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Green reduction of graphene oxide using alanine

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ABSTRACT

There remains a real need for the easy, eco-friendly and scalable preparation method of graphene due to various potential applications. Chemical reduction is the most versatile method for the large scale production of graphene. Here we report the operating conditions for a one-step, economical and green synthesis method for the reduction of graphene oxide using a biomolecule (alanine). Graphene oxide was produced by the oxidation and exfoliation of natural graphite flake with strong oxidants using Hummers method (Hummers and Offeman, 1958), but the method was revised in our laboratory to set up a safe and environmentally friendly route. The reduction of graphene oxide was investigated using alanine at various operating conditions in order to set up optimum conditions (treatment time, temperature and concentration of the reagent). Samples have been characterized by using UV–Visible spectroscopy, Fourier transform infrared spectroscopy, transmission electron microscopy, Raman spectroscopy and X-ray diffraction analysis.

1. Introduction

Graphene is a 2D carbon material made up entirely of conjugated sp^2 carbons arranged in a honeycomb structure. Graphite oxide is an oxygen-containing and water-dispersible derivative of graphite, it can be exfoliated and well suspended in an aqueous medium even down to the single-layer level form of graphene oxide (GO). Deoxygenation of GO sheets offers partial recovery of the graphene-conjugated structure, therefore, GO is a strategic starting point for the large-scale preparation of solution-processable graphene. Reduced graphene oxide (rGO) is the most important among the chemically modified graphenes since its structure and properties are similar to pristine graphene. It has been studied in many applications due to its excellent electrical, mechanical and thermal properties [1–5].

Previous research have shown that graphene oxide and graphene nanosheets have extraordinary potential used as water separation and purification membranes [6]. As adsorbent materials, these materials can be used to remove heavy metal ions [7] and hydrophobic organic contaminants [8]. The application of graphene as biomaterials has also been considered, such as detecting the translocation of DNA [9] and for diabetes monitoring and therapy [10]. In addition, due to its high specific capacitance and excellent conductivity, graphene has also been widely studied as the electrode materials for the electrochemical energy storage devices [11,12] and electrochemical sensors [13].

Large-scale production of graphene is highly desirable but very expensive. Extensive development of graphene for its industrial applications mainly depends upon the availability of efficient and inexpensive methodologies that allow the preparing and manipulating of this material on a large scale [2]. The chemical reduction of GO is a promising route towards the large scale production of graphene for commercial applications [5]. Chemical reduction is the most versatile method as it can be performed in both acidic and alkaline media [3,14] and it is also scalable and economically cheap [15].

Various reducing agents were reported for the reduction of GO. However, most of the chemicals studied are poisonous. Consequently there is a real need for the easy, eco-friendly and scalable preparation of graphene [15,16]. Recently biomolecule-assisted synthetic methods have become the new focus of nanomaterial preparation and these also reported the reduction and functionalization of GO. There are various methods for the green synthesis of reduced graphene oxide [4,5,16–26]; including the use of amino acids for the reduction. Glycine [23] was used as a chemical functionalizer and a reducing agent (with reduction reaction at 95 °C) in the preparation of reduced graphene oxide and L-cysteine followed by a NaOH wash [1] was used for its environment friendly preparation. L-Tryptophan and ascorbic acid with NaOH [24] were employed in the reduction of GO. The reduction of GO with L-lysine to prepare reduced graphene oxide stabilized with polysaccharide polyelectrolyte has been reported [26] but to the best of our knowledge, there is no previous report of using alanine (ALA) as a reducing agent for the reduction of GO to rGO. ALA is an aliphatic amino acid, a simple

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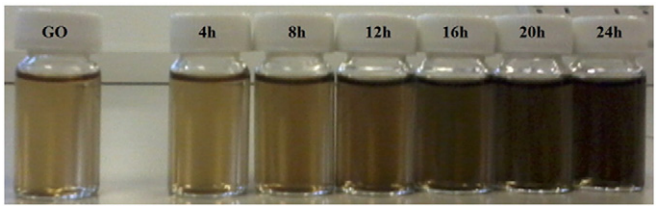


Fig. 1. Photographs of aqueous dispersions of graphene oxide (GO) and reduced graphene oxide (rGO) samples (with treatment times: 4 h, 8 h, 12 h, 16 h, 20 h, 24 h at 85 °C). The photograph shows the gradual color change of the samples from light brown (GO) to black (24 h, rGO) depending on the elapsed treatment time.

molecule which consists of the backbone of the amino acid structure with a methyl group attached as a side chain. Amino acids are advantageous as totally biodegradable and biocompatible reagents [27].

