



Mass production of graphene oxide from expanded graphite



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ARTICLE INFO

Article history:

Received 22 November 2012

Accepted 20 July 2013

Available online 26 July 2013

Keywords:

Expanded graphite

Graphene oxide

Spontaneous expansion

Mass production

ABSTRACT

In a deviation from the conventional Hummers method, a spontaneous expansion approach was introduced with expanded graphite as the precursors. The intercalating agent (H_2SO_4) was able to penetrate into the expanded graphite; this had further expanded the graphite and as a result, a foam-like intermediate was produced. The foam-like graphite was more easily oxidized in reaction with the oxidant (KMnO_4) to form graphene oxide (GO). Fully exfoliated GO was obtained with expanded graphite having the median diameter $\sim 15 \mu\text{m}$ as the precursors. This procedure was much safer and productive in scalable applications than the conventional Hummers methods.

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1. Introduction

Graphene oxide (GO) is of great interest due to its low cost, easy access, and widespread ability to convert to graphene [1–5]. Scalability is also a much desired feature. At present, a conventionally-modified Hummers method is the primary method for preparing GO. Graphite is commonly chosen as the starting material due to its availability and low cost. Proportional amounts of oxidants, such as potassium permanganate, sodium nitrate, and concentrated sulfuric acid, are mixed in order with the graphite. Subsequently, a three-phase procedure is conducted with low, mid, and high temperature reactions, each occurring separately at scheduled times. GO, the oxidized graphene sheet, acquires multiple defects, of which the degree is subject to the additive amount of oxidant and the oxidizing time [6,7].

In regard to the oxidants, some research groups, including that of James M. Tour, excluded sodium nitrate as an additive due to its negligible role in graphite oxidation [8]. A mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (9:1 volume ratio) instead of only H_2SO_4 resulted in increased hydrophilic and oxidized GO without the emission of toxic gas, which differs from the traditional Hummers method [8]. Of these typical processes, the throughput normally benefits from the preparation with a prolonged stirring over time (over 12 h or even 2 d) [3,8]. In addition, proper preparation requires that particular attention be paid to some key steps, for example, the addition of water for high temperature hydrolysis. Unintentionally, the mixed highly explosive oxidants can decompose in an exothermic process or as a large explosion; therefore, off-the-rack methods starting with graphite are still flawed.

Expanded graphite has long been commercially available and its sizes have been optionally chosen. In this paper we report on synthesizing GO with increased safety and productivity from commercial expanded graphite, of which the sizes in a moderate range (the median diameter $D_{50} \sim 15 \mu\text{m}$) as a raw material and with a new modified Hummers method. Therein we introduced a spontaneous-expansion-step modification, which resulted in a preparation that strongly contributes to safety, efficiency, and productivity. Comparisons were also conducted among three raw materials with different sizes. This promising method has applications to the scalable industrialization of graphene.

2. Experimental

Materials and reagent: Commercial expanded graphite (EC300 with $D_{50} \sim 50 \mu\text{m}$, EC1000 with $D_{50} \sim 15 \mu\text{m}$ as manufactured) was purchased from Ito Kokuen Co., Ltd., Mieken, Japan. Highly oriented pyrolytic graphite (HOPGHOPG) was acquired from Bay Carbon, Inc., Michigan, USA. Other chemicals unless specifically noted were from Wako Pure Chemical Industries, Ltd., or Sigma-Aldrich Inc., Japan.

Preparation of GO: Some modifications were made to the Hummers method [9] and applied to the preparation of GO from industrially expanded graphite. In a typical reaction, potassium permanganate (15 g) and expanded graphite (5 g) were initially stirred until homogeneous. Then, in a bottom-round flask (500 mL) with ice-water bath, concentrated sulfuric acid (98%, 100 mL) was added to the mixture with continuously stirring until a uniform liquid paste was formed. Then the water bath was removed. The stirring continued until a foam-like intermediate spontaneously formed (around 30 min) at room temperature with a large volumetric expansion. Deionized water (400 mL) was added, and rapid stirring was restarted to prevent effervescing. Next, the flask was

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placed in a 90 °C water bath, and after 1 h a homogeneous suspension was obtained that was dark yellow in color. The suspension was then filtered and was subjected to repeated washing and centrifugation (10,000 rpm, 2 h per cycle) to remove impurities.

Characterization: The samples were characterized using various analytical methods such as atomic force microscopy (AFM, Agilent series 5500 AFM instrument using the tapping mode at a scanning rate of 0.5 Hz), scanning electron microscopy (SEM, JSM-6300,

JOEL, with accelerating voltage of 30 kV), X-ray photoelectron spectroscopy (XPS, JPC-9010MC, JOEL, using Mg K α , 1×10^{-7} Torr), and X-ray diffraction (XRD) using RINT 2000 (Rigaku Denki, Ltd., X-ray $\lambda_{\text{Cu K}\alpha} = 0.154$ nm), Fourier transform infrared spectroscopy (FTIR, FT/IR-6100 FT-IR Spectrometer, JASCO), and thermogravimetric analysis (TGA, TG/DTA 6200, SII Exstar6000, with a heating rate of 5 °C/min), Transmission Electron Microscopy (Hitachi HD2000 STEM, accelerating voltage 200 kV equipped with an Energy Dispersive X-ray (EDX) detector).

