Preliminary comparison of different reduction methods of graphene oxide

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Abstract. The reduction of graphene oxide (GO) is a promising route to bulk produce graphene-based sheets. Different reduction processes result in reduced graphene oxide (RGO) with different properties. In this paper three reduction methods, chemical, thermal and electrochemical reduction, were compared on three aspects including morphology and structure, reduction degree and electrical conductivity by means of scanning electron microscopy (SEM), X-ray diffraction(XRD), the Fourier transform infrared spectroscopy (FT-IR) spectrum, X-ray photoelectron spectroscopy (XPS) and four-point probe conductivity measurement. Understanding the different characteristics of different RGO by preliminary comparison is helpful in tailoring the characteristics of graphene materials for diverse applications and developing a simple, green, and efficient method for the mass production of graphene.

Keywords. Chemical reduction; thermal reduction; electrochemical reduction; graphene oxide.

1. Introduction

The excellent mechanical, electrical, thermal and optical properties of graphene have driven the search to find methods to produce high-quality graphene on large scale.[1–5] The conversion of graphene oxide (GO) to graphene has been a viable route to afford graphene in considerable quantities, due to its high yield, low-cost and simple process.[6–8] Chemical, thermal and electrochemical reduction of GO are promising routes to bulk produce graphene-based sheets.[8,9]

Chemical reduction of GO sheets has been performed with several reducing agents, including hydrazine,[10,11] sodium hydride, sodium borohydrate ($NaBH_4$)[10,12,13] and ascorbic acid (Vitamin C: VC),[14] etc. Hydrazine is the most common reducing agent. The first use of hydrazine hydrate to prepare graphene was reported by Stankovich *et al*.[15–17] The chemically reduced graphene oxide (CRGO) shows aggregated sheets and crumpled structure because RGO becomes less hydrophilic due to the removal of oxygen atoms. The irreversible agglomerates through van der Waals interaction affect the unique properties that individual sheet has and make further processing difficult.[15,16] There are residual defects and oxide functional groups in CRGO sheets, resulting in degradation of reduction degree and conductivity. However, the highest C/O ratio and conductivity of CRGO by hydrazine reduction could reach 12.5 and 99.6 S cm^{-1}, respectively,[14] and CRGO could be contaminated by hydrazine which is toxic.[18,19]

High reduction level and conductivity could be achieved by thermal reduction of GO. Bulk quantities of single graphene sheets can be prepared by the thermal expansion of GO.[20,21] Aksay's group[22,23] have exfoliated and reduced stacked GO by heating GO to 1050°C, where oxide functional groups were extruded as carbon dioxide. The thermally reduced graphene (TRGO) has a wrinkled structure, with a C/O ratio of 10:1, and is electrically conducting, suggesting the effective reduction of GO.[21] In addition, the degree of thermal reduction can be controlled by heating temperature, duration and gaseous environment (ultrahigh vacuum, Ar, H_2, NH_3).[24–26] This method is readily scalable and also has the ability to produce graphene with a tunable amount of oxygen.

Electrochemical reduction is a promising green strategy for graphene synthesis, and several research works have been reported.[27–29] The reduction usually needs no special chemical agent, and is mainly caused by the electron exchange between GO and electrodes. Hence the 'green synthesis' of graphene under mild conditions is preferred.[30] The oxygen-containing functional groups can be efficiently removed and the conjugated structure can be restored. Zhou *et al*[28] synthesized graphene films by coupling negative reduction and spray coating in various electrolytes. The conductivity of the RGO film produced was measured to be approximately 85 S cm^{-1}. Herein we present a green and facile approach to the synthesis of graphene through electrochemical process in this paper.

