

A facile preparation of reduced graphene oxide papers for electrode and adsorption applications

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This research studied the fabrication of free-standing reduced graphene oxide (rGO) papers by chemical method and flame-induced reduction approach. Graphene oxide (xGO) was first synthesized from graphite powder by modified Hummer's method and the subsequent exfoliation of graphite/graphite oxide via ultrasonication. The resulting free-standing xGO papers were stable and flexible but had low conductivity. As the oxygen functional groups on xGO were eliminated, using flame-induced reduction method, as-prepared rGO papers exhibited a smaller amount of oxygen functional groups and had a better electrical conductivity. In addition, due to their porous network structure, rGO papers possessed an enhanced adsorption capacity toward organic aqueous solutions, in comparison to xGO papers.

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1. Introduction

In the last few years, there is currently a great demand for the development of new inexpensive, flexible, light-weight and environmentally-friendly free-standing materials for electrode and adsorption applications. One of the materials that have been gained a tremendous interest is graphene, a single atomic layer of sp²-hybridized carbon arranged in a two-dimensional honeycomb structure. This is due to its excellent and unique electrical, mechanical, thermal, and optical properties [1-6]. A simple and inexpensive approach to fabricate free-standing graphene is the direct production of reduced graphene oxide (rGO) from graphene oxide (xGO) by the removal of oxygen-functional groups. Although the presence of oxygen moieties provides the hydrophilic character, it can significantly reduce the electrical conductivity of xGO due to enhanced phonon scattering induced by the oxygen defects and disrupted sp² bonding networks [7].

The most common methods to effectively reduce xGO are chemical and thermal treatments. For instance, Vallés et al. (2012) reported the fabrication of conductive graphene papers by direct annealing of xGO papers at 700°C under argon or hydrogen atmosphere [8]. The resulting free-standing rGO papers yielded conductivities as high as 8000 S m⁻¹. Direct fabrication of flexible rGO paper by Li et al. (2008) involved the chemical reduction with hydrazine hydrate, and the optimal electrical conductivity of 7200 S m⁻¹ was achieved [9]. Hydrazine is usually employed as a reducing agent for chemical reduction process. However, it is highly toxic and can functionalize xGO with undesirable nitrogen heteroatom doping [10]. To date, many alternatives, such as NaBH₄

[11], ascorbic acid [12], and sugar [13], have been used and investigated.

Reduction of graphene oxide by the thermal treatment usually involves high temperature annealing under inert or vacuum atmosphere, and, therefore, requires complicated setup and high energy consumption. More recently, the reduction based on flame treatment was reported by several researchers. Liu et al. (2014) fabricated rGO using a novel flame-induced synthesis approach with the assist of flammable polar solvents [14]. The results showed that the flame-reduced methanol-rGO exhibited the excellent supercapacitive performance, which was attributable to the combination of high surface area, residual oxygen containing groups and wrinkled morphologies. Sun et al. (2013) used a flame-induced reduction to synthesize rGO papers with excellent electrochemical properties and capacitive performances [15]. Nevertheless, more investigation on this current technique is still needed to extend the understanding.

In this study, the reduced graphene oxide (rGO) papers were synthesized from graphite oxide via chemical exfoliation method by ultrasonication and flame-induced reduction method using a household lighter. Detailed investigations were performed by scanning electron microscopy (SEM), X-ray diffraction (XRD), fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), as well as conductivity and adsorption capacity measurements. The obtained rGO exhibited improved electrical conductivities with respect to the parent xGO papers. The results showed that the current reduction method could be an alternative for an easy, cost-effective, and environmentally-friendly fabrication route for flexible conducting graphene paper,

and could be of great interest for flexible electrode applications in various fields.

2. Material and methods

2.1 Synthesis of graphite oxide

The processes started with the oxidation of commercial graphite to form graphite oxide (GO), using a modified Hummer's method. 5.0 g of graphite powder (Merck Millipore Corporation) was first added into 100 mL concentrated 9:1 H₂SO₄ (RCI Labscan Limited):H₃PO₄ (Ajax Finechem) solution at room temperature. Under stirring, the mixture was cooled to 0–5°C using an ice bath for 30 min. 15 g KMnO₄ (QRëC™) was then added gradually under stirring and cooling, while keeping the temperature of the mixture not to exceed 5°C for another 60 min. After that, the temperature was raised to 35°C for 30 min, and the resulting solution was treated with 7 mL of 30% H₂O₂ (QRëC™). The suspension was further diluted by adding 200 mL distilled water under continuous stirring for another 30 min. After collected by filtration, the obtained precipitates were washed with 3% HCl aqueous solution (1,000 mL) to remove metal ions and rinsed with distilled water. The resulting graphite oxide (GO) was then dried at 40°C for 24 h.

