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Scalable production of water-dispersible reduced graphene oxide and its integration in a field effect transistor

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ABSTRACT

The development of environmentally benign, low-processing and low-cost approaches to the large-scale preparation of advanced nanomaterials based on the use of biological materials is currently attracting great interest. Here, we report the discovery that aqueous honey solutions reduce graphene oxide in a low-cost and an eco-friendly manner, yielding highly water dispersive functionalized reduced graphene sheets. The roles of honey in the reduction of graphene oxide of as-prepared graphene are demonstrated. The possible mechanism for the de-epoxidation of graphene oxide is elucidated. The fabricated a honey-reduced graphene oxide-based field-effect transistor exhibited ambipolar transfer characteristics, thereby demonstrating that the developed material may therefore have applications in electronic devices and sensors.

Introduction

Since its discovery by Geim in 2004, graphene has attracted considerable interest because of its excellent mechanical, electrical and thermal properties [1–5]. Graphene is a two-dimensional (2D) flat carbon material consisting of closely packed sp^2-hybridized carbon atoms in a honeycomb lattice [6,7]. To facilitate the application of graphene, its bulk production via a low-processing route with aqueous dispersion is highly desirable. Thus far, various methods have been developed to prepare graphene, including mechanical exfoliation, epitaxial growth, chemical vapor deposition, and the deoxygenation/reduction of exfoliated graphite oxide/graphene oxide (GO) with chemicals [8–13]. Among these methods, the chemical reduction of GO has garnered extensive attention because of its potential to enable the scalable production of graphene at low-cost. Several reducing agents (e.g., hydrazine hydrate, sodium borohydride, sodium hydroxide, potassium hydroxide, alcohols and metals) have been used in conjunction with organic solvents to reduce GO; however, these agents are not only toxic and/or explosive, but also limit the aqueous dispersion [7,14–19]. Thus, these reaction conditions restrict the large-scale production of graphene in view of aqueous dispersions and environmental concerns. In this context, great demand exists for the development of high-efficient scalable method for aqueous dispersive graphene involving “green” reducing agents for the reduction of GO.

Natural reducing agents are a potential alternative to toxic/explosive reducing agents for the large-scale preparation of aqueous dispersive graphene in an eco-friendly manner. Only a few biological materials for GO reduction, such as plant extracts (*e.g.*, *Pulicaria glutinosa* (Boiss.) Jaub. & Spach, and *Potamogeton pectinatus* L.) and microorganisms (*e.g.*, *Shewanella oneidensis* and baker's yeast), have been reported in the literature [20–23]. Although some natural chemicals, including sugars, proteins, dopamine and caffeic acid, have been used for this green reduction [21–27], these methods suffer from some limitations, such as the following: (1) natural materials (plant extracts and microorganisms) require an elaborated processes such as the drying of plant

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materials and the maintenance of cell cultures; (2) natural chemicals require harsh reduction conditions, such as an alkaline medium for sugars, proteins, and dopamine and pH adjustments in the case of caffeic acid and (3) aggregation in water. Therefore, the development of a novel, clean, green approach for the bulk preparation of aqueous dispersed graphene by means of a general method with few processing steps remains a great challenge. Honey is a sweet, viscous fluid produced by bees. Honey belongs to the carbohydrate group of foods, and it contains sugars, proteins, vitamins, flavonoids, enzymes, etc. [28]. Certainly, honey-assisted biological synthesis is beneficial for large-scale syntheses and for obviating the elaborated processes involved in biological syntheses that use plant extracts and microorganisms [29].

Great progress in incorporating reduced graphene oxide (rGO) into a field-effect transistor (FET) has been made for the typical electronic application [30–36]. Furthermore, the direct incorporation of rGO as an active channel layer into an FET structure that is responsive to physical [36,37], chemical [30] or biological [32,36,38] stimuli has been demonstrated. Stimuli-responsiver GO-FETs are highly attractive for sensing applications because of their simplicity of design, ease of mass production in a high-density array, facile integration into integrated circuits, compatibility with a large-area conformable substrate, and inherent capability of signal amplification. Therefore, the development of "green" reducing agents for reduction of GO and direct integration into the FET structure is a practical approach for electronics applications.

In view of these facts, we herein report the biological, environmentally benign, simple processing and cost-effective procedure that uses aqueous honey for the scalable preparation of graphene with aqueous dispersion characteristics (Fig. 1a) including it's integrated in a FET for device performance. The honey-reduced GO (Ho-rGO)-based FET demonstrated that the transfer characteristic of the Ho-rGO sheets in the FET structures is ambipolar. These electrical properties confirm that the rGO material prepared from honey has great potential in various applications, including transparent-electrode FETs and sensors.

