Highly controllable and green reduction of graphene oxide to flexible graphene film with high strength

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ABSTRACT

Graphene film with high strength was fabricated by the assembly of graphene sheets derived from graphene oxide (GO) in an effective and environmentally friendly approach. Highly controllable reduction of GO to chemical converted graphene (CCG) was achieved with sodium citrate as a facile reductant, in which the reduction process was monitored by XRD analysis and UV–vis absorption spectra. Self-assembly of the as-made CCG sheets results in a flexible CCG film. This method may open an avenue to the easy and scalable preparation of graphene film with high strength which has promising potentials in many fields where strong, flexible and electrically conductive films are highly demanded.

1. Introduction

Graphene has attracted enormous attention in recent years due to its extraordinary physical and chemical properties [1–3]. However, mass production of high quality graphene sheets at low cost is needed for commercial applications [4]. Recently, several methods have been developed to synthesize graphene sheets [5], such as micromechanical exfoliation of graphite [1], chemical vapor deposition [6] and epitaxial growth on silicon carbide [7,8], but chemical reduction of graphene oxide (GO) is regarded as the most promising approach for large volume synthesis. However, harmful or hazardous chemicals (such as hydrazine and sodium borohydride) are usually employed in the chemical route [9–12]. Therefore, it is important to develop environmentally friendly methods for producing graphene nanosheets in large scale [13–21].

Sodium citrate, a harmless natural food additive, is widely used in Turkevich method for the preparation of monodisperse gold nanoparticles under mild conditions [22]. In the present work, we report on the large scale production of graphene using a citrate reduction of GO. This eco-friendly method has the advantages of low cost and good scalability. Moreover, the as-made chemically converted graphene (CCG) can self-assemble, resulting in high-quality graphene films that are strong, flexible and electrically conductive. Because of this, the graphene films are of great potential in many fields such as in supercapacitors and batteries.

2. Experimental

2.1. Preparation of GO

Graphite oxide was synthesized by the modified Hummers method [23,24]. The exfoliation of graphite oxide to GO was accomplished by ultrasonication of the yellow brown neutral graphite oxide solution for 30 min (see Supplementary Material for details).

2.2. Reduction of GO by sodium citrate

In a typical procedure for the reduction of graphite oxide to graphene, 150 mg of GO was added into 250 ml of deionized (DI) water and then treated by ultrasonication for 30 min. After that, 5 g sodium citrate was added into the GO suspension (corresponding to the concentration of 20 mg/ml), and the reaction was carried out at 95 °C. Finally, the resulting black mixture was cooled to room temperature and the CCG suspension was washed until neutral. In order to investigate the reduction process from GO to CCG, the reaction was conducted under a series of conditions by varying the temperature from 35 °C to 95 °C and the concentration of the reducing agent from 0 to 20 mg/ml.
2.3. Fabrication of graphene films

We used vacuum-assisted self-assembly method to produce graphene films, in which 10 mg CCG was initially dispersed in water (50 ml) and then sonicated for 30 min to form a black dispersion. Finally, the graphene film was fabricated by filtration of the resulting dispersion through a mixed cellulose ester membrane (450 nm pore size, Shanghai Xinya Purification Device Company). The hydrazine reduce graphene film was produced according to the reference [24].

Fig. 1. FE-SEM image of GO with a free-standing sheets (a), inset demonstrates the Tyndall effect of GO. FE-SEM image of CCG nanosheets aggregated after removal of the functional groups (b). Inset picture shows the CCG nanosheets deposited at the bottom of the container.

Fig. 2. (a) FT-IR spectra of GO and CCG. (b) XPS spectra of GO and CCG showing C1s and O1s peaks. High resolution C1s XPS fitting curves of GO (c) and CCG (d) produced using sodium citrate reduction.
2.4. Tensile tests of graphene films

Tensile tests were conducted using a homemade testing system at the cross-head speed of 3 mm/min. The samples were cut into rectangular strips (about 3 mm × 27 mm) and then gripped using film tension clamps.

