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Reduction of Graphene Oxide via Modified Hydrothermal Method

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Abstract

The chemical reduction of graphene oxide (GO) typically involves highly toxic reducing agents that are harmful to human health and environment. Moreover, complicated surface modification is often needed to avoid aggregation of the reduced GO during reduction process. In this paper, GO was synthesized by modified Hummer's method. Modified hydrothermal method was utilized to prepare reduced GO in pH value of 11 adjusted by NaOH at 140 °C for 6 h under continuous stirring. FTIR, Raman, SEM and XRD analyses are performed, which reveal that the labile oxygen functional groups are progressively eliminated, thereby partially restoring the π -conjugated network. Raman spectra show G to D band progression. Furthermore, XRD results confirm proper GO reduction. Carbonyl, carboxyl, ether, and phenolic groups are found to be thermally stable, which hinders complete deoxygenation of GO and makes their dispersion in water stable. In modified hydrothermal method, pressure can be controlled efficiently and temperature is lower than simple hydrothermal method. Also, the final product has homogenous structure, thus facilitating the use of graphene-based materials for large-scale applications.

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1. Introduction

Graphene, a one-atom-thick and two-dimensional honeycomb lattice structure, has remarkable properties such as amazing Young's modulus (~ 1100 GPa), respectable fracture strength (125 GPa), appreciable thermal conductivity (~ 5000 Wm⁻¹ K⁻¹), outstanding charge mobility (200,000 cm²V⁻¹ s⁻¹), very high specific surface area (theoretical value of 2630 m² g⁻¹), magnetism, and fascinating transport phenomena, Park et al. (2009). Recently, there have been

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intense efforts to apply graphene materials in electronic, optoelectronic, capacitor, and sensing applications, Avouris and Dimitrakopoulos (2012).

Among the current methods of graphene synthesis, solution-processed routes are the most suitable method for functionalization and bulk-scale production. Reduction of GO to reduced graphene oxide (RGO) is necessary to recover the conjugated network and electrical conductivity in these methods, Li et al. (2007). The carboxyl, hydroxyl, or epoxy groups bonded on graphene and other atomic-scale lattice defects modify the electronic structure of graphene and serve as strong scattering centres that can affect the electrical transport, Rutter et al. (2007).

Reduction of GO by chemical or thermal routes has widely been accepted to prepare RGO. Hydrazine hydrate, Park et al. (2011) and borohydride, Shin et al. (2009) are well-recognized strong reducing agents and used for the chemical reduction of GO. However, such high temperature reduction method generates various defects by consuming the carbon backbone of GO and eventually releases H₂O, CO₂, and CO, Larciprete et al. (2011) In view of the fact that hydrazine is toxic and dangerously unstable, it is desirable to explore a green chemistry route for the reduction of graphene, Zhou et al. (2009).

In this paper, we explore a simple hydrothermal route to convert GO to RGO in stable graphene suspension in water. The hydrothermal conversion method has several advantages over the common chemical reduction processes such as simplicity, scalability, low defects content (the closed system of relative high temperature and pressure promotes the recovery of π -conjugation after dehydration, which is favourable for minimizing defects). Engineering the parameters of temperature and pressure affords a facile method to control the degree of reduction of the GO.

2. Experimental

2.1. GO synthesis

Graphite oxide was prepared by vigorous oxidation of graphite powder using H₂SO₄ and KMnO₄ as oxidizing reagents according to the modified Hummers method, Krishnamoorthy et al. (2013) 30% H₂O₂ and then 10% HCl solutions were used to rinse the oxidized product. Subsequently, the product was washed with deionized water to remove the extra ions. The prepared graphite oxide solution was exfoliated into the GO using an ultrasonic bath for 1h followed by centrifugation at 4000 rpm for 40 min to remove non exfoliated graphite oxide. The product was dried at room temperature overnight.

2.2. RGO preparation

The GO powders were added into water to form brown dispersions at 0.3 mg/mL concentrations. The solutions were sonicated in an ultrasound bath for 30 min. Then the GO aqueous dispersion was placed into a homemade autoclave and heated at 140 °C for 6 h. The internal pressure of 400 KPa was applied into the autoclave. For proper mixing and faster reaction of precursor materials, a stirring system was used during the reduction process. After the process, the autoclave was allowed to cool naturally to room temperature. The product was collected and washed several times with deionized water to remove the NaOH residues and then dried at room temperature overnight.

2.3. Characterization

X-ray diffraction of reduced-graphene oxide was performed on Philips X-pert pro PW1730, using Cu-K α radiation ($\lambda=1.5405 \text{ \AA}$, 40 kV, 30 mA) in the range 5-60 with step size of 0.02. Raman spectroscopy was performed using an Almega Thermo Nicolet Dispersive 532 nm of an Nd: YLF laser with power of 30 mW on the RGO powders. The surface functional groups of GO and RGO were investigated by a Fourier-transformed infrared (FTIR) spectrophotometer, Bruker TENSOR27. The morphology of the films was investigated by field emission scanning electron microscopy (FESEM), MIRA3 TESCAN.

3. Results and discussion

Fig. 1 shows the XRD patterns of the GO and RGO samples. From the XRD patterns shown in Fig. 1, a dominant peak could be observed at $2\theta=11.45^\circ$ from GO powder, corresponding to an interlayer distance of 0.778 nm calculated by Bragg equation. For the RGO powder obtained by hydrothermal method, this peak completely disappears and broad peaks centered at around 25.25° are observed, corresponding to an interlayer spacing of about 0.33 nm. This spacing is comparable to that of reduced GO platelets obtained by hydrazine treatment of graphene oxide.