Different reduction processes result in RGO with different properties.[9] Therefore, it is of great merit to give a comparison for different reduction methods. Preliminary comparison was carried out between RGO of the three reduction methods on three aspects including morphology and structure, reduction degree and electrical conductivity by means of scanning electron microscopy (SEM), the Fourier transform infrared spectroscopy (FT-IR) spectrum, X-ray diffraction (XRD),

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X-ray photoelectron spectroscopy (XPS) and four-point probe conductivity measurement.[8] Understanding the different characteristic of different RGO by preliminary comparison is helpful in tailoring the characteristics of graphene materials for diverse applications and developing a green and efficient method for the mass production of graphene.

2. Experimental

2.1 *GO synthesis*

Graphite oxide was synthesized from natural graphite by the modified Hummers method.[31,32] H_2SO_4 (120 ml) was added into a 500 ml flask filled with graphite (5 g), which was cooled to 0°C in an ice bath. $KMnO_4$ (15 g) was added slowly, and the mixture was stirred for 30 min. Then the temperature was raised to 35°C with a water bath, and the mixture was stirred for 2 h. Afterward, deionized water (225 ml) was added and the temperature was increased to 95°C. After 30 min, H_2O_2 (30 wt%) was then added until gas evolution ceased. Then the suspension was washed with 5% HCl solution and deionized water. Finally, the graphite oxide was obtained and kept in a vacuum desiccator at 45°C for 48 h.

After drying, the graphite oxide (0.5 g) was dispersed in water (500 ml) and sonicated for 90 min at room temperature. A well-dispersed and stable suspension in water containing 1 mg ml^{-1} of GO platelets was obtained.

2.2 *Reduction of GO*

2.2a *Chemical reduction*: Hydrazine hydrate (1.00 ml) was added into GO suspension (100 ml, 1 mg ml^{-1}) and the solution heated in water bath at 90°C for 2 h.[18] This product was isolated by filtration over a medium fritted glass funnel, washed copiously with water and methanol, and dried at 50°C in vacuum.

2.2b *Thermal reduction*: The GO powder was put in a crucible, and the crucible was quickly inserted into the middle of the furnace preheated to 850°C and held in the furnace for 30 s; then the crucible was taken out.

2.2c *Electrochemical reduction*: Two cleaned copper plates were employed as electrode (figure 1). Electrophoretic deposition (EPD) technique was applied to fabricate GO films on the Cu electrode. Under an applied potential of 30 V for 30 min, the GO was deposited onto the anode completely. Then the direction of electric field was exchanged; in situ electrochemical reduction of the GO films was carried out on the cathode when a direct-current voltage of 60 V was applied for 240 min. All experiments were carried out at room temperature. The electrochemically reduced graphene oxide (ERGO) was taken out from the solution and electrode thoroughly washed with deionized water and dried at 50°C.

2.3 *Characterization*

The morphology and structure of RGO can be reflected from SEM and XRD. Combining XPS with FT-IR, reduction degree was compared. XRDs of the samples were measured using an X-ray diffractometer (D/max2550VB3+/PC, Rigaku, Japan) with reference target: Cu Kα radiation. FT-IR spectra were obtained through a BRUKER EQUINOXSS spectrometer using the attenuated total reflectance. XPS analysis was performed on an RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation ($hν =$ 1253.6 eV). The electrical conductivity of the GO and RGO films was measured by the four-point probe method (SZT-2A). Measurements were repeated on three different areas of the films to ensure sample uniformity and their geometric averages.

3. Results and discussion

3.1 *Morphology and structure*

The morphology and structure of RGO play important role in evaluating the performance of RGO because the unique properties of graphene are associated with them. In our work, SEM and XRD are used to characterize the morphology and structure of RGO. The SEM image of CRGO shows randomly aggregated and crumpled sheets closely associated with each other and formed a disordered structure (figure 2b), while TRGO shows wrinkled shees with a 'fluffy' appearance (figure 2c), which may be caused by release of carbon dioxide. The SEM image of the ERGO (figure 2d) shows the stacked-film structure because GO was deposited onto the anode and formed adsorption film during EPD and then was in situ reduced on the cathode from into outside. The simultaneous film assembly and reduction might be favorable to some electrochemical applications.