2.5. Characterization

The structure of the materials was characterized by powder X-ray diffraction (Rigaku D/Max-2400X) using Cu Kα radiation at 40 kV and 100 mA. The ratio of \( I_{CGG}/I_{Gr} \) in the XRD profiles was used to evaluate the reduction kinetics of CCG during the reaction, \( I_{CGG} \) and \( I_{Gr} \) mean the intensity of GO (graphene oxide) peak at 11° and Gr (graphite) peak at 24° in the XRD profiles, respectively. The morphology and structure were examined by field emission scanning electron microscopy (FESEM, Hitachi S4800) and transmission electron microscopy (TEM, Philips Tecnai G2 F20). The current–voltage curves were recorded using Keithley 6517A Electrometer/High Resistance Meter. UV-vis absorption and transmission spectra were measured by Agilent HP 8453 UV-vis spectrophotometer. The Fourier transform-infrared (FT-IR) spectrum was recorded on a Jasco FT-IR-430 spectrometer. Raman spectra were acquired using a Renishaw 2000 Confocal Raman Microprobe using a 632.8 nm laser. X-ray photoelectron spectroscopy (XPS) characterizations were performed using a Thermo ESCALAB 250 spectrometer equipped with an Al-Kα X-ray source. The thickness of the sample was determined by SEM analysis of the fracture surface. The electrical conductivity of the products was carried out on a S-2A four-point conductivity probe equipped with a Keithley 2400 Digital Sourcecimeter.

3. Results and discussion

3.1. Synthesis of CCG

Due to the hydrophilic oxygen containing functional groups on its surface, GO can be dispersed in water to form a stable colloid, which forms no sediment even after 3 months. As shown in the inset in Fig. 1, GO dispersion features the typical colloid Tyndall effect (a). The Tyndall effect disappears after the chemical reduction, because the produced CCG sheets precipitate at the bottom of the container (right b). SEM images in Fig. 1 shows distinct morphological changes from GO to CCG after the chemical reduction, water soluble GO is consisted of free-standing sheets (Fig. 1a) while the CCG tends to aggregate (Fig. 1b) due to the strong π–π stacking of the CCG sheets. These significant changes in the solubility and color indicate the removal of the oxygen containing functional groups on the surface of GO [25]. In contrast, no aggregates or precipitates are observed in the solution in the absence of reducing agent only the color of the yellow–brown GO dispersion becomes darker and deeper (Fig. S1). This means thermal deoxygenation of GO in water can be excluded under this condition.

The reduction of GO by sodium citrate has been confirmed by FT-IR spectra (Fig. 2a). A typical FT-IR spectrum of GO is characterized by the peaks of stretching vibrations of C=O (1724 cm\(^{-1}\)), deformation vibration of O–H (1362 cm\(^{-1}\)), epoxy C–O stretching vibrations (1160 cm\(^{-1}\)) and C=C stretching vibrations (1620 cm\(^{-1}\)) which account for the abundant oxygen containing groups on the surface of GO [26]. It has been shown in previous studies that oxygen on GO is present in the form of epoxy, hydroxyl and carboxyl groups [27]. After the chemical reduction, the majority of the oxygen functional groups was removed, the peaks at 1724 cm\(^{-1}\) and 1160 cm\(^{-1}\) disappeared and the FT-IR spectrum of CCG was dominated by the peaks of C=C stretching (1618 cm\(^{-1}\)) and aromatic C–H deformation (1123 cm\(^{-1}\)). The formation of graphene upon the chemical reduction was verified by the XPS analysis. For both samples, the XPS spectra demonstrate two main peaks at the binding energy of about 286 eV and 532 eV, respectively, corresponding to the C1s and O1s peaks (Fig. 2b). By curve-fitting analysis, the C1s spectra of GO and CCG were deconvoluted into four peaks that originate from C atoms having different chemical environments. As shown in Fig. 2c, the C1s XPS spectrum of GO has four peaks at 282.6 eV, 286.5 eV, 287.8 eV and 289 eV that come from C=C, C–O, C=O and (C=O)O groups, respectively. The dominant C–O and C=O groups indicate a considerable oxidation degree of GO. After reaction, the sp\(^2\) domains (C–O, C=O, and (C=O)O groups) in the spectra of CCG decreased dramatically. The C1s XPS spectrum of CCG (Fig. 2d) is characterized by a dominant C=C peak at 284.6 eV, indicating the recovery of sp\(^2\) carbon regions in the graphene structure.