In this context, the aim of this study is to investigate a one-step economical and green method for the reduction of graphene oxide using a biomolecule (ALA) without using alkaline medium or additional chemicals. Graphene oxide was produced by the oxidation and exfoliation of natural graphite flake with strong oxidants using Hummers method [28]. This method was revised in our laboratory to set up a safer and environmental friendly route. The reduction of graphene oxide was investigated by using ALA at various operating conditions in order to find the optimum conditions. Experiments explored various treatment time, temperature and concentration of reagents. The extent of reduction was monitored by UV–Visible spectrophotometer and characterization of the samples was done using a Raman spectrometer, Fourier transform infrared (FTIR) spectrometer, X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM).

2. Materials and experimental

Natural graphite flakes (99.8% purity) and sulphuric acid (98%) were purchased from VWR. Phosphoric acid (85%), dihydrogen dioxide (35%), potassium permanganate (99%) were purchased from Sigma. ALA (L-alanine) (≥%98) was also purchased from Sigma. All reagents were used without further purification. Deionised (DI) water (18 MΩ/cm resistivity) from nanopure purification system was used in all experiments.

2.1. Preparation and reduction of GO

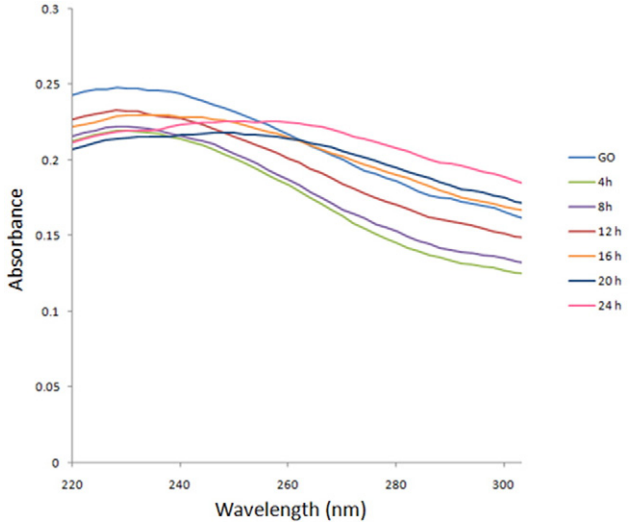
GO was produced by the oxidation and exfoliation of graphite with strong oxidants and mixed acids using Hummers method [28] revised in our laboratory. Briefly, phosphoric acid (20 mL) was slowly added to sulphuric acid (100 mL) at room temperature. A magnetic stirrer was used to mix the solution. Graphite was added to the solution and formed a homogeneous black dispersion. Potassium permanganate (8 g) was then added into the solution slowly to avoid a sudden temperature change which caused the solution to become a dark green dispersion. This solution was left at room temperature for three days to achieve a complete reaction. Dihydrogen dioxide was then dropped into that beaker after the three days to stop reaction at which time solution became bright yellow. The solution was first washed with 5% hydrogen chloride (200 mL) and then washed by DI water several times until the pH value reached 7. The solution was then dried in oven at 70 °C in order to obtain GO. rGO was thereafter prepared by stirring 10 mg of GO with 200 mL of ALA solution at a concentration of 10 g/L for 24 h at various temperatures during various treatment times following the washing with DI water in order to remove the excess of ALA. Washed rGO was finally dried in oven at 70 °C. Experiments were repeated, with a control sample without ALA, using the same conditions.