Figure 3 shows the XRD patterns of graphite, GO, ERGO, CRGO and TRGO. Compared with the pristine graphite,
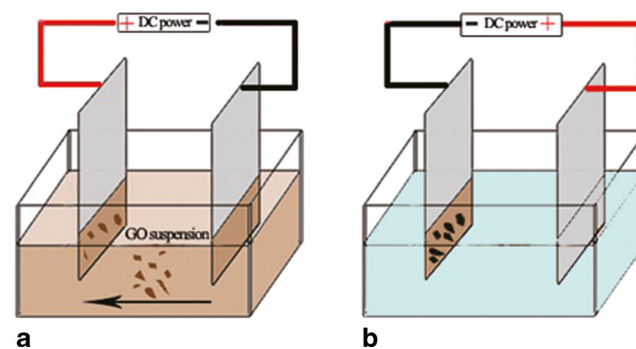

Figure 1. Schematic illustration of electrochemical reduction process: (**a**) electrophoretic deposition (EPD) process and (**b**) negative reduction process.
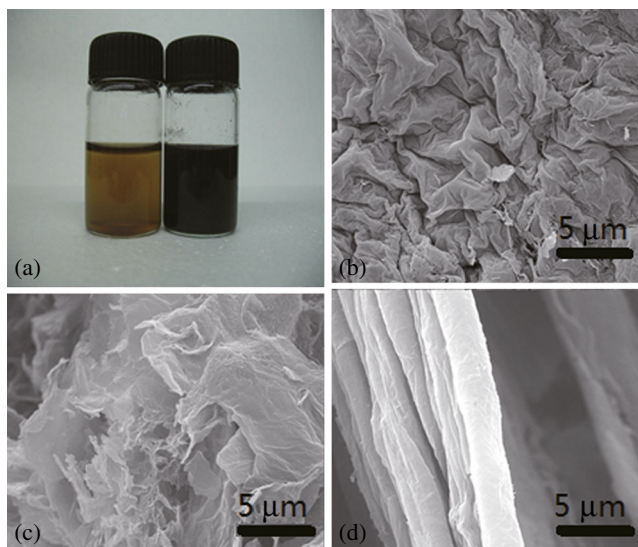
Figure 2. (**a**) Photographs of aqueous colloidal suspension of GO before and after (graphene) reduction. SEM images of (**b**) CRGO (**c**) TRGO and (**d**) ERGO.

Figure 3. XRD spectra of GO and different methods reduced GO.

the sharp diffraction peak at 26.4° (corresponding to the interlayer distance $d = 0.337$ nm) disappeared, and a new diffraction peak appeared at 10.4° with d-spacing of 0.818 nm in GO due to the presence of intercalated H_2O molecules and various oxide groups. The interlayer distance of GO drastically decreased to 0.356 nm for TRGO, 0.369 nm for CRGO and 0.386 nm for ERGO, after thermal, chemical and electrochemical reduction, respectively. The interlayer space of TRGO is the most similar to pristine graphite, which indicates thermal reduction is most effective at removing the intercalated H_2O molecules and surface oxide groups of GO. The interlayer space of ERGO (similar to the result of CRGO) is larger than that of pristine graphite, due to the residual intercalated water molecules between layers. While the XRD pattern (peak shape and intensity) of TRGO displays an amorphous structure. This is mainly because the decomposition of oxygen-containing groups also removes carbon atoms from the carbon plane, which results in lattice defects. CRGO show the better lattice structure than that of TRGO and ERGO.

