

Controllable synthesis of reduced graphene oxide



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ABSTRACT

A controllable fabrication of reduced Graphite oxide (RGO) via different alcohols was reported. Characterized and analyzed by X-ray diffraction, fourier transform infrared spectroscopy, UV–visible spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy and cyclic voltammetry, the chemical and structural properties, together with the electro-conductivities of the RGOs fabricated by ethanol (EtOH), 1-propanol (PrOH), 1-butanol (BuOH) and benzyl alcohol (PhOH) were investigated systematically. The results showed that the reduction degree of GO was strongly dependent on the type of alcohol. The strongest reducibility of PhOH was attributed to the special activity of the benzyl hydrogen of PhOH in comparison with the other primary alcohols. Meanwhile, the reducibility of the primary alcohols decreased with the elongation of carbon chain, which might be explained by the gradual attenuation of hydrogen donation ability and the increase of steric hindrance. The reducibility order of the investigated alcohols was determined as $RGO(PhOH) > RGO(EtOH) > RGO(PrOH) > RGO(BuOH)$, indicating the potential controllability of the RGOs reduced by different alcohols for special use. In addition, the electrical conductivity of RGO(PhOH) was found to be similar to that of Graphite.

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1. Introduction

Graphene, a monoatomic layer of sp^2 -bonded hexagonal carbon, has stimulated high attention due to its extraordinary electrical, thermal, optical and mechanical properties, as well as its high specific surface areas [1–5]. Since the discovery of graphene in 2004 [6], it has been used in diverse fields, such as electronics [7], batteries [8,9], biological sensors [10] and supercapacitors [11,12], etc. In recent years, graphene has been prepared by a variety of methods, for instance, mechanical exfoliation [6], chemical vapor deposition [13], epitaxial growth [14] and chemical reduction of graphite oxide (GO) [15,16], etc. Thereinto, chemical reduction has drawn special attention on account of its simplicity, reliability and well-controlled reduction degree [17,18]. To date, researchers have studied a number of chemical reductants to reduce GO, for example, anhydrous hydrazine [19], hydrazine monohydrate [20] and sodium borohydride [21]. However, the above mentioned reducing agents are possession of high toxicity and explosion hazard [22], which makes them unattractive for production of reduced graphene oxide (RGO) in large-scale [23]. Hence, seeking a

safer, lower or non-toxic reductants for controllable reduction of graphene oxide in a single step is demanded. Very recently, many efforts have been devoted to study green reductants for preparation of RGO, such as water [24], L-ascorbic acid [25,26], birch [27], alcohols [23,28,29], and so on. Among these agents, alcohols have shown a special attraction due to their inherent reduction power or the ability to donate hydrogen [23]. Su and co-workers [28] fabricated graphene via alcohol reduction (at 900 °C with Ar as a carrier gas), alcohol/ H_2 reduction (at 900 °C with 20% H_2 /Ar as a carrier gas) and other two reduction methods, respectively. The results showed that RGOs reduced by high-temperature alcohol vapor showed highly graphitic structures and excellent electrical conductivity. Dreyer et al. [29] reported a mild reduction of GO with various alcohols by heating at reflux for 5 days, and a high carbon-to-oxygen (C/O) atomic ratio of 30 and bulk powder conductivities as high as 4600 S m^{-1} were achieved when benzyl alcohol was used as a neat reductant. Seo and co-workers [23] investigated the effect of supercritical alcohols on the properties of the resulting graphene. The results showed that the RGO reduced by supercritical ethanol exhibited a higher C/O atomic ratio of 14.4 and a larger surface area of $203\text{ m}^2/\text{g}$ in comparison with those RGOs reduced by the other supercritical alcohols. However, the above mentioned green alcoholic reduction methods are challenged by high reaction temperature [27], long reaction period [28] and harsh experimental

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conditions [23], etc. Here we present a simple hydrothermal process with mild conditions for reducing GO sheets by using different alcohols as the reductants. The effects of the alcohols on the C/O atomic ratio, the interlayer distance and other properties of RGOs were investigated systematically. The results showed that the reduction degree of RGOs could be controlled by selecting proper alcohols.

2. Experimental

2.1. Chemicals and materials

Pristine Graphite(Gr) was purchased from Alfa Aesar. GO was synthesized using a modified Hummers method [30,31]. Ethanol (EtOH), 1-propanol (PrOH), 1-butanol (BuOH), benzyl alcohol (PhOH) and N, N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. The ultra-pure water used throughout all experiments was purified to $18.2 \text{ M}\Omega \text{ cm}^{-1}$ from a laboratory water purification system (Research UF, Hitech Instruments Co., Ltd).

