

Comparative study of synthesis and reduction methods for graphene oxide



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ABSTRACT

Graphene oxide (GO) and reduced graphene oxide (rGO) have congregated much interest as promising active materials for a variety of applications such as electrodes for supercapacitors. Yet, partially given the absence of comparative studies in synthesis methodologies, a lack of understanding persists on how to best tailor these materials. In this work, the effect of using different graphene oxidation–reduction strategies in the structure and chemistry of rGOs is systematically discussed. Two of the most popular oxidation routes in the literature were used to obtain GO. Subsequently, two sets of rGO powders were synthesized employing three different reduction routes, totalling six separate products. It is shown that the extension of the structural rearrangement in rGOs is not just dependent on the reduction step but also on the approach followed for the initial graphite oxidation.

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1. Introduction

Graphene is a remarkable two-dimensional material [1] which has been receiving tremendous attention from academics and industrialists alike [2]. Amongst its many potential applications are supercapacitors [3], conductive coatings composites [4], catalysis [5] and flat panel displays [6]. While the latter requires large-area films, other applications such as supercapacitors are better realised via particulates (or “flakes”) [7]. With respect to this, tailoring of the graphene’s shape, structure and chemistry is highly desirable. The challenge of a cost-effective mass production method of application-specific graphene flakes remains quite present, however. To this end, much work has been carried out on the synthesis of rGO. One of the most popular chemical methods to obtain rGO is to first oxidize graphite flakes in aqueous medium and subsequently reduce them. For both steps, a myriad of approaches have been reported with the most common being oxidation via the classical Hummer’s method (or an adaptation of this) [1,8] followed by a reduction step resorting to heat [9] or chemical reactions [10]. Although it has been recognised that the use of different oxidation–reduction routes has a considerable effect on the final rGO properties [1], comparative studies on this issue have been lacking. This is particularly important if one is to understand

by which means each approach influences the final structure and chemistry of the rGO flakes and to which extent can we control/tailor this. On the other hand, different reduction methods will have an important effect on the surface’s chemical structure of rGO. For instance, as regards energy-related applications, several studies in the literature have delved on the supercapacitance performance of rGO-based electrodes synthesized either by the classical Hummer’s method [11] or an adaption of this [8b]. Still, these authors do not justify their rGO synthesis approach or analyze systematically what is the best oxidation–reduction synthesis strategy for such applications. In this comparative study, we describe how using common methodologies for rGO synthesis affects the final product’s oxidation degree, structure and chemical signature.

2. Materials and methods

2.1. Synthesis of graphene oxide

Graphite powder (Sigma–Aldrich, particle-size <45 μm or Alfa Aesar, <50 μm) was first oxidized using one of two commonly used chemical processes: the Hummer’s method [12] or the so-called Improved-Hummers’ method [8b] (with additional KMnO₄). Note that the two graphite powders are equivalent as they have similar particle size and XRD patterns (Fig. S1). For the classical Hummer’s synthesis, 3 g of graphite powder (Sigma–Aldrich) and 1.5 g of NaNO₃ (Fisher Scientific, 99%) were mixed with 75 mL of concentrated H₂SO₄ (Sigma Aldrich, 99%). The reaction was cooled to <5 °C in an ice bath and stirred for 2 h. 9 g of KMnO₄

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(Acros, 99%) was added in small portions, to maintain the reaction temperature below 20 °C, and constantly stirred for another hour. Then, the suspension was warmed to room temperature, by removing the cooling bath, at which time deionized water (100 mL) was slowly added (caution: the reaction is highly exothermic and evolution of gas was noticed). An oil bath was used to keep the reaction temperature constant at 90 °C. Subsequently, 300 mL of deionized water was added and the mixture was continuously stirred for another hour and a half. An extra 1 L of deionized water was poured into the mixture followed by the slow addition of 30 mL H₂O₂ (Sigma Aldrich, 30%). This action turned the colour of the mixture from dark brown to yellow and was accompanied by the release of heat. After cooling to room temperature, the product was diluted with deionized water to a total volume of 2 L. Finally, the suspension was repeatedly washed with water and centrifuged (Hettich U320, 9000 rpm, 10 min) until the pH was nearly neutral. At this point, the suspension was vacuum dried in the centrifuge tubes (60 °C, 12 h) and the resulting powder collected.

For the Improved-Hummers' synthesis, 3 g of graphite powder (Alfa Aesar) was added to a mixture of 360 mL H₂SO₄ (Sigma Aldrich, 99%) and 40 mL H₃PO₄ (Sigma Aldrich, 85 wt.%). This was followed by the slow addition of 18 g of KMnO₄ (Acros, 99%), taking care that the reaction temperature was maintained at <20 °C. Then, the resulting suspension was heated, in an oil bath, to 50 °C and stirred for 12 h. The colour of the mixture turned from black to mud-brown. The reaction was allowed to cool to room temperature and treated with 400 mL of cold deionised water plus 3 mL of H₂O₂ (Sigma Aldrich, 30%). The product was washed and dried using the same procedures described above.