Experimental

Materials

Graphite powder, sulfuric acid (H_2SO_4), hydrochloric acid (HCl), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), and hydrazine hydrate (N_2H_2), Hydrogen peroxide (H_2O_2, 30 wt.%) were procured from Sigma–Aldrich (USA). Natural honey was obtained from the local apicultural industry in Korea.

Characterization

The synthesized GO, Ho-rGO and Hy-rGO samples were characterized by ultraviolet–visible (UV–vis) spectroscopy (NANO-DROP 2000c, Thermo Scientific, USA), Fourier transform infrared spectroscopy (FT-IR) spectroscopy (Nicolet 6700, Thermo Scientific, USA), Raman spectroscopy (Almega XR, Thermo Scientific, USA), X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Scientific, USA), X-ray diffraction (XRD) (Empyrean, Panalytical, the Netherlands), Transmission electron microscopy (TEM) (SU8020, Hitachi, Japan) and Atomic force microscopy (AFM) (XE-150, Park Systems, Korea). The green and blue light emitting diode (LED) beams (Shenzhen Huangshi Junwei Aluminum & Kitchenware Co., Ltd., Mainland, China) were used to study the water dispersion properties (Tyndall effect) of as-prepared rGO samples.

Synthesis of graphitic oxide

Graphitic oxide was synthesized using a modified Hummer's method, a process that has been detailed elsewhere [39]. One gram of graphite powder and 0.5 g $NaNO_3$ were added to 23 mL of concentrated H_2SO_4 at 0 °C using an ice bath. Then, 3 g $KMnO_4$ was slowly added to the reaction mixture maintaining the temperature at 20 °C or less. The resulting reaction mixture was subsequently stirred for 4 h while immersed in a water bath at 35 °C and was subsequently mixed with 200 mL of deionized water. Three milliliters of aqueous H_2O_2 (30 wt.%) was then mixed into the

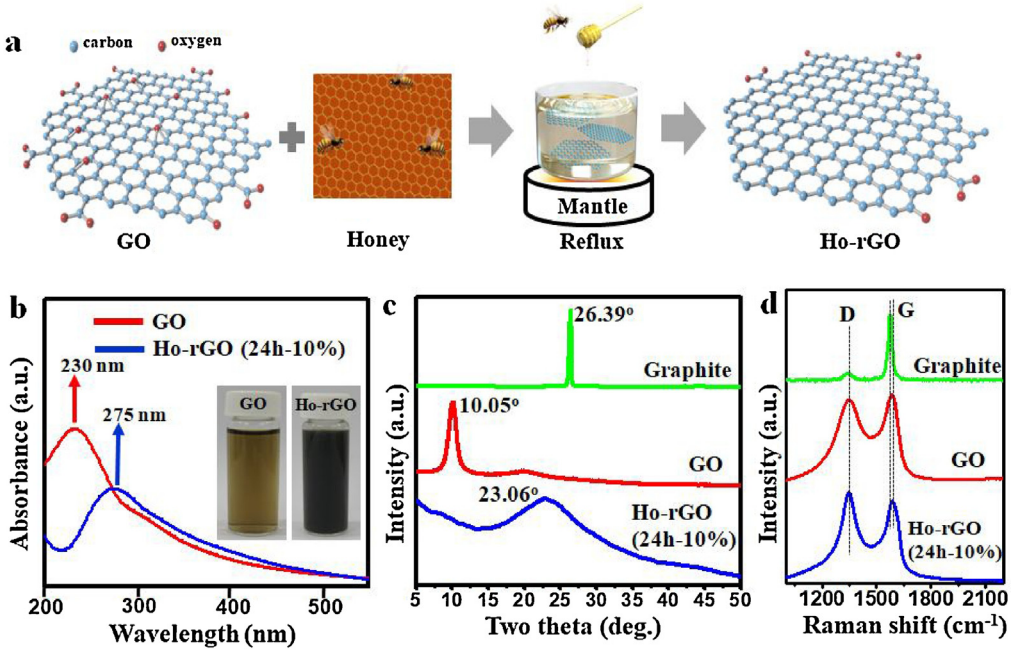

Fig. 1. (a) Schematic illustration of reduced graphene oxide production using aqueous honey solutions. (b) UV–vis absorption spectra of as-prepared GO (red) and 24 h-10% Ho-rGO (blue) samples. Insets in figure (b) represent the digital photographs of GO and 24 h-100%Ho-rGOsamples. (c) XRD patterns and (d) Raman spectra (1000to 2200 cm^{-1}) of graphite (green) and as-prepared GO (red) as well as 24 h-10%Ho-rGO (blue) samples.

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