2.2 Synthesis of graphene oxide and reduced graphene oxide papers

2 g GO was then dispersed into 1,000 mL of distilled water, followed by subsequent ultrasonication and centrifugation for 2 hr. The obtained brown-yellow xGO aqueous solution was then collected and dried at 40°C. Free-standing xGO papers could be achieved by a simple solution-casting method. In a typical procedure, xGO powders were re-dispersed in distilled water using an ultrasonic bath. The resultant xGO aqueous solution was then poured onto a polytetrafluoroethylene (PTFE) plate and dried at 40°C. As the water evaporation was ongoing, the xGO sheets were self-assembled in aqueous solution, resulting in xGO papers, which could be easily peeled off the plate. Different thicknesses (20–40 µm) of xGO papers were prepared by varying concentration of xGO aqueous solution (2 and 4 mg/mL). Flame-induced reduction method was finally applied to free-standing xGO papers to obtain corresponding rGO papers. A common lighter was used, and the xGO paper was burned for 3 s.

2.3 Characterization

X-ray diffraction (XRD) patterns were collected on a Miniflex II, Rigaku X-ray diffractometer using CuK α irradiation ($\lambda = 0.15406$ nm). Fourier-transform infrared spectra were measured on a Vertex 70, Bruker FTIR spectrometer. Electrical conductivity of the prepared samples was measured with a four-point probe method using a Keithley 2040 System Sourcemeter. The

microstructure of xGO and rGO samples were observed by scanning electron microscopy (SEM, Camscan MX2000).

The adsorption capability of rGO papers was evaluated by using methylene blue (MB) (Ajax Finechem) as the model dye. The rGO papers was first cut into 1 cm \times 1 cm in size and put into 10 mL 1 mg/L MB aqueous solution under vigorous stirring. The dye was allowed to be adsorbed into rGO papers until saturated absorption capability was reached. The decrease in MB concentration was then measured by monitoring the absorbance signal,

3. Results and discussion

The structural and chemical properties of graphite, GO, and xGO were characterized using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR), as shown in Fig. 1. The XRD patterns (Fig. 1a) of graphite exhibited a strong peak at 2-Theta = 26.4°, which corresponded to the diffraction from the (002) plane of graphite. After oxidation, oxygen-containing functional groups such as hydroxyl, epoxy, alkoxy and carboxy, were intercalated in the interlayers of graphite structure, leading to an increase in the interlayer spacing. The broad peak at 2-Theta = 10.3° in Fig. 1b confirmed that the d-spacing of GO increased from 0.34 nm in graphite to 0.86 nm. xGO, on the other hand, had broader diffraction peak around 2-Theta = 23.8° (Fig. 1a), which indicated poor ordering of the graphene sheets along the stacking direction. This implied that the sample was comprised mainly from single or only a few layers of graphene sheets.

Consistent with the XRD data, FTIR spectra (Fig. 1b) clearly showed the presence of oxygen functionalities in GO and xGO. As shown in Fig. 1b, FTIR spectrum of GO consisted of –OH stretching vibration at 3418 cm⁻¹, C=O stretching of carboxylic groups at 1720 cm⁻¹, stretching vibration peaks of epoxy and alkoxy groups at 1225 cm⁻¹, and C-O vibration of alkoxy at 1054 cm⁻¹, which confirmed the oxidation of graphite. The peak at 1619 cm⁻¹ could be attributed to in plane C=C group and the skeletal vibration of the graphene sheets.

The morphology of graphite, GO, and xGO was characterized by SEM technique (Fig. 2). The SEM image of graphite clearly showed the rigid and condensed layers (Fig. 2a). On the other hand, the surface of GO was relatively rough due to the aggregation of irregular graphite flakes caused by the acid oxidation (Fig. 2b). After ultrasonication, the sheets were exfoliated and folding. The edges of wrinkled individual sheets could be distinguished on the surfaces and edges of xGO, as seen in Fig. 2c.