2.2. Measurements and characterization

Spectra of GO and rGO samples were recorded by UV–Visible spectrophotometer (Cary 100 UV–Visible). Fourier transform infrared (FTIR) spectra of the samples were recorded with a Varian 800 FTIR spectrometer. The Raman spectrometer used in this work was WiTec Confocal Raman Microscope model CRM 200, Ulm Germany with the excitation wavelength at 488 nm. The morphology of the prepared sample was characterized by TEM (Philps CM-100 with a tungsten filament). XRD data was collected by the X'Pert ProMultipurpose from PANalytical Company.

3. Results

Aqueous dispersions of rGO was prepared by chemical reduction of GO at 85 °C using ALA as a reducing agent. Photographs of aqueous dispersion of GO before and after the reduction are shown in the Fig. 1. A gradual color change was observed from yellowish brown to dark



	λ_{max}
GO	228
4 h	230
8 h	230
12 h	230
16 h	239
20 h	250
24 h (rGO)	258
36 h	258
48 h	258

Fig. 2. UV spectra of aqueous dispersions of graphene oxide (GO) and reduced GO samples with various reduction times at 85 °C and variation of λ_{max} with the treatment time for the reduction of graphene oxide (GO) at 85 °C.

Table 1
Variation of λ_{max} with the concentration of alanine (ALA) used for reduction of graphene oxide (GO) at 85 °C for 24 h.

	λ_{max}
GO	228
rGO (C_{ALA} = 1 g/L)	236
rGO (C_{ALA} = 5 g/L)	249
rGO (C_{ALA} = 10 g/L)	258
rGO (C_{ALA} = 20 g/L)	258

black during the reduction process which can be taken as a sign of GO reduction. Similar color change due to the formation of dark black dispersion in water was observed as the primary indication of the reduction of GO to rGO [16,24,29]. Experiments were repeated with control samples without ALA. The color change was not observed in the control samples tested under the same conditions.

The extent of the reduction reaction of GO to rGO was monitored using a UV–Vis spectrophotometer. The absorption spectrum of GO and rGO samples (Fig. 2) shows the red-shift of the C═C plasmon peak from 228 nm to 258 nm. The absorption peak at 228 nm corresponds to the π-π* transitions of aromatic C═C bonds [30]. The red shift is a result of the revival of the conjugated C═C bonds which shows the restoration of the sp^2 hybridized carbon network due to the removal of the oxygen bearing functional groups [31,32]. A similar shift was observed for the reduction of GO by L-ascorbic acid [21,33], L-cysteine [1], glycine [23], L-lysine [26] and 2,4-dihydroxy phenyl alanine [16].

The extent of the reduction reaction monitored by UV–Visible spectra of GO and rGO samples with various operating conditions showed the effect of the operating conditions on the reduction of GO with ALA. Fig. 2 shows the effect of treatment time on the reduction of GO using ALA. The red-shift of the C═C plasmon peak was increased with increasing treatment time and maximum reduction was observed at 24 h and C═C plasmon peak shifted from 228 nm to 258 nm.

