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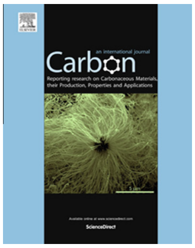

Facile synthesis of graphene oxide in a Couette–Taylor flow reactor

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ABSTRACT

A practical approach to bulk-scale graphene-based materials is critically important for their use in the industrial applications. Here, we describe a facile method to prepare graphite oxide (GO) using a Couette–Taylor flow reactor for the oxidation of bulk graphite flakes. We found that the turbulent Couette–Taylor flow in the reactor could be engineered to result in the efficient mixing and mass transfer of graphite and oxidizing agents ($KMnO_4$ and H_2SO_4), thereby improving the efficiency of graphite into GO. As compared to the standard Hummers' method, higher fraction of a single- and few-layer graphene oxide (G-O) can be yielded in a dramatically shortened reaction time, by optimizing the processing parameters, we have shown that ~93% of G-O yield could be achieved within 60 min of reaction time. This method also allowed for the in-situ functionalization of G-O with metal oxide nanoparticles to give a nanoparticle-decorated G-O hybrid material. Our method for facile and large-scale production of graphite oxide may find utility in a range of applications including energy storage, composites and supporting frameworks of catalyst.

1. Introduction

Graphene oxide (G-O) is a two-dimensional material derived from graphene with hydrophilic surface functional groups such as hydroxy, epoxide, and carboxy groups on the basal plane and edges of the graphene. [1,2]. G-O has attracted great attention due to its nature to remain exfoliated in polar solvents as individual layers and be easily reduced back to conductive graphitic materials, referred to as reduced graphene oxide (r-GO) [3–5]. With large surface area and the aforementioned properties, G-O has shown a wide range of applications including electronics, conductive films, energy storage, sensors and composites. [1,6–9].

G-O can be produced in large quantity from bulk graphite by chemical oxidation and subsequent exfoliation [4,10]. While graphite oxide (GO), a stacked galleries of G-O sheets, is synthesized by either the Brodie, Staudenmaier or Hummers method, the most common approach is the use of Hummers method or some variation of this method [3,11,12]. This method involve the oxidation of graphite with strong oxidizing agents such as potassium permanganate ($KMnO_4$) and sulfuric acid (H_2SO_4), which introduces polar oxygen functional groups on the graphene sheet and render it hydrophilic [13–18]. Hence, GO can be readily exfoliated in many polar solvents and disperse particularly well in water, which then can be deposited on substrates to prepare graphitic films by means

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of common processing methods such as drop-casting, spraying, or spin-coating [19–22]. In addition, the surface functional groups on GO can serve as sites for functionalization with various active species including metals, oxides, and organic molecules [23,24]. Therefore, the oxidation of graphite into G-O layers provides advantages such as solution processing and derivatization of graphene-based materials for practical use in numerous applications [21,22].

However, oxidation of graphite using the conventional Hummers' method yielded graphite oxide along with a significant amount of non- or under-oxidized graphitic particles under a certain reaction time. To increase yields of graphite oxides that can be exfoliated into single- or few-layer graphene, it often requires either pre-oxidation steps, sequential addition of excess $KMnO_4$, or extended reaction time to several hours [25–27].

To achieve large scale production of individual or few-layer G-O sheets, it is important to oxidize graphite with oxidizing agents penetrating between stacked graphene layers and overcome the strong interlayer van der Waals forces. Efficient oxidation process would give high yields of homogeneously exfoliated G-O sheets in a reduced reaction time.

Herein, we report on a new method to produce a single- or few-layer graphene oxide from bulk graphite with high yields in a significantly shortened reaction time. This method employs Couette–Taylor flow reactor, in which the oxidation of graphite with oxidizing agents (*i.e.* $KMnO_4$, H_2SO_4 and $NaNO_3$) is accelerated by the turbulent Couette–Taylor vortex flow. The Couette–Taylor reactor consists of two coaxial cylinders with the inner one rotating. At a critical rotating speed, toroidal vortices are created and regularly spaced along the cylinder axis [28–30]. We found that this toroidal motion of fluids leads to highly efficient radial mixing of graphite and oxidizing agents in the system, thereby enhancing the oxidation efficiency. As compared to the conventional Hummers method, the use of this system allows for the production of a single or few-layer G-O at a high yield within an hour of reaction time. In this work, a series of oxidation reaction was carried out in a Couette–Taylor reactor with respect to processing parameters such as rotating speeds and reaction time, and the results will be discussed in terms of yield of G-O. This method is also compatible with the continuous production of G-O sheets and the functionalization of G-O with other species such as metal oxides can be achieved simultaneously.

