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Graphene prepared by thermal reduction–exfoliation of graphite oxide: Effect of raw graphite particle size on the properties of graphite oxide and graphene

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ABSTRACT

We report the effect of raw graphite size on the properties of graphite oxide and graphene prepared by thermal reduction–exfoliation of graphite oxide. Transmission electron microscope analysis shows that the lateral size of graphene becomes smaller when smaller size graphite is used. X-ray diffraction analysis confirms that graphite with smaller size is more effectively oxidized, resulting in a more effective subsequent exfoliation of the obtained graphite oxide toward graphene. X-ray photoelectron spectroscopy demonstrates that reduction of the graphite oxide derived from smaller size graphite into graphene is more efficient. However, Raman analysis suggests that the average size of the in-plane sp^2-carbon domains on graphene is smaller when smaller size graphite is used. The enhanced reduction degree and the reduced size of sp^2-carbon domains contribute contradictively to the electrical conductivity of graphene when the particle size of raw graphite reduces.

1. Introduction

Graphene is a single-atom-thick sheet of hexagonally arrayed sp^2-bonded carbon atoms. It has attracted a great deal of attention because of its extraordinary electronic, electrochemical, thermal, and mechanical properties, large surface area, and high aspect ratio. The novel properties of graphene ensure its potential for a variety of applications such as in electronic and energy devices, catalysis, sensors, biomedicines, and composite materials [1–6]. Graphene can be prepared using various methods such as micromechanical exfoliation of graphite [7], exfoliation of graphite intercalation compounds [8], thermal or chemical reduction of graphene oxide [9,10], epitaxial growth on silicon carbide [11], or chemical vapor deposition on metal substrates [12].

The top-down methods used to prepare graphene from graphite via graphite oxide (GO) routes have been considered as the promising approaches for the mass production of graphene. Graphite is readily available and inexpensive, and a simple chemical oxidation of graphite can readily form bulk quantities of GO for further uses. Thermal exfoliation of GO can produce bulk quantities of graphene. In this process, GO is reduced and exfoliated simultaneously upon rapid heating due to the thermal decomposition of the oxygen-containing functional groups of GO and the pressure of the gas products (mainly CO_2) that built up instantaneously between the sheets [13,14]. This method is ultra-fast, economical and eco-friendly because it does not use any solvent or reducing agent. The obtained graphene can readily disperse in polar organic solvents such as acetone or dimethylformamide for further processing without need of any additional modifications. That is due to the polar oxygen-containing functional groups remained on the graphene as well as the wrinkled nature of this graphene which prevents the graphene sheets from restacking [13–15]. This graphene has found numerous applications, involving the uses as electrode material for batteries, supercapacitors, sensors and solar cells [16–20], the use in fabrication of conductive, high surface area tapes [21], and the uses as fillers for the preparation of polymer composites [22,23], showing excellent performance.

The properties of graphene prepared by thermal reduction–exfoliation of GO depend strongly on the preparation conditions. For example, the oxygen to carbon element ratio (O/C) and the electrical conductivity of graphene can be tunable by the reduction–exfoliation time and temperature [24]. Other recent works have also reported the preparations of high quality graphene having less structural and topological defects at a lower reduction–exfoliation temperature under vacuum, or with the assistance of a reduction–exfoliation accelerating agent such as H_2 or HCl, or with microwave or irradiation assistance [25–27]. In addition, the

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characteristics of the raw graphite such as its type and particle size, pre-treatments, and the properties of obtained GO which used for reduction–exfoliation may be important factors that affect the properties of the resulting graphene. However, to the best of our knowledge, such factors have not yet been investigated in-depth.

In this paper, we report the effect of raw graphite particle size on the properties of resulting GO and the graphene obtained from the thermal reduction–exfoliation of the GO. The expandable graphites with various particle sizes were used for the preparation of GOs, to examine the effect of graphite size on the size, oxidation degree, and chemical structure of GO. In addition, the effect on the exfoliation and reduction efficiency of the GO toward graphene as well as on the lateral size and the electrical conductivity of the resulting graphene were examined.

2. Materials and methods

2.1. Materials

The large-sized expandable graphite (ES350 F5) was purchased from Qingdao Kropfmuehl Graphite Co., Ltd., China. The medium-sized and small-sized graphite samples were obtained by grinding the large-sized graphite in different durations of time of 8 and 15 min using a 4-blade kitchen blender. These three graphite samples were used for the preparation of graphenes. Fuming nitric acid (Matsunoen Chemical) and potassium chlorate (Kanto Chemical Co., Inc.) were used as received.

2.2. Preparation of GO and graphene

GO was prepared by the chemical oxidation of expandable graphite using the Brodie method, as described elsewhere [28]. Briefly, a reaction flask containing 200 mL of fuming nitric acid was cooled in an ice bath to 0 °C, and graphite powder (10 g) was added with stirring. Potassium chlorate (85 g) was then slowly added to the reaction mixture over one hour with stirring at 25 °C. After 24 h, the mixture was poured into 3 L of distilled water. The obtained GO was filtered, washed with distilled water until the pH of the filtrate was neutral, and then dried in a vacuum at 60 °C for 1 day.