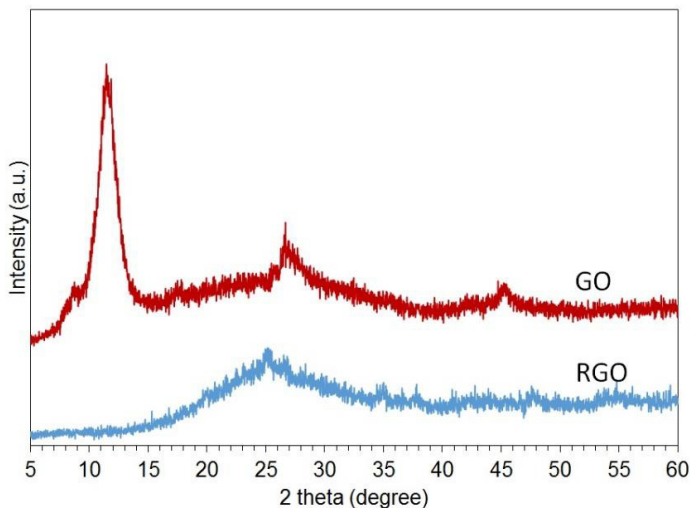


Fig. 1. X-ray diffraction patterns of GO and RGO powders.

The Raman spectra of GO and RGO are shown in Fig. 2. The Raman spectrum of GO has been used to compare the degree of defects in RGO. The I_D/I_G ratio increases from 1.08 in GO to 1.5 in RGO, which is attributed to the removal of oxygen functional groups and the decrease of the average size of the sp^2 domains formed in the RGO.

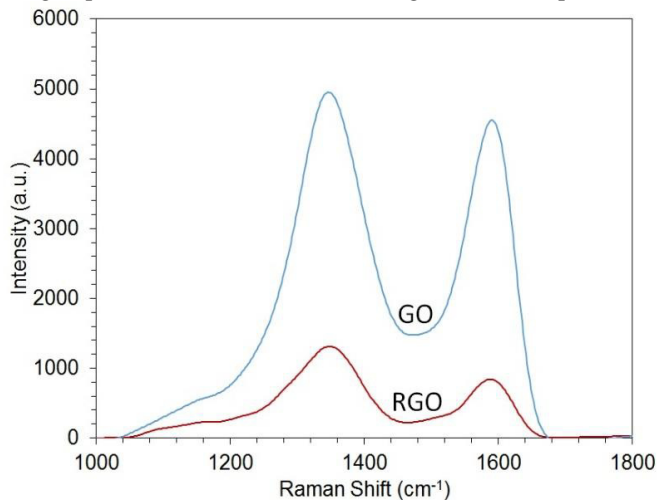


Fig. 2. Raman spectra patterns of GO and RGO powders.

The FT-IR spectra of GO and RGO are shown in Figure 3. The stretching and bending vibration of the hydroxyl groups of GO appears at 3407 cm^{-1} . A strong peak at 1730 cm^{-1} corresponds to the stretching vibration of carboxyl groups (-COOH). A peak at 1629 cm^{-1} is due to the presence of sp^2 bond of graphite in GO. The presence of these oxygen-containing groups reveals graphite oxidation. It is noteworthy that the characteristic peaks of GO vanish (or appear with significantly lower intensity) after reduction. These results indicate that the GO is reduced to a great extent.

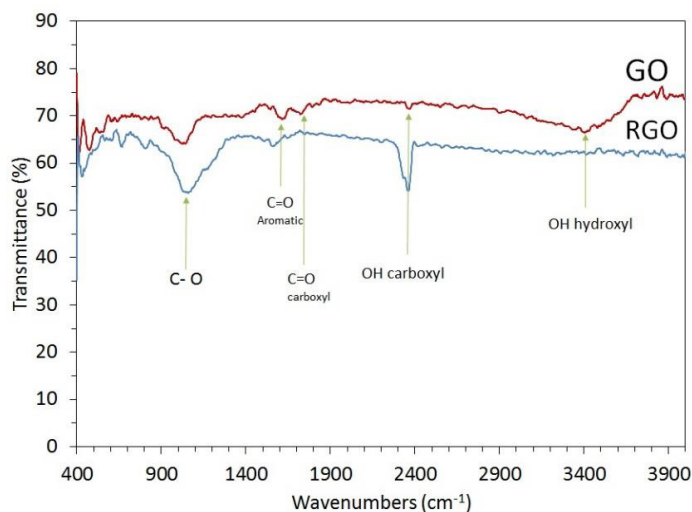


Fig. 3. FT-IR spectra of GO and RGO.

4. Conclusion

In conclusion, a green method was introduced for the partial deoxygenation of GO in water at moderate temperature (140°C), under basic pH conditions. The hydrothermal treatment of GO evolved significant chemical and structural changes, which were examined by XRD, FTIR, and Raman analyses. The present “water-based” route is advantageous compared to conventional chemical reduction processes based on hydrazine treatment because it is very convenient to use, environmentally friendly, and industrially scalable and shows the ability to recover aromatic structures via repairing the post reduction defects.

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