



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.

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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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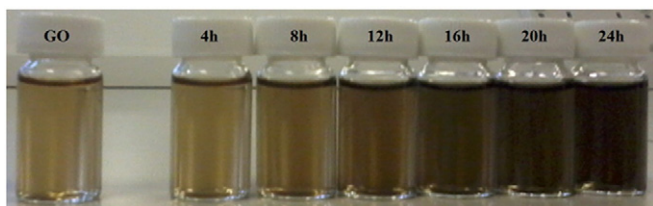


Fig. 1. Photographs of aqueous dispersions of graphene oxide (GO) and reduced graphene oxide (rGO) samples (with treatment times: 4 h, 8 h, 12 h, 16 h, 20 h, 24 h at 85 °C). The photograph shows the gradual color change of the samples from light brown (GO) to black (24 h, rGO) depending on the elapsed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

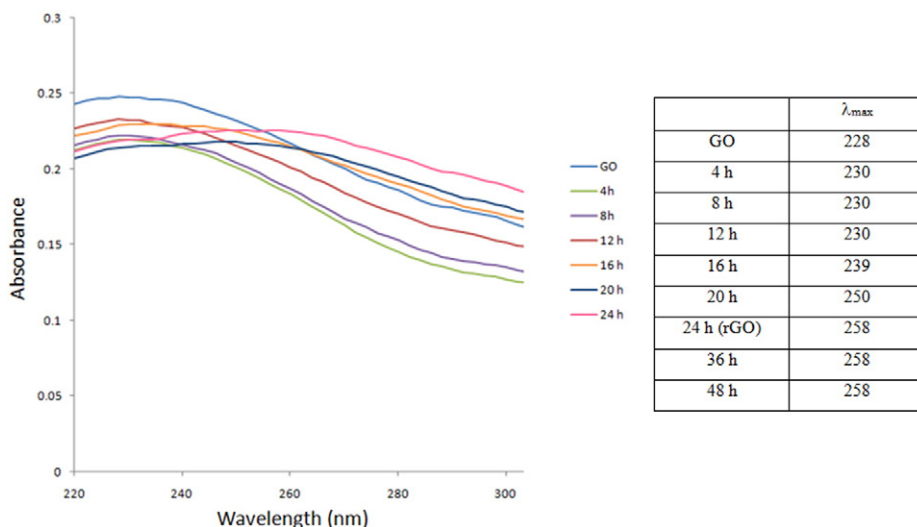


Fig. 2. UV spectra of aqueous dispersions of graphene oxide (GO) and reduced GO samples with various reduction times at 85 °C and variation of λ_{max} with the treatment time for the reduction of graphene oxide (GO) at 85 °C.

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