

# Selective reduction of graphene oxide

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**Abstract:** The reduction of graphene oxide has been widely used to control the properties of graphene-based materials. Traditional methods thoroughly remove oxygenated functional groups in graphene oxides. We show that ethanol, ethylene glycol and glycerol can selectively reduce epoxy groups in graphene oxide while hydroxyl and carboxyl groups remain unchanged. Hydrazine hydrate can reduce oxygen functional groups except carboxyl groups. These selective removals can be used to control the reduction degree of graphene oxides and their properties. The electrical conductivity of the reduced graphene oxides with different types of oxygen functional groups varied significantly and increased with the degree of reduction.

**Key Words:** Graphene oxide; Oxygenated functional groups; Alcohols; Selective reduction

## 1 Introduction

Graphene oxide (GO), utilized as precursor for a large-scale production of graphene-based materials, has attracted a great deal of attention in recent years<sup>[1-5]</sup>. GO sheets are electrically insulating, owing to their oxygenated functional groups (hydroxyl, carboxyl and epoxy groups) on surface, which usually need further treatments to restore the electrical conductivity for specific applications<sup>[6]</sup>. A lot of methods, such as chemical reduction<sup>[7-9]</sup>, laser irradiation<sup>[10,11]</sup>, microwave irradiation<sup>[12,13]</sup>, photocatalysis<sup>[14,15]</sup>, solvothermal reduction<sup>[16,17]</sup>, have been explored to remove these attached groups thoroughly and to recover graphene networks of sp<sup>2</sup> bonds.

Actually, researchers recently have found that the reduction degree of graphene oxide or oxidation degree of graphene has certain influences on their properties, such as electrical conductivity, catalysis activity and semi-conductive band positions<sup>[18-20]</sup>. Among these research work, the reduction degree of graphene oxide sheets (or oxidation degree of graphene) is controlled by adjusting the reactive temperature or time<sup>[19-21]</sup>. It is very difficult for these methods to control the reduction degree precisely and the repeatability is usually far from satisfactory, which limit further studies on their inherent characteristics. It is well known that the oxygenated functional groups on GO sheets mainly consist of hydroxyl, carboxyl and epoxy groups<sup>[22]</sup>. In theory, these functional groups should have different reaction activities. Accordingly, it is possible to utilize such diversified

reactivities to remove these functional groups selectively through a stepwise manner, resulting in a controllable reduction of GO.

Herein, we will show that under manipulative conditions, alcohols such as ethanol, ethylene glycol and glycerol can act as mild reducing agents to reduce GO selectively. Although some of these alcohols have been utilized to reduce GO, few attention is paid to their special reducing abilities<sup>[17,23,24]</sup>. Our experimental results indicate that when GO was treated with these alcohols under appropriate conditions, only the signals from epoxy groups have been attenuated, but no obvious reactions are observed for the hydroxyl and carboxyl groups on GO. Such selective elimination of functional groups could enable us to manipulate the reduction degree of GO in a well-controlled manner and to obtain certain functional groups-involved graphene consequently.

## 2 Experimental

### 2.1 Chemical reduction of GO

GO was prepared from purified natural graphite with a mean particle size of 325 mesh according to the method reported by Hummers and Offeman<sup>[25]</sup>. All other reagents were purchased from Shanghai Lingfeng Chemical Reagents Co. Ltd., China.

Three types of alcohols (ethanol, ethylene glycol and glycerol) were used to react with GO. Typically, GO powder was dispersed in 50 mL of ethylene glycol under sonication for 30 min at room temperature. Then the as-obtained

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suspension was heated in an oil bath at 160 °C for 6 h under vigorous stirring. Subsequently, the mixture was centrifuged while still hot, which was further washed with anhydrous alcohol and deionized water completely and dried at 60 °C. The as-prepared products are labeled as RGO-EG. Samples reduced by glycerol were prepared using the same procedure, and the products are labeled as RGO-GL. Reduction of GO by ethanol was carried out in a sealed autoclave and heated at 160 °C for 6 h, and the as-prepared samples are labeled as RGO-ET. The hydrazine hydrate, a typically strong reducing agent for GO, was also used here as a comparison<sup>[8]</sup>. 200 mg of GO was dispersed in 100 mL of water by sonication for 30 min to form a suspension. 2 mL of hydrazine hydrate (50 % w/v) was then added to the suspension that was refluxed (100 °C) for 24 h. After the reaction, the solid product (RGO-Hy) was isolated by filtration and washed with water and anhydrous alcohol, and finally dried at 60 °C in vacuum.