Raman spectroscopy is a powerful non-destructive tool to track the structure change from GO to CCG. Carbon materials are characterized by the G band (~1580 cm\(^{-1}\)), which comes from stretching vibration of carbon bonds in the hexagonal graphene network – the first order scattering of the E2g mode [28,29], and the double-resonance D band (~1350 cm\(^{-1}\), excitation wavelength dependent), which is an indicator of disorder in the carbon layer. In

![Fig. 3. Raman spectra of Graphite, GO and CCG, inset pictures show the detailed 2D peaks at the wavelength from 2400 cm\(^{-1}\) to 3000 cm\(^{-1}\).](image)

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<tr>
<th>Time (h)</th>
<th>0</th>
<th>1</th>
<th>4</th>
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<tr>
<td>( I_{CGG}/I_{Gr} )</td>
<td>GO</td>
<td>6</td>
<td>1.17</td>
<td>0.71</td>
<td>0 (CCG)</td>
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Table 1 Absolute intensity ratio of \( I_{CGG}/I_{Gr} \) as a function of reaction time.
our experiment (Fig. 3), graphite has the dominant G band at 1580 cm\(^{-1}\), and for GO the G and D bands are at 1600 cm\(^{-1}\) and 1333 cm\(^{-1}\), respectively. They are broad and overlaid onto a strong fluorescence background, which indicates defects and functional groups in the sample. After chemical reduction, the peaks become narrower, meanwhile the intensity ratio \((I_D/I_G)\) changes from 0.85 to 1.17. The increased \(I_D/I_G\) value is consistent with the published data\cite{30} and can be explained by the increasing number of sp\(^2\) domains, while the size of the created graphitic areas is smaller than that of GO\cite{9}. The insets show that pristine graphite and CCG exhibit a distinct 2D band, while GO displays no obvious 2D band, which could disappear under the fluorescence background.

3.2. Investigation of the reduction process from GO to CCG

The sodium citrate reduction was carried out under mild conditions, giving us an opportunity to investigate the transformation of GO to CCG. In a continuous reaction process, the
intermediate products were extracted from the system at different reduction times, and examined by XRD (Fig. 4a). GO showed a typical strong and sharp (0 0 1) peak at 2θ = 11°, corresponding to d-spacing of 0.758 nm. After 1 h of reaction, a very broad peak appeared at about 24°, corresponding to the (0 0 2) peak of CCG. As time elapsed, the peak of GO at 11° became weaker and broader, meanwhile the graphite peak became stronger with the increasing time. Finally, after reaction for 20 h, the GO peak disappeared completely. The ratio of I(GO)/I(Gr) in the XRD profiles was used to evaluate the reduction kinetics of CCG during the reaction, as shown in Table 1. Along the reaction pathway from GO to CCG, the intensity (peak height) ratio decreased as a function of reaction time. We attribute this obvious changes of the XRD patterns to the reduction of GO as well as the partial recovery of the π→π conjugated structure within the graphene nanosheets during the reduction.

Using XRD analysis, we systematically investigated the variations of the XRD patterns as a function of temperature and amount of reducing agent employed in the reaction. The reduction of GO by sodium citrate is sensitive to temperature. According to the XRD data, the reduction of GO by sodium citrate can only efficiently take place above 75 °C (Fig. 5a). It was found that I(GO)/I(Gr) ratio decreases with the increasing content of sodium citrate, which means that the GO reduction rate increases with the increasing concentration of the reducing agent, as shown in Fig. S3. This allows us to control the reduction degree by varying the sodium citrate concentration. Thus, the XRD analysis can provide a simple way to monitor the GO reduction by sodium citrate and consequently precisely control the reduction process to obtain CCG with different oxygen contents for specific applications.