3.2 *Reduction degree*

The reduction degree of RGO will significantly influence the performance of reduced graphene oxide materials. Therefore, the reduction degree is an important parameter to evaluate the property of RGO. FT-IR transmittance spectra and XPS are the two major characterization techniques.[8] As shown in figure 4, the C 1s spectrum of GO consists of four different peaks: C = C in aromatic rings (284.6 eV); C–O (286.3 eV); C=O (287.8 eV); COOH (289.0 eV).[33] In the C 1s XPS spectrum of RGO, the intensities of all C 1s peaks of the carbons binding to oxygen decreased obviously, revealing
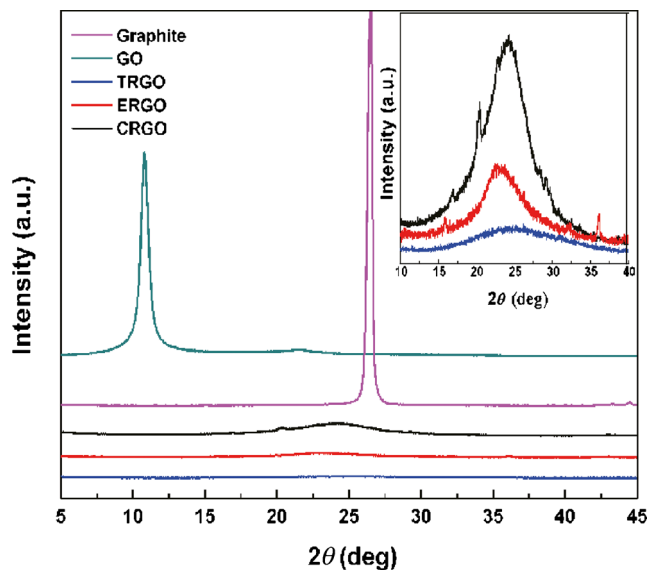
that considerable oxygen containing functional groups were removed. Although the C 1s XPS spectrum of CRGO also exhibits their peak intensities are much smaller than those in GO, there is an additional component at 285.9 eV corresponding to C bound to nitrogen, indicating both considerable deoxygenation as well as nitrogen incorporation. Thermal reduction is quite powerful to remove most of the C = O groups on the GO flakes, which is possibly by forming CO or CO_2. The changes of C/O ratio of RGO indicate the different reduction degrees. After thermal reduction, the C/O ratio can be improved to approximately 9:1. The C 1s XPS spectrum of ERGO shows suppression of the epoxy/ether groups (286.3 eV) peak while a small peak at 289 eV remains, indicating that there are still oxygen-containing groups on ERGO. The C/O ratio was improved to approximately 6:1.