## 2.2 Characterization

Powder X-ray diffraction (XRD) were performed on a Bruker D8 Advance diffractometer with Cu  $K\alpha$  radiation. The diffraction data were recorded for  $2\theta$  angles between 5° and 60°. Scanning electron microscopy (SEM) were carried out on a JEOL JSM-6380LV scanning electron microscope. Fourier-transformed infrared spectroscopy (FT-IR) were carried out on a Bruker Vector-22, for which samples were prepared in potassium bromide pellets. The X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer PHI5300 X-ray photoelectron spectrometer, using Mg  $K\alpha$  ( $h\nu = 1253.6$  eV) X-ray as the excitation source. The elemental analysis were carried out on a Vario EL III, and before test all samples were dried at 100 °C in vacuum for two days. Raman spectra were recorded from 200 to 2000  $\text{cm}^{-1}$  on a Renishaw Invia Raman Microprobe using a 514.5 nm argon ion laser. The electrical conductivity of each sample was analyzed by a SDY-4 four-point probe instrument.

## 3 Results and discussion

Hydrazine hydrate is a strong reducing agent which was employed here to reduce GO as a comparison for other methods in this study<sup>[8]</sup>. Fig. 1 shows the XRD patterns of GO and its derivatives treated by ethylene glycol and hydrazine hydrate (the resulting materials are labeled as RGO-EG and RGO-Hy, respectively). It can be clearly seen that the XRD patterns of RGO-EG are quite different from that of GO. The characteristic diffraction peak (001) of GO almost disappears, while a new broad peak at around 24° is formed, which is one characteristic diffraction peak observed in the traditional reduced GO<sup>[8,17]</sup>. Furthermore, the XRD patterns of RGO-ET and RGO-GL are similar to that of RGO-EG and RGO-Hy, indicating structure of GO could be changed by reducing with these alcohols<sup>[17,26,27]</sup>.

Fig. 2 displays SEM images of GO, RGO-EG and RGO-Hy. By comparison, it can be found that GO sheets

possess a plat lamellar structure (Fig. 2a, b), whereas RGO-EG and RGO-Hy possess a flocculent morphology, forming a disordered solid (Fig. 2b), which is similar to that of reduced GOs reported in previous literatures<sup>[8,17]</sup>.

It is worth noting that there are some differences between these reduced GO using alcohols and hydrazine hydrate. Fig. 3 shows the FT-IR spectra of GO, RGO-EG and RGO-Hy. As shown in Fig. 3, the characteristic features in the FT-IR spectra of GO are the absorption bands corresponding to the C=O carbonyl stretching at 1720  $\text{cm}^{-1}$ , the C-OH stretching at 1224  $\text{cm}^{-1}$ , and the C-O stretching at 1050  $\text{cm}^{-1}$ <sup>[28,29]</sup>. The spectra also show a C=C peak at 1620  $\text{cm}^{-1}$  corresponding to the remaining  $\text{sp}^2$  character<sup>[30]</sup>. These absorption bands in the RGO-Hy are not pronounced, indicative of an apparent removal of the oxygen-containing groups<sup>[31]</sup>. Several absorption bands at around 1721, 1568 and 1210  $\text{cm}^{-1}$  are still observable in the spectrum of RGO-EG. It has been demonstrated that C=O carbonyl stretching at around 1720  $\text{cm}^{-1}$  is hard to be reduced, even with hydrazine hydrate. The same phenomenon is observed in our samples<sup>[7]</sup>. The bands at around 1568 and 1210  $\text{cm}^{-1}$  may be attributed to the vibrations of skeleton and C-OH bonds of RGO-EG, respectively<sup>[17]</sup>. It is worth noting that the absorption of epoxy groups (around 1050  $\text{cm}^{-1}$ ) almost disappear as the arrow, which may be ascribe to the reactions between the epoxy groups and alcohols. Analogously, the RGO-ET and RGO-GL possess almost the same absorption bands.

The functional groups present in these samples are further analyzed by XPS. The C1s XPS spectrum of GO (Fig. 4a) clearly indicates that there are four kinds of carbon: the  $\text{sp}^2$ -hybridized C-C, the C in C-OH bonds, the epoxy C, and the carboxylate carbon<sup>[8,32]</sup>. Strong reductants such as hydrazine hydrate can usually remove oxygen in GO considerably (Fig. 4c). However, by comparison, it can be clearly seen that only epoxy C1s peak intensity of RGO-EG reduced significantly after reduction with ethylene glycol, and the change of the C1s peak intensities of hydroxyl and carboxyl groups in RGO-EG is not noticeable (as shown in Fig. 4b), which is consistent with the results of FT-IR spectra. On the other hand, the increased area percentage of the peak associated with  $\text{sp}^2$ -hybridized C indicates the formation of

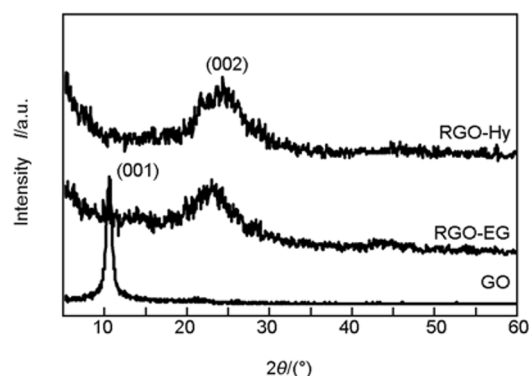


Fig. 1 XRD patterns of GO, RGO-EG and RGO-Hy.

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