



Fractionation and characterization of graphene oxide by oxidation extent through emulsion stabilization



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ARTICLE INFO

Article history:

Received 16 June 2015

Received in revised form

22 October 2015

Accepted 26 October 2015

Available online 4 November 2015

ABSTRACT

The conversion of graphite to graphite oxide (GO) is an effective and widely used method for solubilizing and exfoliating graphite. The oxidation is not uniform however, and wide variations in the degree of oxidation exist between and within batches of GO. In this article we introduce an approach to both quantify the global degree of oxidation in GO and to separate GO into fractions with more uniform extents of oxidation. Using the formation of GO stabilized oil-in-water emulsions, GO is separated into an emulsion fraction and a water fraction. We find GO sheets that stabilize the emulsion droplets are less oxidized than sheets suspended in water as shown by XRD, Raman spectroscopy, FTIR, elemental analysis and electrical conductance. The use of successive fractionation allows not only for the preparation of GO fractions with more narrowly defined properties, but also provides a method for characterizing GO batches. This promises to provide the field with a critical missing piece: a straightforward and standard method for the global characterization and comparison of GO made by different procedures and by different investigators.

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1. Introduction

The oxidation of graphite to graphite oxide (GO) is a widely used approach for the exfoliation and dispersion of oxidized graphene sheets in water [1] with hundreds of thousands of research articles describing research utilizing GO. Despite the enormous amount of attention however, there is currently no routine method for the global characterization or fractionation of the highly disperse material produced by the oxidation of graphite. In this article we present such a method based on our finding that the degree of oxidation of graphene sheets has a direct correlation to their ability to stabilize oil-in-water emulsions. Inspired by the early work in the polymer field to quantify the polydispersity of polymers by fractionation [2], we introduce a fractionation approach to quantify the dispersity found in the degree of oxidation within batches of GO.

The oxidation of graphite was first reported over 150 years ago by Brodie in an attempt to determine the atomic weight of carbon [3]. The approach has changed and been improved over the years

[4–7], but the mechanism of oxidation is still an active area of research [7]. Two things are clear about GO however: it is a very polydisperse material in terms of the level of oxidation of individual sheets [6,8], and every batch of GO has a unique distribution of oxidized sheets [6,9]. The oxidation process requires the use of harsh conditions, often involving sulfuric acid and potassium permanganate, and produces sheets with a wide range of oxidation levels, with some sheets highly oxidized and others having nearly no oxidation. That the GO is not a mixture of oxidized and unoxidized sheets is supported our observation that unoxidized graphite cannot be suspended in water even upon extensive mixing, where as GO can give a suspension stable for at least several weeks. Additionally, a recent study of the mechanism of GO formation convincingly argues that oxidation of the graphene sheets in graphite is a diffusion controlled reaction, and they found the use of 2 wt equivalents of oxidizing agent produced sheets that varied from lightly to fully oxidized [7].

This is problematic, however, as different synthetic approaches, and even the same approach but with different batches, can yield GO with very different extents of oxidation, and thus different properties, making the characterization of the batches a critical need for GO based research. The availability of more uniform and better characterized GO would be of great utility for controlling the

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chemical, physical, electrical, and thermal properties of GO and accelerating the pace of GO utilization in medical devices [10], nanoelectronics [11], electromechanical systems [12], sensors [13], composites [14], catalysis [15], energy storage devices [16], and optics [17].

Currently the characterization of GO batches is done by methods that look at individual sheets, such as AFM or electron microscopy, requiring time consuming and tedious work to obtain any global data, or by methods that give an overall average of the batch. Although knowing the overall average degree of oxidation is useful, it does not give any information as to how the oxidation is distributed: is the GO batch composed of a few highly oxidized sheets or do all the sheets have roughly the same level of oxidation? The answer to that question has a significant impact on understanding the properties of devices and materials made with that batch of GO.

2. Experimental

For a typical fractionation procedure, 20 mg of GO was added to 5 mL of DI water in a 20 mL scintillation vial. The mixture was then bath sonicated for 1 min. After sonication, the GO was dispersed and the suspension appeared black. Next, 5 mL of chloroform was added to the suspension. This GO in a chloroform/water system was then mixed for 1 min using a Kinematica Brinkmann Polytron Homogenizer mixer (Model PT 10-35), leading to the formation of a stable emulsion. As the oil phase is chloroform, with a density greater than water, the spheres were seen at the bottom of the vial (GO_e fraction). The top region (containing GO_w) consisted of a uniformly black water/GO suspension. Other organic solvents, such as heptane and benzene, form water and emulsion phases as well, but the emulsion phase is the top layer in those cases.

Both types of GO fractions (GO_e & GO_w) were obtained from the fractionation vial using a glass pipette. GO_e emulsions were very stable (hours/minutes) so the emulsion phase could be obtained, even with multiple pipetting, without disturbing the phase separation. In all cases the fractions were dried in air at 70 °C. For XRD analysis, each GO sample was drop cast onto a glass slide (20 mm × 5 mm) and dried at 70 °C, and for FTIR, 1 mg of the GO sample was mixed with 99 mg of KBr and pressed into a pellet.