2.2. Synthesis of RGO

The reduction reaction for synthesizing RGOs was formulated in Scheme 1. In a typical experiment, 50 mg as-synthesized GO was dispersed in 50 mL of each alcohol with ultrasonic treatment (40 KHz) for 1 h (It has been proven that the ultrasonic technology could be applied to large scale preparation of graphene [26,32]). Then the as-obtained brown suspension was sealed in a 100 mL Teflon-lined autoclave and maintained at $150 \text{ }^\circ\text{C}$ for 12 h. Subsequently, the resulting black slurry was filtered, washed with anhydrous alcohol and dried in a vacuum oven at $60 \text{ }^\circ\text{C}$ for overnight. The RGO samples prepared using the different alcohols were labeled as RGO (BuOH), RGO (PrOH), RGO (EtOH) and RGO (PhOH), respectively. All the samples were kept sealed at the same condition once prepared and the time gap between the RGO preparation and the analyses was controlled in a week.

2.3. Characterization

The X-ray diffraction (XRD) analysis was performed on a Bruker D8 Advance (Bruker, Germany) with Gr crystal monochromatized Cu $K\alpha$ radiation at 40 kV and 40 mA, the d-spacing was calculated according to Bragg's law. Fourier transform infrared spectroscopy (FT-IR) was carried out on a Bruker Tensor 27 (Bruker, Germany). The UV-visible spectroscopy was recorded using a double-beam UV-Vis spectrophotometer (TU-1900, Beijing Purkinje General Instrument Co., Ltd.). The morphology of the samples was characterized by transmission electron microscopy (TEM, Hitachi H-800) and scanning electron microscope (SEM, British Cambridge S-250).

X-ray photoelectron spectroscopy (XPS) was recorded on a PHI 5300 ESCA spectrometer (Pekin-Elmer, US).

2.4. Electrochemical test

Electrochemical experiments were performed with a CHI 600C electrochemistry workstation (CH Instruments, Chenhua. Co., Shanghai), and a three-electrode cell using a saturated calomel electrode (SCE), a platinum foil, and a modified glassy carbon electrode (GCE) with 3 mm in diameter as the reference, counter, and working electrodes, respectively. The GCE was polished with $0.5 \mu\text{m}$ alumina slurry, and then washed ultrasonically in DI water and ethanol for a few minutes, respectively. The cleaned GCE was dried in a nitrogen flow for the next modification. A total of $10 \mu\text{L}$ of GO or RGO-DMF suspension (1 mg/mL) was dropped on the GCE surface and dried at ambient temperature.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of Gr, GO and RGOs reduced by different alcohols are presented in Fig. 1. The calculated d-spacing data corresponding to the XRD patterns are listed in Table 1 as well. For pristine Gr (Fig. 1), the single sharp peak presented at 26.61° is ascribed to (002) face of Gr, the corresponding d-spacing is 3.35 \AA (see Table 1). Whereas for GO (Fig. 1), a typical diffraction peak of GO (001) is observed at 10.36° along with the disappearance of the peak at 26.61° , indicating the complete oxidation of pristine Gr. The

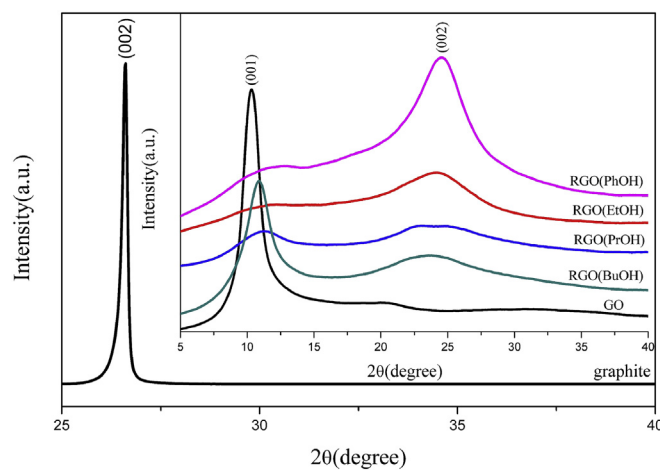
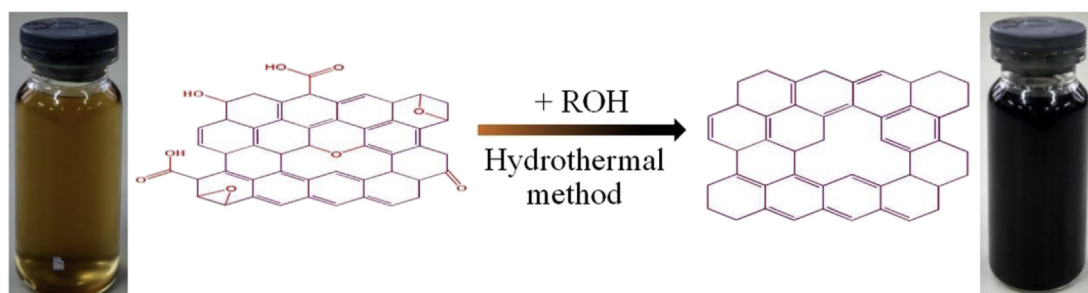


Fig. 1. XRD spectra of Gr, GO and RGOs.



Scheme 1. Illustration of the reduction process, including photographs of (a) the GO aqueous solution and (b) the stable RGO aqueous dispersion.

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