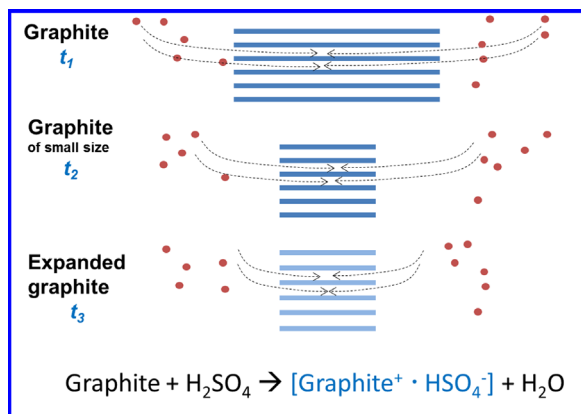


Fig. 1. The schematic regarding the intercalation of graphite by H_2SO_4 .

3. Results and discussion

Intercalation of graphite (Fig. 1) is required for subsequent exfoliation when preparing GO. H_2SO_4 is the most common intercalating agent. Under identical conditions, graphite with relatively small lateral sizes would help save considerable time because of a lower resistance than in the case of large graphite ($t_1 > t_2$). Further, if such graphite is pre-expanded with the inter-layer space being larger, the intercalation would then complete even sooner ($t_2 > t_3$). Meanwhile the intercalation emits heat as well as produces water. With these points of view, expanded graphite was used as the starting material. A spontaneous full intercalation along with the evaporation of water at room temperature would prepare a foam-like graphite-intercalating intermediate.

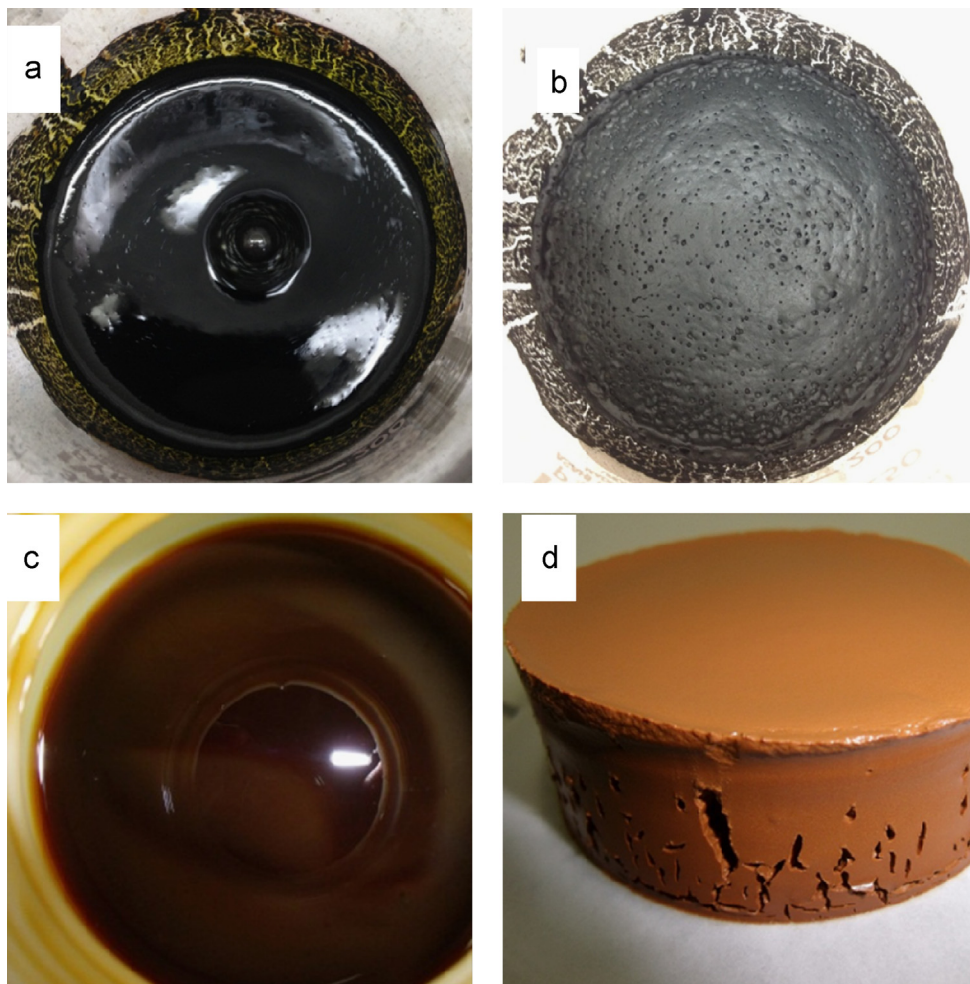


Fig. 2. Photos of preparation of GO from EC1000 with the proposed method. (a) A mixing of raw materials, (b) the scene at the moment of spontaneous-expansion: foam-like volumetrically expanded graphite intermediate, (c) the product of high-temperature hydrolysis: a homogeneous light-brown GO “cake”, and (d) concentrated GO solution in dark brown after purification.

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