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Chrysanthemum extract assisted green reduction of graphene oxide

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HIGHLIGHTS

- The chrysanthemum extract was used for the reduction of graphene oxide.
- The obtained few layered graphene exhibited high carbon to oxygen ratio.
- The mechanism for reduction of graphene oxide with chrysanthemum was proposed.
- This approach can be applied in the preparation of graphene-based bio-materials.

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ABSTRACT

The chemical reduction of graphene oxide (GO) usually involves highly toxic reducing agents which are injurious to the environment and human health. In the present study, chrysanthemum extract, as a natural and harmless reductant, mediated facile and green approach for the preparation of reduced GO (RGO) was reported for the first time. The reduction experiments of GO were conducted at room temperature, and the obtained RGO was few layered and exhibited high carbon to oxygen ratio (4.96) as demonstrated by transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS), respectively. The mechanism for removing of oxygen-containing functional groups from GO with chrysanthemum extract was proposed. The features of environmentally friendly and cost-effectively endow this approach with great promise in the preparation of various graphene-based materials, especially for biomaterials.

1. Introduction

Graphene, a two-dimensional hexagonal form of elemental carbon, as one of the revolutionary materials, has attracted enormous attention due to its outstanding optical, electronic, thermal, and mechanical properties [1]. During the past decades, several procedures have been developed for the production of graphene-like products, such as mechanical or ultrasonic exfoliation [2], chemical vapor deposition [3], microwave irradiation [4], solvothermal reduction [5] and chemical reduction of graphene oxide (GO) [6]. Indeed, the cost effectiveness and bulk productivity make chemical reduction of GO become the most widely applied approach [7]. It should be noted, however, the chemical reduction method typically involves highly toxic reducing agents, such as hydrazine, hydrazine hydrate, dimethyl hydrazine, hydroquinone, and sodium borohydride. And most of these are harmful to human health and the environment, that is, trace amount of these poisonous agents could have detrimental effects, especially in bio-related applications [8]. Therefore, reduction of GO using natural reagents has attracted a great deal of scientific interest, with the purpose ultimately to synthesize graphene in bulk for its commercial applications [9]. So far, a number of nature-based reducing agents, e.g., vitamin C [10,11], alcohols [12], tea solution [13,14], reducing sugar [15], glucose [16], and bacteria [17] have been applied in GO reduction thanks to the hard work of scientists. However, the products treated by the above-mentioned natural agents without adding an external stabilizer usually exhibited a highly agglomerated morphology, so the advanced applications of these green methods have not been fully realized. Thus, more research is still strongly desirable to develop an optimal, environmental-friendly, low-cost green reducing reagent for the production of graphene in large-scale.

The chrysanthemum flower, a traditional Chinese medicinal herb and grown in large quantities, has been used as a tea or a drug

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for thousands of years [18]. In addition, the dried flowers of chrysanthemum were reported to contain alkanes, flavonoids, unsaturated fatty acids, polysaccharides, which have a high tendency to get oxidized [19]. Generally, this trend was found to be due, at least in part, to that these types of phytochemicals are easily converted to the corresponding quinone forms in the presence of reactive oxygen.

In the present study, a green and facile method conducted with a simple procedure using chrysanthemum extract as the reductant was employed in the chemical reduction of GO. Compared with other reported traditional agents [20], chrysanthemum extract shows advantages of mild reaction conditions, high reduction capacity, easy isolation, and the most importantly, the environmentally friendly preparation procedure.

2. Experimental

2.1. Materials

GO was obtained from the Tangshan Jianhua Science and Technology Development Co., Ltd., Hebei, China, which was synthesized through Hummer's method and its features are shown in Table 1. The details of how the Hummer's method was carried out and a wider discussion of the oxidation mechanism are provided elsewhere [21]. Dried chrysanthemum flowers were purchased from a local supermarket. All chemicals were of analytical reagent grade and used without further purification. Deionized water (DI-water) was used throughout.

2.2. Preparation of chrysanthemum extract

Dried chrysanthemum flowers 45 g were firstly soaked in 600 mL DI-water at 95 °C for 30 min. Then, the aqueous extracted suspension was filtered through a 0.45 μm cellulose membrane under ambient conditions (~20 °C) to obtain a clear solution. Eventually, only about 300 mL chrysanthemum extract was obtained, because dried chrysanthemum flowers can absorb a part of DI-water.

