Study on efficient and green reduction of graphene oxide by a one-step hydrothermal method

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Abstract. This work reports an efficient and green reduction method of graphene oxide (GO) by a one-step hydrothermal process. GO was prepared by the oxidation of graphite using a modified Hummers method. The reduced graphene oxide (rGO) were characterised and studied by means of UV-vis absorption spectra, Raman spectroscopy and transmission electron microscope (TEM) techniques. UV-vis absorption spectra revealed that GO was successfully reduced to rGO and the π-conjugated structure was restored. Raman spectroscopy suggested that rGO had a smaller average size of the in-plane sp² domains and more sp² domains than that of GO. Fourier transform infrared (FTIR) spectra demonstrated that most oxygen functionalities on the GO were removed after the reduction. TEM images further confirmed that there was no irreversible agglomeration of rGO layers. Furthermore, we proposed a possible mechanism for the reduction of GO with subcritical water under hydrothermal condition. This study provides a novel idea for developing environmentally friendly reduction methods of GO.

1. Introduction

As a single layer of carbon atoms arranged in a honeycomb lattice, graphene has triggered tremendous interest for its excellent mechanical, thermal, chemical, optical and electrical properties [1], and exhibits broad application prospects in the field of household appliances, automobile, electronic devices and aerospace industries. There are various synthesis methods of graphene, such as mechanical exfoliation of highly oriented pyrolytic graphite, chemical vapor deposition, liquid-phase stripping, epitaxial growth, and the chemical reduction of graphene oxide (GO). Although graphene prepared by the first four methods show fewer structural defects and excellent comprehensive properties, its large-scale application is limited because of the high production cost. To our delight, GO can be prepared from inexpensive graphite as raw material using low cost and high efficiency chemical oxidation methods [2]. Because there are many functional groups on the surface of GO, such as hydroxyl, carboxyl and epoxy groups, which seriously affect the properties of GO, it is necessary to reduce GO to reduced graphene oxide (rGO). Unfortunately, some reducing agents are toxic, such as hydrazine hydrate, phenylhydrazine and sodium borohydride [3]. Therefore, it is of great significance to develop environment-friendly reducing agents for GO reduction.

According to the Arrhenius equation, the rate of ion reaction increases remarkably when water is heated above the boiling point under closed and pressurized conditions. Thus ionic reactions rate constant are generally increased with temperature in subcritical water [4], and the occurrence of ionic reactions is more probable in subcritical water than in below-subcritical water [5]. Therefore, it is likely that subcritical water acts as a reductant and accelerate the ion reaction. In this work, we report
an efficient reduction method of GO with subcritical water under hydrothermal condition, and the possible mechanism of reduction of GO with subcritical water is proposed.

2. Experimental section

2.1. Materials
Natural flake graphite (purity>99.9%) with an average particle size of 30 μm was kindly provided by Qingdao Xingyuan Graphite Co., Ltd (China). KMnO4, NaNO3, H2SO4 (98%), H2O2 (30%), HCl (36%) were purchased from Chengdu Kelong Chemical Co., Ltd (China). All the chemicals were used as received without further purification.

2.2. Synthesis of GO and rGO
Graphite oxide was prepared from the oxidation of natural flake graphite using a modified Hummers method [6]. In a typical procedure, 92 ml of 98% H2SO4 was added to the three round bottom flask, and 4 g flake graphite and 2 g NaNO3 were slowly added into the flask added under stirring in an ice bath. After 1 hour of stirring, the temperature was raised up to 35 °C and kept for 2 hours in a water bath. Then, 200 mL deionized water was added slowly into the mixture, and the temperature was raised up to 95 °C and kept for 20 minutes. After the addition of 14 mL of 30% H2O2 and 120 mL deionized water, the color of the mixture becomes golden yellow. Finally, the precipitate in the mixture was collected by centrifugation at 4000 rpm, and was repeatedly rinsed with 5% HCl solution and deionized water. Graphite oxide was transformed to GO using ultrasonic stripping treatment for 30 minutes in an ultrasonic bath cleaner [7]. The graphene oxide powder was obtained from centrifugation at 10000 rpm for 10 minutes, and dried in vacuum drier at 50 °C.

The reduction of GO was carried out through a facile hydrothermal method. In detail, 50 mg of GO powder was loaded in a beaker, and 100 mL deionized water was then added. The dispersion was sonicated using an ultrasonic bath cleaner for 30 min to form a homogeneous yellow-brown dispersion. Then, the dispersion was transferred to a Teflon-lined stainless steel autoclave, which was tightly sealed and heated at 150 °C for 4 h in a hot air oven. Thereafter, the prepared products were filtered and washed with deionized water for several times, and the rGO powder was obtained by drying in a vacuum oven at 60 °C for overnight.

2.3. Characterization
UV-vis adsorption spectra were performed on a Specord 200 UV–vis spectrophotometer at room temperature. Raman spectra were recorded with a Horiba Jobin Yvon LabRAM HR Raman spectrometer at an excitation laser wavelength of 632.8 nm. Fourier transform infrared spectroscopy (FTIR) was carried out on a Bruker Tensor 27 spectrophotometer with KBr pellets in the range of 4000–400 cm⁻¹. The flake graphite powder was observed using Hitachi S-4800 scanning electron microscopy (SEM) at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) was carried out with a JEOL JEM-2100F transmission electron microscope at 200 kV to investigate the morphology of GO and rGO, and the sample was dispersed in water by ultrasonication for 10 min and then the dispersion was drop casted on a copper grid for observation.