Figure 5 shows the FT-IR transmittance spectra of GO, ERGO, TRGO and CRGO. The spectrum of graphene oxide illustrates C–O (ν (alkoxy)) at 1045 cm^{-1}, C–O–C (ν (epoxy)) at 1226 cm^{-1}, and C=O in carboxylic acid and carbonyl moieties (ν (carbonyl)) at 1722 cm^{-1}; C=C at 1620 cm^{-1} assigns to skeletal vibrations of unoxidized graphitic domains. The band at 3397 and 1396 cm^{-1} could be due to the O–H stretching mode and deformation vibration of intercalated water, respectively.[26] The intensity of the peaks related to oxygen functional groups of RGO all decreased dramatically, demonstrating graphene oxide were reduced by using the different approach. However, FT-IR just gives us an average reflection of reduction degree of RGO. This shows, along with the chemical analysis by XPS, that the oxygen functional groups were significantly reduced. After the GO is thermally reduced, the C=O vibration band disappears and the C–O stretching bands remain. Therefore, after comparison, the reduction
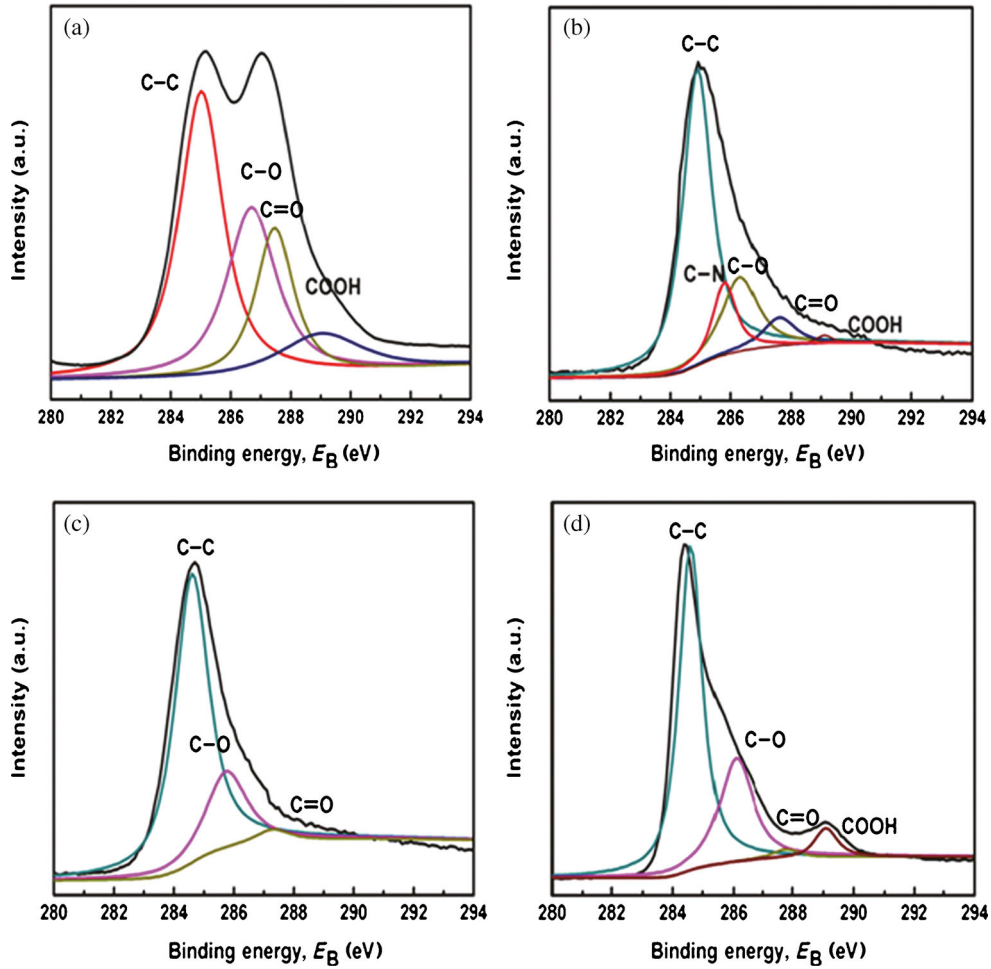
Figure 4. XPS spectra of (**a**) GO, (**b**) CRGO, (**c**) TRGO and (**d**) ERGO.
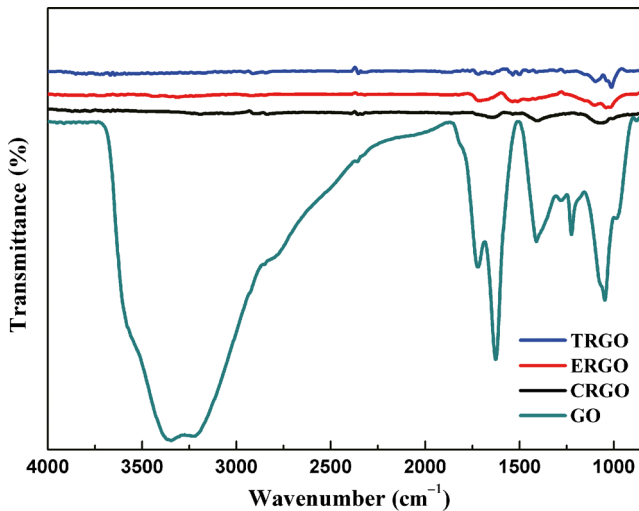

Figure 5. FT-IR spectra of GO and different methods RGO.

degree of TRGO is highest and CRGO has similar reduction level to ERGO. However, nitrogen was induced to CRGO, which contaminated the products.