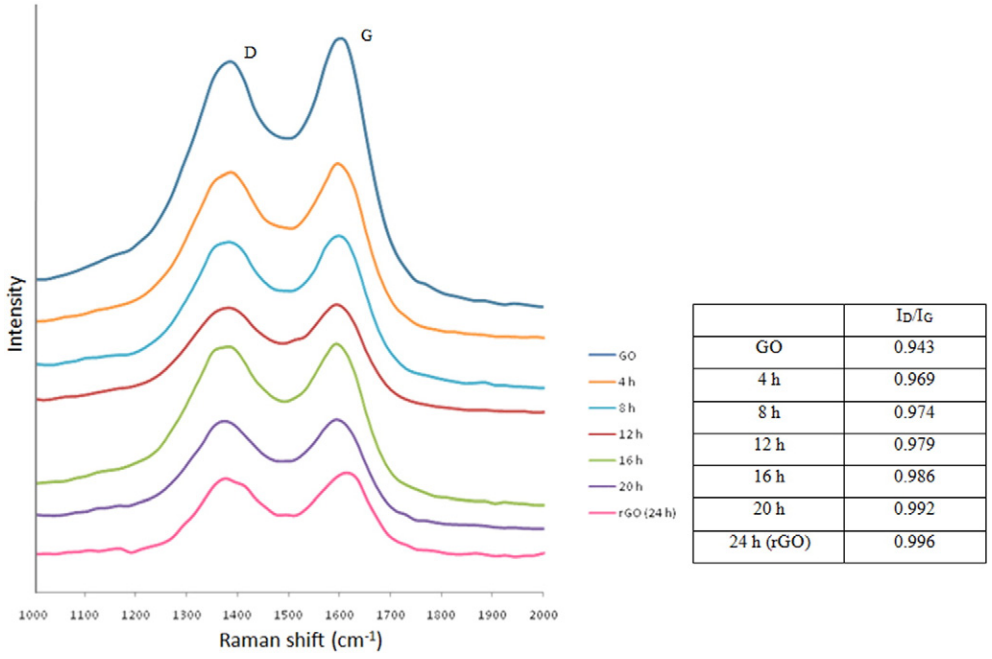
The effect of temperature (in range between room temperature and 85 °C) on the reduction of GO with ALA during 24 h was investigated. No shift in the plasmon absorption peak were observed for the temperatures below 85 °C and maximum reduction was achieved at 85 °C. Table 1 shows the concentration of ALA used for the reduction of GO at 85 °C during 24 h. Maximum reduction is achieved with 10 g/L ALA.

rGO samples prepared using the optimum conditions (treatment time: 24 h, temperature: 85 °C, concentration of ALA: 10 g/L) found were characterized by using Raman spectrometer, Fourier transform infrared (FTIR) spectrometer, X-ray diffraction (XRD) analysis and electron microscopy (TEM).

The Raman spectra (Fig. 3) shows the structural changes after the reduction of GO. The Raman spectrum of GO is generally characterized by a typical D band at around 1359 cm^{-1} (the breathing mode of C-sp^2 atoms in rings is related with disorder within the structure) and a G band at around 1598 cm^{-1} (the in-plane bond stretching motion of C-sp^2 atoms) [34]. Changes in the relative intensities of the D and G bands (I_D/I_G) indicate changes in the electronic conjugation state of the GO during reduction and are useful for predicting the size of the in-plane sp^2 domain [35]. Fig. 3 shows the I_D/I_G intensity ratio that increases with the treatment time during reduction due to the restoration of the sp^2 network. Since the Raman I_D/I_G intensity ratio is inversely proportional to the average size of the sp^2 domains, the increase of the I_D/I_G intensity ratio suggests that smaller in-plane sp^2 domains are formed during the reduction of GO which also indicates an effective reduction of GO [23,26].

FTIR analysis (Fig. 4) was used in order to further characterize the rGO samples. The broad absorption band at between 3000 and 3500 cm^{-1} can be attributed to OH groups. Absorption bands at around 1650 cm^{-1} are due to carbonyl and carboxyl groups. Bands at around 1400 and 950 cm^{-1} are due to C—O bonds of hydroxyl or epoxy groups [36–38]. The peaks for oxygen functional groups decreased with the reduction or disappeared completely which confirms the removal of most of the oxygen functionalities in the GO. The peak around 1550 cm^{-1} is attributed to the aromatic C═C groups of the rGO sample. It suggests that the frame of sp^2 carbon atoms after reduction by amino acid is well retained, as before. Chen et al. have reported similar result for the reduction of GO to rGO by L-cysteine [1].

To evaluate the structural information and confirm the removal of the oxygen-containing groups, XRD patterns of graphite, GO and rGO



	I_D/I_G
GO	0.943
4 h	0.969
8 h	0.974
12 h	0.979
16 h	0.986
20 h	0.992
24 h (rGO)	0.996

Fig. 3. Raman spectra of aqueous dispersions of graphene oxide (GO) and reduced GO (rGO) samples with various reduction times and D/G intensity ratios of graphene oxide (GO) and reduced GO (rGO) samples with various treatment times at 85 °C.