3. Results and discussion
UV–vis absorption spectroscopy was employed to analyze the structure of GO and rGO. As shown in figure 1(a), there is two strong absorption peaks centered at 232 nm and 301 nm for the GO solution, which corresponds to the π–π* transitions of C=C bond and n–π* transitions of C=O bond, respectively [8]. After the reduction (figure 1(b)), the π–π* transition band is red-shifted from 232 to 269 nm, and the absorption intensity of the whole spectrum increases dramatically, indicating that GO was reduced to rGO and the π-conjugated structure might be restored [9]. The inset shows the photographs of GO and rGO dispersions in water. The GO dispersion with bright yellow color revealed the successful oxidation of graphite to GO [10]. It is also observed that the color of GO solution changed from bright
yellow to the homogeneous black after hydrothermal process, suggesting the partial restoration of the conjugation structure.

Figure 1. UV-vis absorption spectra of (a) GO and (b) rGO. The inset is photographs of GO and rGO dispersion in water with a concentration of 0.2 mg ml$^{-1}$.

Figure 2. Raman spectra of (a) graphite, (b) GO and (c) rGO.

Raman spectroscopy has proven to be a powerful tool to characterize the structure and quality of graphene and related materials. Figure 2 shows Raman spectra of graphite, GO and rGO. Raman spectrum of graphite in figure 2(a) displays a prominent G-band at 1582 cm$^{-1}$, which is caused by the first-order scattering of tangential stretching ($E_{2g}$) [11]. It can be seen from the Raman spectrum of GO (figure 2(b)) that the G-band is broadened and shifts from 1582 cm$^{-1}$ to 1592 cm$^{-1}$. In addition, the D-band at 1325 cm$^{-1}$ becomes prominent, and the D-band originated from a breathing mode of $\kappa$-point phonons of $A_{1g}$ symmetry of the defects [12]. In the Raman spectrum of rGO (figure 2(c)), both the G-band and D-band are widened and shifted to 1590 cm$^{-1}$ and 1339 cm$^{-1}$, respectively. The D/G intensity ratio is used for measuring the $sp^2$ domain size of graphene [13]. The D/G intensity ratio of rGO (1.6) is higher than that of GO (1.2), suggesting a decrease in the average size of the in-plane $sp^2$ domains and a partially recovery of the structure of the rGO. Furthermore, this change can be attributed to that more $sp^2$ domains were created during the reduction. And the result agrees very well with the Raman spectrum of the GO reduced by L-ascorbic acid [14].

The oxygen-containing groups of GO and rGO were investigated by FTIR spectroscopy. As shown in figure 3(a), the natural flake graphite shows no obvious sharp absorption peak in the range 4000–400 cm$^{-1}$. Figure 3(b) shows the FTIR spectra of GO, and the characteristic peaks of are corresponding to many characteristic functional groups of GO [15], such as the stretching and bending vibration peaks of O–H groups at 3406 cm$^{-1}$ and 1402 cm$^{-1}$, respectively, the C=O stretching vibration peak at 1731 cm$^{-1}$, the O–H vibrations of water at 1623 cm$^{-1}$, the C–O stretching vibration peak at 1230 cm$^{-1}$, and the C–O–C stretching vibration peak at 1078 cm$^{-1}$. The results clearly demonstrate that GO has been successfully synthesized by the modified Hummers method. After the reduction of GO (figure 3(c)), the intensities of the FTIR peaks of the above oxygen-containing groups are decreased.
dramatically, revealing that most oxygen functionalities were removed and GO has been reduced to rGO. In addition, the appearance of a new peak at about 1565 cm$^{-1}$ is ascribed to C=C skeletal vibration of graphene [16], suggesting that the oxidized sp$^2$ carbons are partly transformed to sp$^3$ carbons, and it is consistent with the results from UV-vis absorption spectra and Raman spectra.

Figure 3. FTIR spectra of (a) graphite, (b) GO and (c) rGO.

Figure 4(a) shows the SEM image of natural flake graphite, and it exhibits a layered structure and the lateral size of the graphite flakes is around 20–40 µm. As shown in Figure 4(b), GO shows smooth surfaces and wrinkled edges, which is mainly attribute to the epoxy groups forming chains on the surface of GO [17], and that wrinkles and ripples formed on the GO sheets improved the thermodynamic stability because perfect two-dimensional GO sheets were thermodynamically unstable [18]. Figure 4(c) presents TEM image of rGO and it shows a transparent and curled “paper like” structure, suggesting that there was no irreversible restacking and agglomeration of rGO layers during hydrothermal process. This is probably due to the presence of residual oxygen-containing functional groups on the surfaces of rGO sheets.

Figure 4. (a) SEM image of graphite, and TEM images of (b) GO and (c) rGO.

The possible mechanism of the reduction of GO with subcritical water is proposed on the basis of above experiments, and shown in Figure 5. There are more hydrogen and hydroxide ions in subcritical water than below-subcritical water at normal temperature and pressure, functioning as an acid catalyst or alkaline catalyst. Therefore, subcritical water is believed to be an effective reductant, and the
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reduction reaction is similar to the dehydration of ethanol catalyzed by H+. In the dehydration process, the H+ protons usually have the high binding affinity for hydroxyl groups and epoxide groups on the surfaces of GO, together with the formation of H2O molecules [14]. Fortunately, the prepared rGO has good water dispersibility, and this is probably due to residual carboxyl and carbonyl groups on the surfaces and edges of rGO sheets [9].

4. Conclusions
In conclusion, this paper reports an effective method to reduce GO to rGO using a simple hydrothermal method and environmental friendly water as the reducing agent. UV–vis absorption spectroscopy, Raman spectroscopy and FTIR spectra confirmed that GO was successfully reduced to rGO and the π−π conjugated structure was restored after the reduction. And morphological observation showed that GO was prepared from graphite using the modified Hummers method. Furthermore, the possible mechanism of the reduction of GO with subcritical water was proposed.

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