Fig. 3a presents the TGA curves of XGO and rGO. After reduction, most of oxygen functional groups in XGO were removed. Unlike xGO, rGO did not have any mass losses at 150–450°C, which was corresponded to the decomposition of oxygen-containing groups such as hydroxyl and carboxyl. The major weight loss above 450°C for rGO, however, could be due to the decomposition of defective carbon structure after reduction process. This result was confirmed by the FTIR

analysis (Fig. 3b). In addition, removing intercalated water molecules and the oxide groups also caused a broad

diffraction peak in XRD pattern (Fig. 3c), indicating the exfoliated structure of reduced graphene oxide.

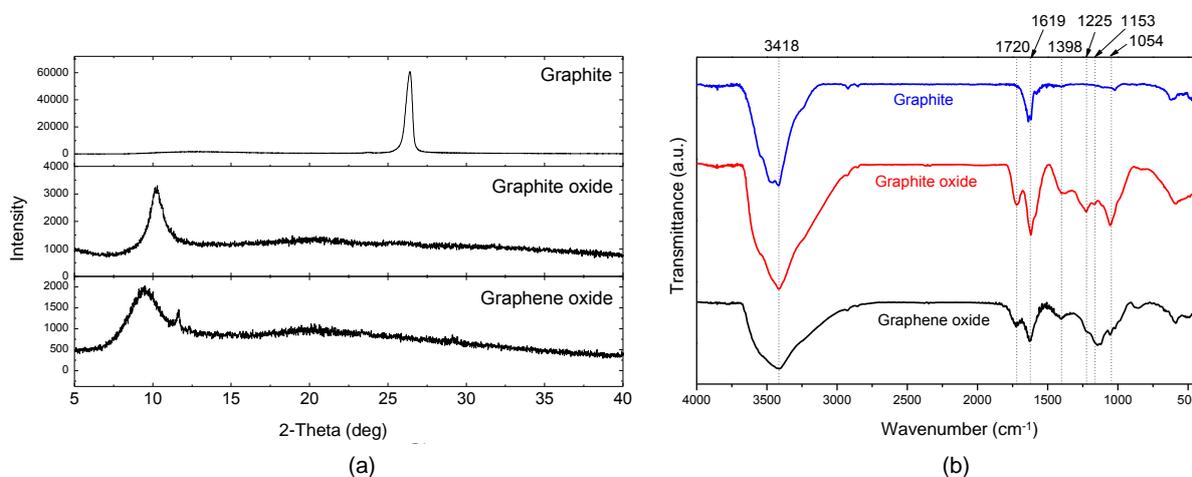


Fig. 1. XRD patterns and FTIR spectra of graphite, GO, and xGO.

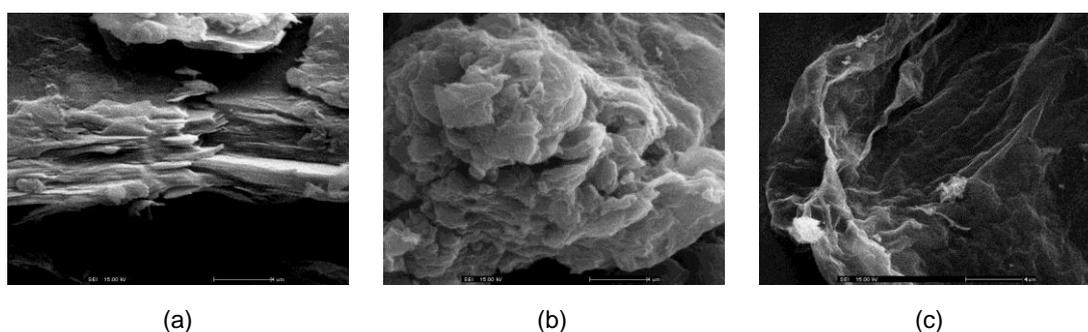


Fig. 2. SEM images of (a) graphite, (b) GO, and (c) xGO.