The nomenclature used is as follows: the region the fraction is taken from (w for water and e for emulsion) is used as a subscript to denote the route from the original GO to the current fraction. For instance, if GO is fractionated by separating the water and emulsion phases, the material obtained from the water phase is denoted GO_w and the material isolated from the emulsion phase is denoted GO_e. If the GO_e material is then fractionated, the sample from the water phase is GO_w_e and the sample from the emulsion phase is GO_e_e.

Hummers GO. For GO synthesized using the Hummer's method, 625 mL of concentrated sulfuric acid and 12.5 g sodium nitrate was stirred for 30 min and 25 g graphite (Ashbury Mills grade 3243, avg sheet size 50 μm) was added over 20 min, followed by the slow addition of 75 g potassium permanganate. After 2 h, the reaction was quenched by adding 1.5 L water and 625 mL 30% hydrogen peroxide. For workup, 625 mL concentrated hydrochloric acid was added. The GO used for fractionation was obtained after purification using filtration and centrifugation. This GO was used in all experiments except for the data shown in Fig. 3, where the GO was reacted for 5 h rather than 2 h.

Improved GO [6]. A 9:1 mixture of H₂SO₄/H₃PO₄ (360:40 mL) was added to a mixture of 3.0 g graphite flakes (Ashbury Mills grade 3243, avg sheet size 50 μm) and 18.0 g KMnO₄. After 15 min of stirring, the reaction was heated to 50 °C and stirred for an additional 12 h. The reaction was allowed to cool to room temperature

and poured onto 400 mL ice and 3.0 mL 30% H₂O₂. The filtrate was centrifuged (5000 rpm for 3 h), and the supernatant was decanted off. The remaining solid material was then washed in succession with 200 mL of water, 200 mL of concentrated HCl, and two additional centrifugations, removing the supernatant each time. The final pH was observed to be 6.5. The solid obtained on the filter was vacuum-dried overnight at room temperature.

CabGO. Commercial sample whose preparation is proprietary.

Electrical Conductivity. Electrical conductivity of dried GO films of size 2 cm × 1 cm × 190 μm was calculated using a FLUKE 25 multimeter. The two test leads of the multimeter were put on the two ends of the GO film and conductance was measured. To ensure maximum contact of GO film surface and the test lead ends, carbon tape was used at both ends of GO film. Electrical conductivity was calculated using the conductance value and GO film dimensions.

3. Results and discussion

We have previously found that pristine (never oxidized) graphene sheets behave as two dimensional surfactants in stabilizing the high energy interface between immiscible oil and water phases to form water-in-oil emulsions [18,19]. Likewise, when GO is agitated in a water/oil mixture, we and others [20] have found that oil-in-water emulsions can be stabilized. However, we also find that the more intact, less oxidized sheets in the GO batch are better at stabilizing the interface and give rise to a stable emulsion phase, while the more oxidized sheets partition to the water phase. Separating these two phases fractionates the GO into a more and a less oxidized sheet population. Such an emulsion, with an upper water phase and lower emulsion phase, is shown in Fig. 1A. Although oil phases such as heptane and toluene also give rise to emulsions, having the emulsion as the lower phase is advantageous for separation, and thus chloroform/water is the system used in all of our reported investigations.

After forming two phases, the water phase, termed the GO_w phase, is separated from the emulsion phase, termed the GO_e phase, and both are analyzed. Fig. 1B compares the XRD spectra of the original GO and the GO_w and GO_e fractions. XRD analysis indicates the spacing of the stacked sheets, with the smaller peak at 2θ = 26.6 arising from the 0.33 nm graphite stacking and the larger peak at 2θ = 10–13.5 arising from the increased spacing due to the oxidation of the graphene sheets [21–24]. To quantify the observed differences, we use the area of the peak assigned to graphite stacking, A_G, and the area of the peak assigned to GO stacking, A_{GO}, to calculate the value of r.

$$r = A_{GO}/(A_{GO} + A_G)$$

We find the value of r decreases in the order of GO_w > GO > GO_e, indicating an increasing fraction of graphitic spacing in the samples going from water soluble fraction to original material to emulsion fraction. Table 1 shows the values, as well as the value for a sample in which the emulsion fraction is fractionated two additional times, GO_e_e.

XRD, however, does not directly measure the extent of oxidation. For that, elemental analysis of the fractions is obtained, and the results are shown in the second column of Table 1. The ratio of carbon to oxygen is observed to directly correlate with the trend seen by XRD, with the C/O ratio increasing from GO_w to GO to GO_e. This same trend is also observed in measurements of the electrical conductance of films made with each fraction with the most oxidized material, GO_w, showing the least conductance. This is to be expected, as oxidation is known to disrupt the conjugation in graphene responsible for electrical conductivity [25].

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