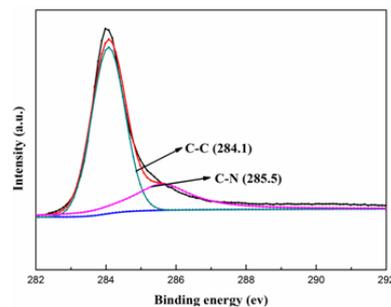
(c) GO-EDA



(d) rGO-EDA

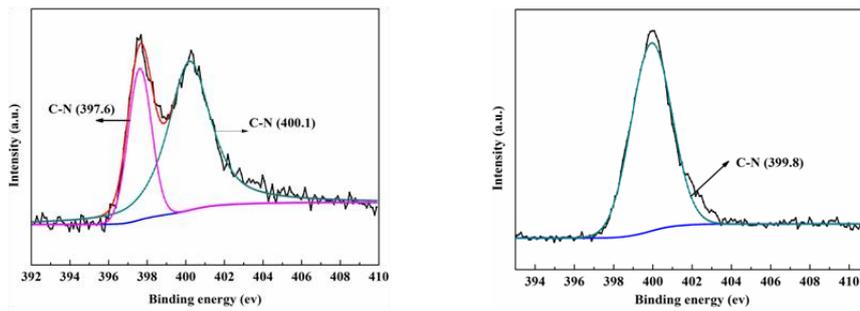


(e) GO-EA



(f) rGO-EA

Figure 2 C1s XPS spectra of GO, GO-EDA, and GO-EA before and after thermal annealing



(a) GO-EDA

(b) GO-EA

Figure 3 N1s XPS spectra of GO-EDA, and GO-EA

3.4 XRD analysis

Furthermore, the surface modification and reduction of GO with amine monomers is also well-reflected in its XRD pattern as shown in Figure 4. The characteristic diffraction peak of GO is at 11.7° corresponding to an interlayer distance of 0.76 nm. The XRD pattern of the GO-EDA shows that the 002 reflection peak almost disappears after reduction of GO. Compared with that of GO, the 002 reflection peak of GO-EA has been shifted to a lower angle (2θ , 9.2°). This is attributed to the insertion of ethylamine in GO layers with covalent bonds between ethylamine and GO sheets. Based on these results, it can be inferred that ethylenediamine possesses better reduction effects on GO than ethylamine, as verified by XPS results in Table 1. After thermal annealing at 800°C for 2 h, 002 reflection peak disappeared and a sharp peak was observed at $2\theta=26.4^\circ$ for rGO, rGO-EDA and rGO-EA, indicating the sufficient restore of conjugated graphene structure.

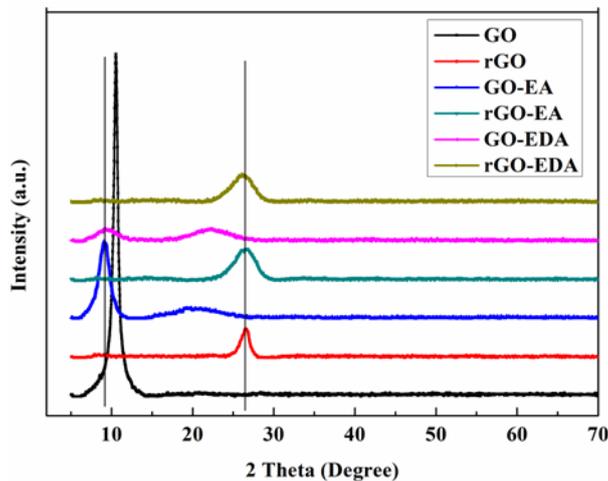
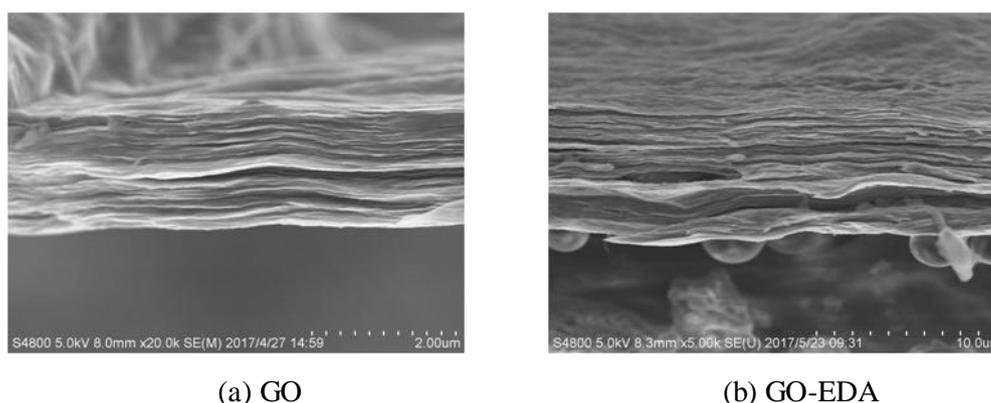