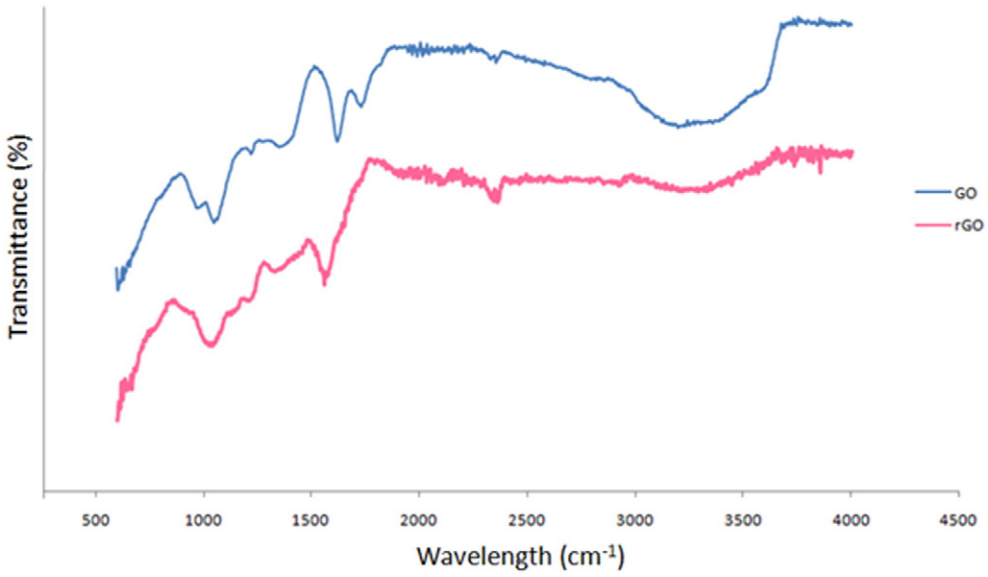


Fig. 4. FT-IR spectra of graphene oxide (GO) and reduced GO (rGO).

were examined (see Fig. 5). There is a sharp diffraction peak at about 26° for the pristine graphite which corresponds to an interlayer d-spacing of 0.34 nm. For GO, there is a diffraction peak at around 11° which corresponds to an interlayer d-spacing of 0.78 nm, which is larger than that of graphite (0.34 nm). The enlarged interlayer distance is attributed to the formation of hydroxyl, epoxy and carboxyl groups which causes the intercalation of water molecules and increases the distance between the layers [26,39]. There is no diffraction peak in the XRD pattern of rGO due to the disappearance of the long-term ordering of the graphitic structure. These results confirm the successful exfoliation of the single or few-layered stacking sheets as rGO [40].

Fig. 6 shows the transmission electron microscopy (TEM) images of rGO samples. TEM images of the samples show that the samples consist of aggregated and wrinkled few layer of rGO wrapped together. TEM analysis indicates the formation of transparent few layered graphene due to the reduction.

These results show the succesful reduction of GO to rGO without using any stabilizer or alkaline medium. After the reduction reaction, rGO was separated from the dispersion and the supernatant was kept for further analysis. The supernatant was dried and the mass obtained analysed by FT-IR. It was seen (FT-IR spectra not shown here) that the sediment has the same spectra as ALA itself. This may be evidence that ALA is playing the role of a catalyst.

A possible reduction mechanism was given in Fig. 7. ALA molecules can attach to the GO surface due to the peptide bond forming [41,42] which may be followed by a thermal elimination. GO has mainly two types of reactive oxygen species, including hydroxyl and epoxy functional groups on the basal plane. Epoxy group could be opened by the nucleophilic attack of the amine group of ALA resulting in the formation of an intermediate ⟨1⟩. The amine group of ALA can also attack the β-carbon atom of the hydroxyl group on the GO with release of a H_2O molecule resulting in the formation of a second intermediate ⟨2⟩. Then two ALA molecules which are already attached to the surface may leave the surface (elimination of the intermediate) in order to form a dipeptide (diALA: L-alanyl-L-alanine). A simultaneous destruction of peptide bonds may occur in the aqueous phase due to accelerated hydrolysis of the dipeptide upon heating. The further details of the reduction phenomenon should be investigated in future.