Graphene was prepared by rapid heating of the dry GO. Typically, dry GO (2 g) was charged into a quartz tube followed by flushing with nitrogen for 5 min. The quartz tube was then quickly inserted into a furnace preheated at 1100 °C and kept for one minute to obtain graphene by the thermal reduction–exfoliation of the GO [13,14].

2.3. Measurements

The morphology of the samples was observed using a field emission scanning electron microscope (FE-SEM, JSM-6500F, Jeol)

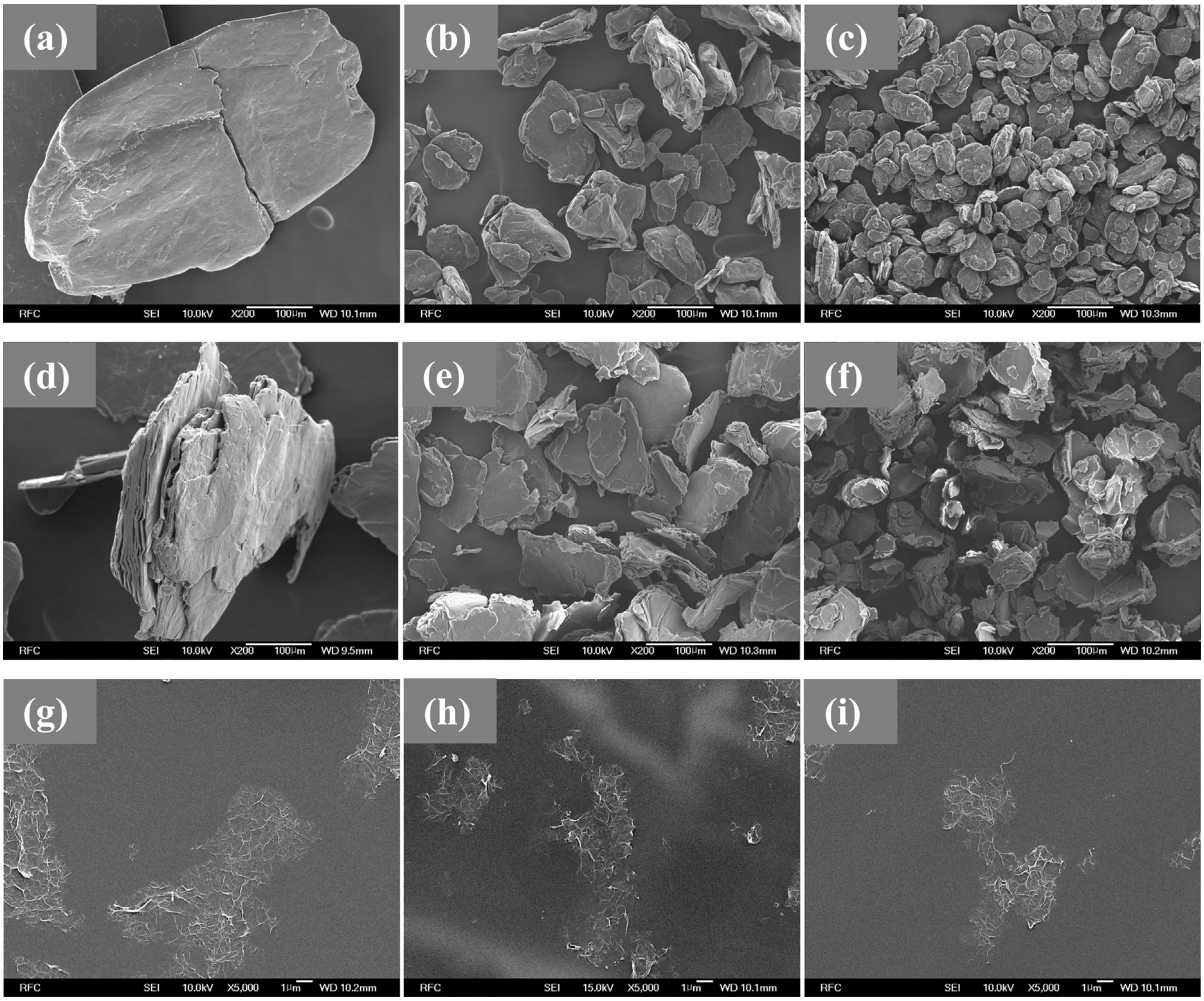

Fig. 1. SEM images of (a, d, g) large-sized graphite and the derived graphite oxide and graphene; (b, e, h) medium-sized graphite and the derived graphite oxide and graphene; (c, f, i) small-sized graphite and the derived graphite oxide and graphene.