Fig. 4b shows the UV–vis spectra of GO with different concentrations, GO dispersion has the absorbance peak at 231 nm, which originates from the π→π* transitions of aromatic C=C bonds within GO sheets. The inset demonstrates the linear relationship between the absorbance maximum at 231 nm and the concentration of GO. It obeys the Beer–Lambert law very well. The water solubility of GO originates from the oxygen containing functional groups on its surface, which is consistent with the Tyndall effect (Fig. 1). During the chemical reduction process, the absorption peak of GO gradually shifts from 231 nm to 268 nm (Fig. 4c), at the same time, the shoulder peak at about 300 nm disappears and the absorption in the whole spectral region increases. All of these observations clearly suggest the gradual restoration of the π→π conjugated structure within the graphene nanosheets [24]. The recovery of the conjugated π-system after chemical reduction is also reflected by the I–V curve (Fig. 5a) [9,31]. At the same voltage, the current increases with reaction time, that is a reflection of reduction process of GO. The electron transport in

Fig. 6. (a) Digital photograph of a free-standing self-assembled graphene film, inset picture shows a strip of the film. (b) TEM image of CCG. (c) Cross sectional views of a self-assembled film, inset SEM image shows the side view of a CCG film at a higher magnification. (d) Optical transmittance of GO and CCG films. Inset shows photographs of GO (left) and CCG (right) films.
CCG is about 4 orders of magnitude faster than in GO (Fig. S5b). The improvement in the electrical conductivity (From $5.7 \times 10^{-3}$ to $30.6 \, S/m$) suggests the recovery of $\pi$-conjugated system in the graphene sheets. As a lot of method has been developed to achieve CCG, herein the electrical conductivity as well as the C/O ratio of different chemical reduction methods are compared (Table S1). It is found that the reduction degree of our produced graphene is comparable to the graphene prepared by sodium borohydride reduction. Table S1 also reveal that CCG produced by chemical reduction can hold the conductivity varying from 1 to $29800 \, S/m$ depending on the reducing agent and reaction condition. In addition, the conductivity of the product goes differently even with the same reducing agent, that may be caused by different testing and calculation method employed in different literature. Another main reason for this result is that the GO used for the synthesis of graphene is always different in references. For comparison, we have also prepared graphene films reduced by hydrazine, the conductivity of the hydrazine reduced graphene film in our experiment is $1338 \, S/m$, which is much higher than that of the sodium citrate reduced graphene film.

Sodium citrate is a widely used reducing agent in Turkevich–Frens method for the preparation of monodisperse gold nanoparticles [32,33], the intermediates formed during the reaction process have been widely investigated [34]. According to these studies, sodium citrate serves as an excellent electron donor in the production of gold nanoparticles [35]. In the case of GO reduction, it is supposed that in the initial step of the reaction, a citrate is oxidized by GO at elevated temperature and will release electrons simultaneously. After that, GO will undergo chemical reduction as it obtains electrons.