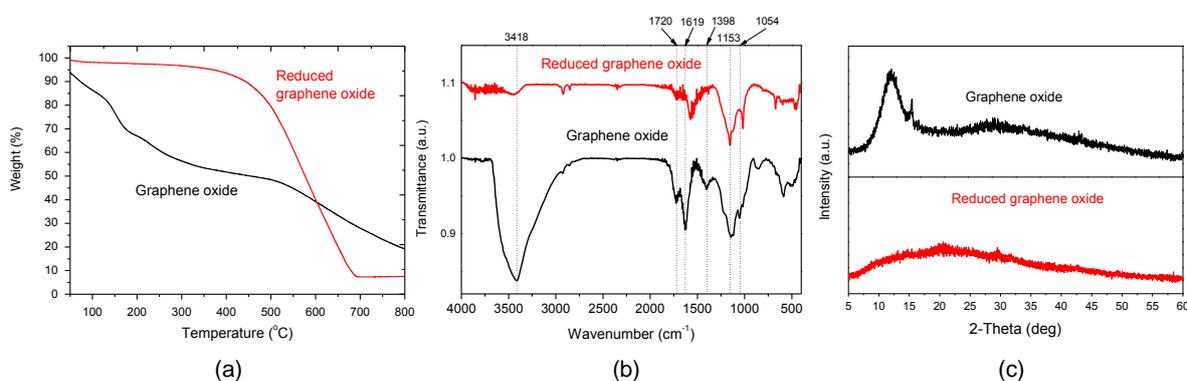


Fig. 3. TGA curves, XRD spectra, FTIR spectra, and Raman spectrum of xGO and rGO.

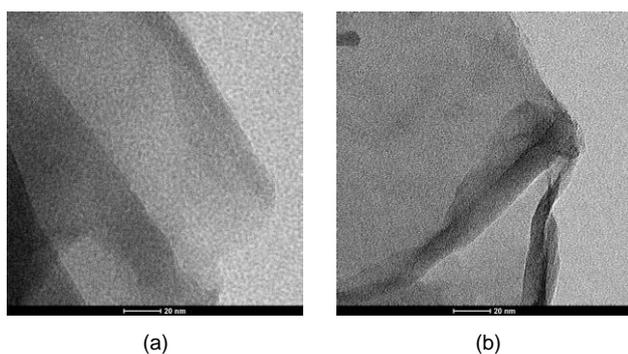


Fig. 4. TEM images of (a) xGO and (b) rGO.

The morphology of xGO and rGO was investigated through TEM, as shown in Fig. 4. TEM images of both xGO and rGO showed transparent sheets, which were so thin that electron beam can be passed through sample (Fig. 4). This results illustrated the successful exfoliation process. The reduced graphene oxide, however, exhibited wrinkled structure and sheet folding.

Fig. 5 showed SEM images and digital images of xGO and rGO papers. From the figure, all of the obtained papers revealed flexible characteristics, which were due to continuous networks and layered structure, and hence provided structural and mechanical integrity without

adding any binders. However, rGO paper exhibited more crumpled and rippled structure, which was the result of deformation upon the flame-induced reduction process. In addition, the rGO papers contained lots of wrinkles, and,

upon SEM observation, their structures were more swollen and formed a porous network. This type of structure would enable rGO papers to perform excellently as conductive electrode materials and organic adsorbents.

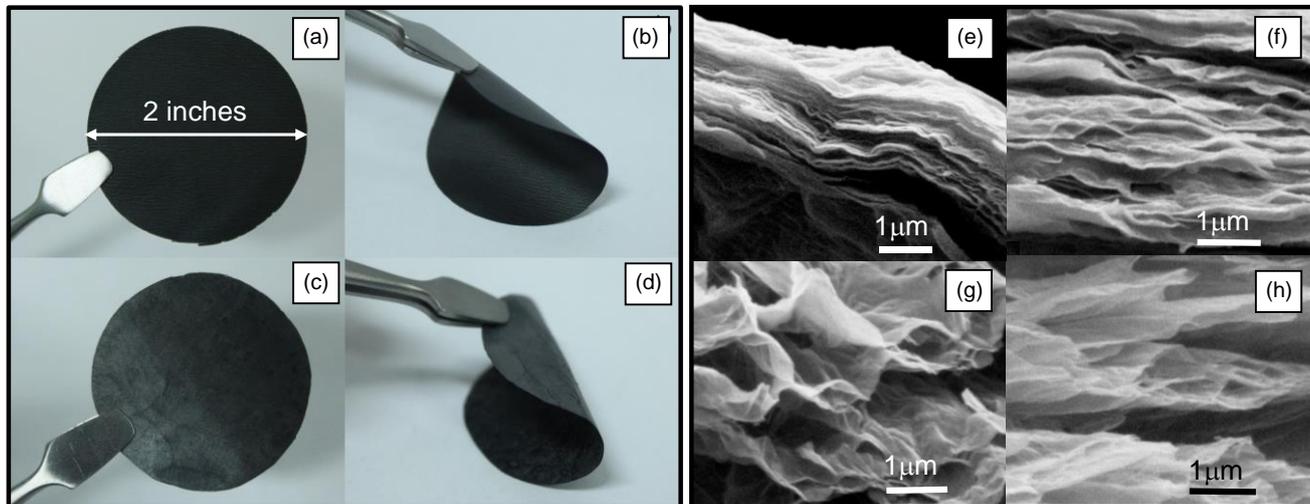


Fig. 5. TGA curves, XRD spectra, FTIR spectra, and Raman spectrum of xGO and rGO.