2. Experimental details

2.1. *Synthesis of G-O*

Graphite flakes were oxidized using Couette–Taylor flow reactor. 5 g of graphite flakes (SP-1 graphite, 50 μm) and 3.75 g of sodium nitrate ($NaNO_3$) were added to 169 mL of sulfuric acid (H_2SO_4, 95%). Then, 23 g of potassium permanganate ($KMnO_4$) was slowly added to this mixture at 10 °C or lower and the mixture was stirred for 30 min. The Couette–Taylor flow reactor (length: 400 mm) consists of two coaxial cylinders with the fixed outer cylinder (radius: 125 mm) and the rotating inner cylinder (radius: 25 mm). After the mixture was introduced into the gap between the two cylinders, the inner cylinder was rotated. The rotating speed of the inner cylinder was varied from 400 to 1200 rpm for the reaction time of 15, 30, 45 and 60 min. Oxidation of graphite in a Couette–Taylor flow reactor led to a brown-colored pasty slurry within 60 min. For a work-up, 200 mL of purified water and 10 mL of peroxide (H_2O_2, 30%) were added to the mixture, and then stirred for 60 min. For purification, a filter press system was used to separate GO and impurities. As detailed in Supporting Information, the filter press system consists of a membrane filter plates with a pore size of 5 μm. GO slurry and a large volume of DI water was continually fed into the system until the water and impurities is squeezed out. The purification step was done for 6 h. The remaining GO solids were collected, dispersed and sonicated in water. Then, non- or under-oxidized graphitic particles were precipitated out by further centrifugation at 4000 rpm for 30 min. The supernatant containing single- or few-layer G-O was filtered over a PTFE membrane with a 1 μm pore size and vacuum- or freeze-dried for characterization.

2.2. *Characterization*

The microstructure of the samples was investigated using a field emission scanning electron microscopy (FESEM, JSM-7600F, JEOL), and a high resolution transition electron microscopy (HRTEM, JEM-3010, JEOL). The thickness of the G-O sheets were obtained using atomic force microscopy (AFM, SPA-300HV, SII). X-ray diffraction (XRD) patterns of oxidized graphite prepared were determined by a D8 ADVANCE (Bruker Corporation) with Cu-Kα X-ray source. Raman spectra were obtained by micro-Raman system (Bruker FRA 160/S, Burker) with an excitation energy of 2.41 eV (514 nm). X-ray photoelectron spectroscopy (XPS) spectrum of the G-O sample were performed by a VG Microtech ESCA2000 (JEOL) with a monochromatic Al-Kα X-ray source at 250 W.

3. Results and discussion

According to the modified Hummers method, graphite oxide is produced by the oxidation of bulk graphite in the acidic oxidizing medium [4,10]. In the course of the reaction, the oxidation begins by the oxidizing agent attacking graphene layer. To afford the efficient oxidation of graphite, it would be important to enhance the rate of diffusion of the oxidizing agent into the graphite interlayer and the subsequent oxidation reaction. To this end, we used a Couette–Taylor flow reactor for the efficient mixing and mass transfer of graphite and oxidizing agents, thereby enhancing an efficiency of oxidation reaction of graphite into graphite oxide.

Fig. 1 illustrates the reaction system used for the oxidation of bulk graphite with oxidizing agent. As shown in Fig. 1a, the Couette–Taylor reactor consists of two concentric cylinders and the inner cylinder rotates at a controlled speed while the outer cylinder is kept stationary [28–30]. Then, a mixture of graphite flakes, the concentrated acids and oxidizing agents were fed into the reactor. As the rotation speed of the inner cylinder reaches a critical value, it develops the counter-rotating toroidal vortices in a regular arrangement