The GO products prepared by the classical and improved Hummers' methods are hereafter designated as HGO and IGO, respectively.

2.2. Thermal reduction

A sample of HGO or IGO, typically in the order of 400 mg, was thermally reduced for 2 h in a horizontal tube furnace under N₂ atmosphere at 900 °C (heating rate of 5 °C min⁻¹). The thermally reduced GO is hereafter designated as rHGO/N₂ or rIGO/N₂ [9b].

2.3. Chemical reduction

The chemically-induced reduction of HGO (or IGO) was carried out by loading 100 mg of the GO powder into a 500 mL round-bottom flask and then disperse it in 100 mL of deionised water. This yielded a brown slurry that, upon stirring for 12 h, became clear. 1 mL of a hydrazine hydrate solution (NH₂NH₂·H₂O, Sigma Aldrich, 25%) was then added and the mixture heated in an oil bath at 100 °C. A water-cooled condenser was fitted to the flask and the reaction allowed to proceed for 24 h, after which a black solid had precipitated. The chemically reduced GO is hereafter designated as rHGO/hydrazine or rIGO/hydrazine [13].

2.4. Hydrothermal reduction

100 mg of HGO (or IGO) powder was dispersed in 40 mL of deionized water and stirred for 24 h to form an aqueous dispersion. Then, the mixture was transferred to a 50 mL Teflon-lined autoclave and kept in an oven at 180 °C for 24 h. The product was collected, washed several times with deionized water and dried at 50 °C for 24 h. The hydrothermally reduced GO is hereafter designated as rHGO/hydrothermal or rIGO/hydrothermal [14].

2.5. Characterization

The Fourier transform infrared (FTIR) spectral analysis was carried out on a Thermo Scientific spectrometer (Nicolet iS10) and performed in transmission mode using KBr pellets. Raman spectra were obtained with a WITec Alpha300RA spectrometer using an excitation wavelength of 488 nm. Thermogravimetric analysis (TGA) data was recorded on a Netzsch TG209-F1 instrument at a heating rate of 10 °C min⁻¹ in N₂. Thermogravimetric analysis with mass spectrometry (TGA-MS) was carried out in a Netzsch TG209-F1 coupled to a QMS 403 C Aëolos using a He flow with a heating rate of 10 °C min⁻¹. The powder X-ray diffraction (XRD) analysis was performed on a diffractometer (Bruker D8 Advance) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology of the samples was observed with scanning electron microscopy (SEM) (FEI Quanta 600, 4 kV) and the structure of the flakes studied with transmission electron microscopy (TEM) (FEI Tecnai BioTwin, 120 kV).

3. Results and discussion

3.1. Sample tree

The two methods we selected for the oxidation step, just as for the subsequent reductions, are the most common procedures referred to by other teams. The first oxidation method is the Hummers' method (KMnO₄, NaNO₃, H₂SO₄), which is the most common approach used for producing GO. The second method is the Improved-Hummers' method (KMnO₄, 9:1 H₂SO₄/H₃PO₄). In this regard, Tour et al. have demonstrated that preparing GO in 9:1 H₂SO₄/H₃PO₄ while excluding NaNO₃ clearly improves the efficiency of the oxidation process and subsequently the quality of the produced GO [8b]. Overall, the amounts used and conditions employed were also in order with those commonly described in the literature [12,8b,14,13,9b]. The final rGO products are correlated with the parent graphite powder as schematised in Fig. 1.

3.2. Structural analysis

The morphologies of aggregates and individual flakes derived from the parent graphite and its oxidized counterparts are shown

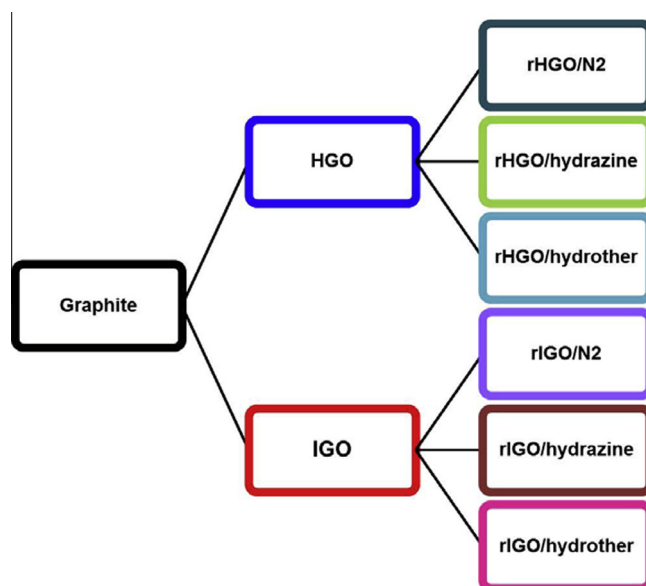


Fig. 1. Sample tree diagram of the graphite-derived materials studied. Acronyms are explained in Section 2.

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