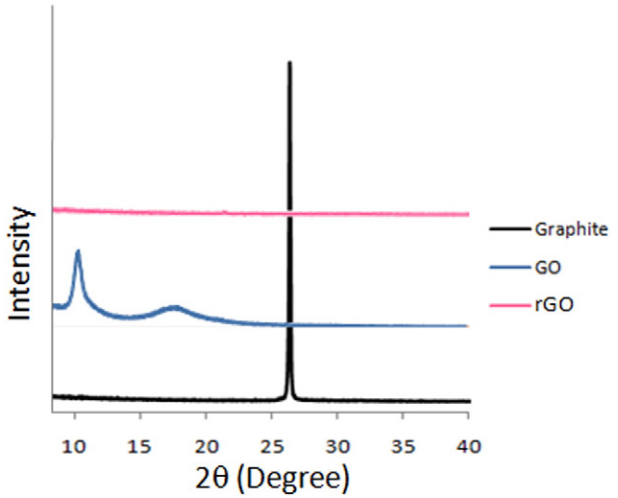


Fig. 5. XRD patterns of graphene oxide (GO) and reduced GO (rGO).

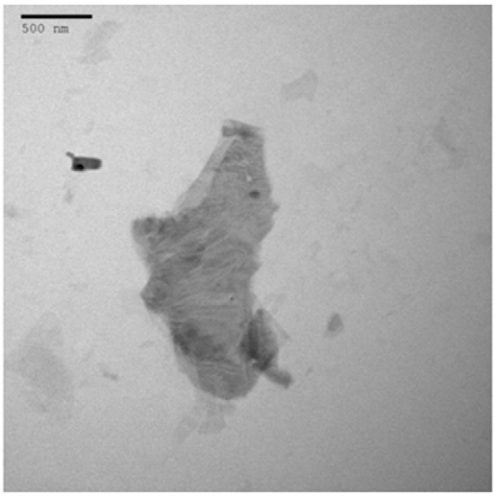


Fig. 6. TEM images of reduced graphene oxide (rGO).

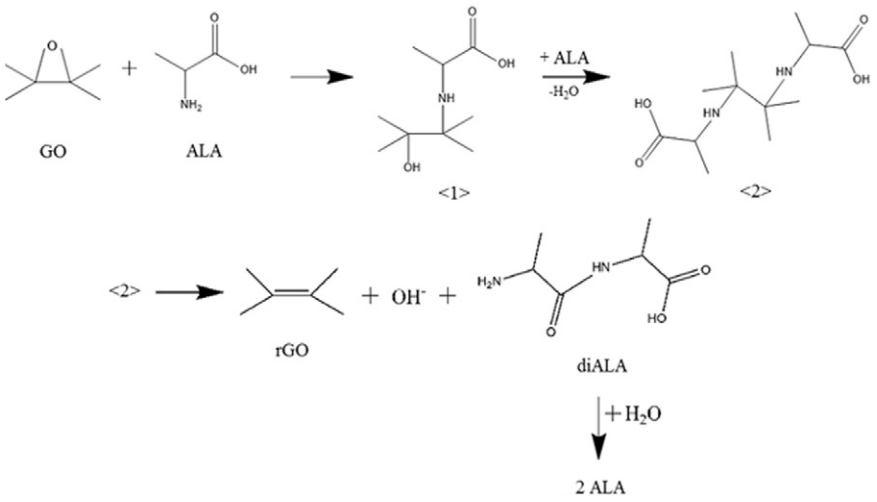


Fig. 7. Possible mechanism for the reduction of GO using ALA (heat applied was not shown in the scheme).

4. Conclusions

Chemical reduction of graphene oxide is important for large-scale production of graphene because it is the most versatile method. Various reducing agents have been reported for the reduction of graphene oxide but most of them are poisonous. Consequently there is still a need to find a method for easy, environmentally friendly and scalable production of graphene. Results presented show the succesful reduction of GO by ALA. ALA can be used for the effective, easy, one step and environmentally friendly reduction of GO. This procedure offers a 'green route' for the scalable production of graphene without using alcaline medium or additional chemicals. Reduced GO, produced through this route, may be a potential alternative for the production of biomaterials.

Acknowledgments

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