2.3. Reduction of GO by chrysanthemum extract

GO dispersions with concentration of 0.1 mg/mL and 1 mg/mL were prepared by dispersing 10 mg and 100 mg GO in 100 mL DI-water, respectively, with sonication for 1 h. And then 100 mL of chrysanthemum extract was added into the GO dispersion. After that, the result suspension was placed in a thermostatic bath at 95 °C for 24 h. For comparing the reduction efficacy of the chrysanthemum extract with routine methods [11], 100 mL of GO suspension was reduced by DI-water and hydrazine hydrate (2 mL), a common and standard reducing agent, at 95 °C for 24 h, respectively. The experiment of reduction of GO by DI-water was conducted by placing 100 mL GO dispersions (0.1 mg/mL and 1 mg/mL) in a water-bath at 95 °C for 24 h, without adding any more DI-water. After reduction, the reduced GO (RGO) was washed three times with ethanol and DI-water, respectively, to remove the impurities. To test the reproducibility of the experiments, the above procedures were repeated three times respectively to acquire the ideal results.

Table 1
Features of GO.

GO	Unit	Value	Test method
Thickness	nm	0.5–4	TEM
Lateral dimension	μm	0.5–3	SEM
Number of layers	–	1–10	TEM
Oxygen content	at.%	>30	XPS

2.4. Characterization

The X-ray diffraction (XRD) study was carried out on a Rigaku D/max 2500 PC X-ray diffractometer (Japan) with Cu ($\lambda = 1.54178$ Å) irradiation over the range of $2\theta = 2.5–70°$ with a scanning rate of 4°/min operating at 40 kV and 150 mA. Raman spectra were taken with an inVia Raman spectrometer (Renishaw, UK). The samples were excited with an air cooled argon ion laser of wavelength 514 nm. Scanning electron microscopy (SEM) was carried out on a S4800 scanning electron microscopy (HITACHI, Japan). Field emission transmission electron microscopy (TEM) images were recorded by using Tecnai G2 F30 (FEI, USA). X-ray photoelectron spectroscopy (XPS) analysis was performed by an Escalab 250Xi photoelectron spectrometer (Thermo Fisher Scientific, USA) with monochromatic Al Kα radiation (hv = 1486.6 eV). Fourier transform infrared spectroscopy (FT-IR) was performed on a Thermo Fisher Nicolet 6700 spectrometer (USA). The FT-IR spectra were obtained within the range of 400–4000 cm^{-1} in KBr pellet form (2 mg sample in 300 mg KBr). Thermogravimetric analysis (TGA) was carried out on a thermal analyzer, 1/1600HT (Mettler Toledo, Switzerland) with a nitrogen flow rate of 30 mL/min at a heating rate of 10 °C/min. And all RGO samples used for the above characterization were reduced from GO with the concentration of 1 mg/mL.

3. Results and discussion

3.1. Reduction of GO by chrysanthemum extract

To compare the performance of different reducing agents towards the deoxygenation of GO, dispersions at concentration of 0.1 mg/mL and 1 mg/mL were reacted in a thermostatic bath at 95 °C for 24 h with the following reductants: DI-water, chrysanthemum extract, and hydrazine hydrate. The reduced products were labeled as D-RGO, C-RGO, and H-RGO, respectively. As shown

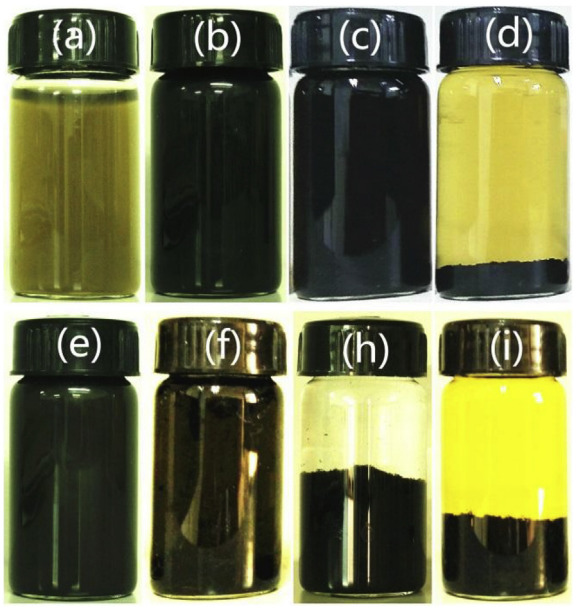

Fig. 1. Digital photographs of GO aqueous dispersion 0.1 mg/mL (a) and its reduction products H-RGO (b), D-RGO (c), and C-RGO (d); H-RGO (f), D-RGO (h), C-RGO (i), all reduced from GO dispersion with concentration of 1 mg/mL (e).

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