Table 1. Electrical conductivity data of GO and different methods RGO.

	GO	CRGO	ERGO	TRGO
Sheet resistance (Ω S^{-1})		406	284	215
Electrical conductivity (S m^{-1})	Insulator	164	176	232

3.3 *Electrical conductivity*

The electrical conductivity is a direct indicator of the reduction degree and defect repair degree.[19,34] GO and RGO films were formed by vacuum filtration method. The electrical conductivity of GO and RGO is calculated by

$$R_s = \frac{1}{\sigma t}. \tag{1}$$

Sheet resistance (R_s; Ω S^{-1}) is a measure of the electrical resistance of a sheet, independent of its thickness. It can be measured by four-probe method. σ is the bulk conductivity (S m^{-1}) and t the sample thickness. The electrical

Table 2. Comparison of the reducing effect of GO by different methods.

Reduction method	Morphology and structure	C/O ratio	σ (S m^{-1})	Reduction condition
Electrochemical reduction	Stacked-film	6:1	176	Room temperature; no chemical regent
Chemical reduction	Aggregated and crumpled	7:1	164	Hydrazine; 90°C
Thermal reduction	'Fluffy' appearance of amorphous structure	9:1	232	High temperature (850°C)

conductivity of graphene nanosheets obtained by chemical, electrochemical and thermal routes are calculated to be 164, 176, 232 S m^{-1}, respectively (table 1). All the electrical conductivity has been improved compared with GO after performing different reduction, which indicates the reduction of GO and the restoration of the sp^2 carbon reestablished conductive pathways. The electrical conductivity of TRGO is the highest; combining with the results of XPS reveals that considerable deoxygenation, especially of the remove of C=O groups, can help enhance the electrical conductivity.

4. Conclusion

In summary, after preliminary comparation, we found that different RGO have different characteristics (table 2). The morphology and structure of RGO can be reflected from SEM and XRD. Combining XPS with FT-IR, reduction degree was compared. Finally, following conclusions can be drawn:

(1) The reduction degree and the electrical conductivity of TRGO are higher than those of CRGO and ERGO. Thermal reduction is mainly to remove most of the C=O groups on the GO flakes, which is possibly by forming CO or CO_2. That is also why TRGO displays an amorphous structure. while TRGO shows wrinkled sheets with a 'fluffy' appearance.

(2) CRGO shows disordered structure Sheets randomly aggregated and crumpled, which affects the unique properties that individual sheet has and make further processing difficult. The reduction degree of the CRGO is lower compared to TRGO due to the residual oxide functional groups and defects. Hydrazine is most effective at reducing C–O–C species but has low to moderate efficiency in the reduction of carboxylic acids and it still includes N-containing species, according to results of XPS.

(3) ERGO shows stacked-film structure. The simultaneous film assembly and reduction might be favorable to some electrochemical applications. The electrical conductivity of the ERGO is higher than the results of CRGO and electrochemical reduction could also avoid being contaminated by hydrazine or other chemical regents which are toxic. Also electrochemical reduction process is under mild conditions compared with thermal reduction, which is preferred. ERGO has better lattice structure than TRGO, because this reduction is mainly

caused by the electron exchange between GO and electrodes and fewer defects is formed. Electrochemical reduction is a promising green and effective strategy for the mass production of graphene.

Understanding the different characteristics of different RGO is helpful in tailoring the characteristics of graphene materials for diverse applications and develop a green and efficient method for the mass production of high quality graphene. Because the electrochemical reduction method we reported in this paper can remove the oxygen under mild and green conditions and introduce less defects. According to the results, thermal reduction at high temperature possesses some defects because of the fast reduction. Therefore, combining electrochemical reduction with thermal anneal together may be a green, effective way to prepare high quality graphene.

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