### 3.3. Self-assembly of flexible graphene film

Solution chemistry is a versatile method for synthesis and assembly of nanomaterials [36–38], including free-standing graphene films, which are known to have excellent mechanical properties [24]. In this study, high-strength flexible graphene films were fabricated by the widely used vacuum induced self-assembly method [39]. We find that a uniform black film can form on the filter membrane after filtration (Fig. S4). However, the as formed wet film is in the form of a hydrogel containing 90 wt% of water. The water molecules between the CCG layers can prevent the stacking of individual graphene sheets. As a result, the initial wet film is not mechanically strong at all, which is impossible to peel off from the filter membrane as an intact film structure (Fig. S4a and b). SEM images of the freeze dried wet film reveal that the graphene layers in the sample are loosely attached with each other to form porous structure (Fig. S4c and d). Therefore, in order to get strong graphene film, we need to get rid of the water in the wet film. For the formation of mechanically strong graphene film, the graphene nanosheets must regularly attach to each other to form a well compact graphene film during the water evaporation process. It is found that air dry is the best way to get flexible and smooth CCG film. In contrast, the oven dried films tend to shrink and become fragile which is unable to peel off from the membrane (Fig. S5). In conclusion, the water evaporation process is critical to form mechanically strong graphene films. The smooth and uniform CCG film exhibits a shiny metallic luster with a typical light silver-gray color of graphene (Fig. 6a). Inset picture shows a CCG ribbon fabricated by cutting the film that displays the flexibility of the product. The microstructure of the prepared graphene film is revealed by SEM images. Fig. 6c is the side view of a graphene film, inset picture reveals the detailed microstructure of a CCG film at a higher magnification. The fracture surfaces exhibit a uniform layered structure along the entire cross section, in which the flexible graphene sheets are aligned and attached to each other. The thickness of the self-assembled graphene film can be controlled by adjusting the volume of the CCG (Fig. S7). For comparison, we also fabricated a self-assembled GO film. As can be seen, GO film is semitransparent while CCG film is opaque. Those dramatic differences in the optical properties can be reflected by UV–vis spectroscopy (Fig. 6d). It is apparent that the transmission of GO increases gradually as a function of the wavelength, while the conductive CCG film absorbs in the whole wavelength range.

Recently, Cheng and his colleagues have reported the direct reduction of graphene oxide films into graphene films by hydrohalic acids [40]. For comparison, we have tried the reduction of GO film directly by sodium citrate solution. However, our GO film will swell in the sodium citrate solution and become fragile after about 1 h of reaction. As a consequence, the GO film was broken into small parts when we tried to take it out of water (Fig. S6). It was reported by Brinson and his colleagues that GO film swelled in polar solvent [39] (such as water). The SEM image of the expended GO film shows that the adjacent nanosheets become separated which is totally different from the well compacted film structure in Fig. S6. In addition, the reduction process from GO to CCG by sodium citrate reduction usually needs about 18 h, therefore, the initial prepared GO film will swell and become

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**Fig. 7.** (a) Tensile strength of CCG films prepared at different reaction times. (b) Digital photograph of a strip of graphene film supporting 275 g of load (the weight and the clamp), which is equal to 48 MPa of stress.
fragile during the reaction. It was demonstrated that the defect-free individual graphene sheet was extremely strong with the Young’s modulus as high as 1.01 TPa [41], low mechanical properties of graphite were explained by the weak van der Waals forces between the layers. Fig. 7a shows the tensile strength of the CCG films prepared at different reaction times (four samples were tested for every point, complete tensile test results are summarized in Table S4). As shown in Fig. 7a, the sample derived from eight hours of reduction exhibits the greatest tensile strength reaching 80 MPa, while longer time reduction gave rise to less tensile strength. This may be caused by the poor dispersibility of graphene after long time reducing treatment evidenced by the fact that the graphene nanosheets tend to aggregate together to form small aggregations in the solution after the reaction. This is an unfavorable condition for the graphene sheets to reconstruct themselves into well packed uniform thin film structure. Fig. 7b demonstrates the digital photograph of a CCG strip supporting ~275 g of load (the weight and the clamp), which equals to 48 MPa of stress.

The CCG produced by this simple method may find applications in a variety of fields where graphene is being used or tested, such as catalyst supports, electrodes of supercapacitors and conductive fillers in polymers. These graphene films produced by CCG self-assembly may find applications in current collectors of supercapacitors and batteries, and wherever else graphene papers are used.

4. Conclusions

CCG has been synthesized by a facile and eco-friendly approach – reduction of GO by sodium citrate. The restoration of the electron $\pi-\pi$ conjugated network within the graphene sheets leads to increased ordering as well as a much higher electrical conductivity. The reduction process from GO to CCG can be controlled by adjusting the temperature, time and citrate concentration. This green and facile graphene synthesis approach provides a scalable and effective alternative to the traditional chemical reduction method. The obtained CCG was self-assembled into macro-graphene film with strong tensile strength.

Supplementary data

Experimental details, XRD patterns, cross sectional SEM images and tensile test results are listed in the supplementary material.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.materresbull.2013.08.031.

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