xGO and rGO have been used for the adsorption of methylene blue. Fig. 6 shows the UV-Vis absorption spectra of MB solutions in the presence of xGO or rGO papers. It could be seen that both rGO papers had more superior absorption capacity, in which all of the MB molecules were removed in the aqueous system, despite less oxygen-containing functional groups. This could be attributed to their porous network structure and hence a high surface area, as discussed in SEM analysis.

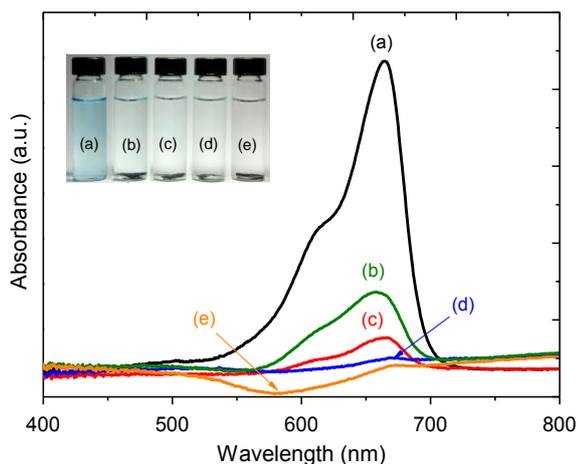


Fig. 6. Absorption spectra of aqueous methylene blue solutions in the presence of various adsorbents: (a) none, (b) xGO (2 mg/mL) paper, (c) xGO (4 mg/mL) paper, (d) rGO (2 mg/mL) paper, and (e) rGO (4 mg/mL) paper.

Due to the presence of oxygen functional groups, xGO exhibited very low electrical conductivity, as seen in Figs. 7(a)-(b). Upon flame-induced reduction process, the

removal of these oxygen-containing functional groups from the xGO papers could restore the conjugated structure of sp^2 carbon domains, and, therefore, higher electrical conductivities are observed (Figs. 7(c)-(d)) [8,14]. As seen in the figure, the rGO papers prepared from higher concentration of xGO solution tended to be more conductive. This could be due to its denser structure (Fig. 5g (2mg/mL) and Fig. 5h (4mg/mL)). Rani et al. (2010) have reported that denser materials would have higher electrical conductivity [16]. For example, they found that an increase in electrical conductivity tended to be in the following order: natural graphene < synthetic graphene < CNTs < synthetic graphite < natural graphite < expanded graphite.

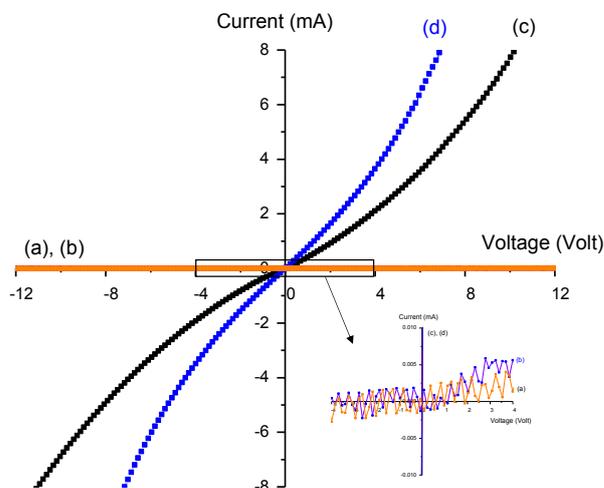


Fig. 7. Current-voltage characteristics of (a) xGO (2 mg/mL) paper, (b) xGO (4 mg/mL) paper, (c) rGO (2 mg/mL) paper, and (d) rGO (4 mg/mL) paper.

4. Conclusions

In this study, flexible and conductive free standing rGO papers could be fabricated through flame-induced reduction of xGO papers. This is a very simple, inexpensive, and efficient method to remove oxygen-containing function groups and to restore the carbon sp² network. The resulting rGO papers exhibited improved electrical conductivity and electron transfer, while maintaining the structural integrity and mechanical flexibility of the parent xGO papers.

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Conflict of interest

The authors declare no competing financial interest.

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