Figure 4 XRD pattern of GO, GO-EDA and GO-EA before and after thermal annealing

3.5 Electrical conductivity analysis

As is shown in Figure 5, GO films possess well-order stacked structure, as well as for GO-EDA films, indicating that functionalization of amine monomers has minimal disturbance on the well order of GO-EDA films.



(a) GO (b) GO-EDA

Figure 5 SEM cross-section images of GO, GO-EDA

As expected, unmodified GO film was nonconductive, with sheet resistance values as high as $1 \text{ G}\Omega$ approximately. On the contrary, an improvement was achieved both in the electricity of GO-EA and GO-EDA films. As could be seen in Table 2, sheet resistance has declined about four orders of magnitude for GO-EDA and two orders of magnitude for GO-EA, respectively, compared with that of GO films. A proper reason for the above phenomenon is that GO was successfully reduced by EA or EDA, and GO-EDA possesses better degree of reduction than GO-EA.

However, the effect of cross-linking between adjacent GO sheets on the electrical conductivity of GO films modified with amine monomers is hard to distinguish from the chemical reduction. Therefore, these films were thermally annealing at $800 \text{ }^\circ\text{C}$ for 2 h, to obtain nearly the same C/O ratio (as shown in Table 1) and well electrical conductivity. Compared with that of rGO films, decreases of the sheet resistance of rGO-EDA and rGO-EA could be observed, attributing to surface modification of GO. Moreover, a decline about 5 times was achieved in the sheet resistance of rGO-EDA films, compared with that of rGO-EA films. Based on the above results, this is believed to be due to the presence of diamine monomers (EDA) acting as cross-linked nanoscale spacers impeding the layer-by-layer stacking of GO sheets, which is in favour of the formation of more electron conduct channels. In future research, the effect of cross-linked GO sheets modified with EDA could be investigated by materials studio simulation.

Table 2 Sheet resistance of GO, GO-EDA and GO-EA before and after thermal annealing

Sample	Sheet resistance (Ω)	Sheet resistance (Ω) annealing at $800 \text{ }^\circ\text{C}$ for 2h
GO	$(8.07 \pm 5.10) \times 10^8$	10.63 ± 1.32
GO-EDA	$(6.19 \pm 0.12) \times 10^4$	1.07 ± 0.07
GO-EA	$(5.26 \pm 2.19) \times 10^6$	5.77 ± 0.04

4 CONCLUSIONS

In summary, GO was reduced and functionalized simultaneously by simple refluxing with EA or EDA, which could be confirmed by TGA, FTIR, XPS and XRD characterizations. The covalent bonds between GO and amine monomers were formed by the nucleophilic substitution reaction between amine groups of amine monomers and oxygen-containing groups of GO. The sheet resistance of GO-EDA films was greatly decreased to $6.19 \pm 0.12 \times 10^4$, nearly 4 orders of magnitude lower than that of GO films. Also, after thermal annealing, rGO-EDA films possess five times lower sheet resistance

than that of rGO-EA, with nearly the same C/O ratio, indicating that the cross-linked structure between adjacent GO sheets is formed by the chemical reaction with EDA.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the Research Project (No. JC 15-01-03) of National University of Defense Technology.

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