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ScienceDirect

Ceramics International 41 (2015) 4810–4813

CERAMICS INTERNATIONAL

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Spinach assisted green reduction of graphene oxide and its antioxidant and dye absorption properties

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Received 21 October 2014; received in revised form 6 December 2014; accepted 7 December 2014

Available online 12 December 2014

Abstract

Spinach (*Spinacia oleracea*) leaves mediated efficient green reduction of graphene oxide (GO) was achieved to produce multifunctional reduced graphene oxide (rGO). GO was mixed with spinach juice and refluxed for 30 min at 100 °C. Powder XRD, TEM and UV–visible techniques demonstrate the formation of well-organized layered rGO. Industrially important carcinogenic Methylene blue (MB) and Malachite green (MG) dyes absorption experiments with rGO were performed under dark condition. Complete removal of MB and MG occurs in spans of 60 and 40 min respectively in the presence of 20 mg rGO. Potential antioxidant activity was exhibited by the rGO with 50% inhibitory concentration of 1590 μg/mL against the scavenging of 2, 2-diphenyl-1-picrylhydrazyl (DPPH) free radicals. Environment friendly, economical and facile reduction method is suggested for the efficient reduction of GO.

Keywords: B. X-ray methods; D. Carbon; E. Functional applications; Graphene oxide; TEM

1. Introduction

The synthesis of graphene has been one of the most exciting benchmark scientific advancements in recent years due to its outstanding properties and applications [1–3]. A variety of attempts have been made for the synthesis of graphene such as mechanical routes [1], chemical vapor deposition [4], epitaxial growth [5] and chemical reduction of graphene oxide (GO). Currently, solution-based chemical reduction of GO presents very easier route for the production of good quality graphene [6]. The resultant graphene could be utilized in a variety of applications [7,8]. However, the solution-based chemical reduction methods employ hazardous chemicals such as Sodium borohydride, hydrazine and dimethyl hydrazine which are highly toxic and trace amounts of these in final product could pose harmful effects. Superior quality reduced graphene oxide (rGO) was obtained using Hydriodic acid [9], but it is highly corrosive in nature. Handling of hazardous waste generated out of these processes could counter the environment protection and add up to the production cost. Further, the graphene produced by these methods lead to aggregation of graphene sheets and an additional step needs to be incorporated to avoid these aggregations [10]. A solvothermal method of reduction has been one of the recent approaches for the synthesis of graphene. But it involves elevated temperatures during reduction that could produce hazardous gases and wastes [11]. Recently, green approaches have employed natural products in place of toxic reducing agents. Vitamin C was shown to be efficient for reduction of GO; however, the product had highly agglomerated morphology and the reduction process

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http://dx.doi.org/10.1016/j.ceramint.2014.12.036

0272-8842/

involve high temperatures that results in increased defects in graphene [12]. Bovine serum albumin [13] was utilized in reducing GO, but an alkali is needed as a coreductant. Therefore an efficient, economical and eco-friendly reducing agent is highly desirable for reduction to obtain soluble graphene in bulk quantity.

Spinach (*Spinacia oleracea*), an edible plant belongs to Amaranthaceae family is native to central and southwestern Asia and consumed in most of the countries. It is a very rich source of essential nutrients such as vitamin A, vitamin C, vitamin K, magnesium, manganese, folate and iron. Spinach leaves consist of glucuronic acid derivatives of flavonoids, tartarate derivatives of p-coumaric acid and found to be antioxidant [14]. The proximate composition studies reveal that crude protein and ash contents were 2.89% and 1.96% and total lipid content was 0–61% [15]. In view of the presence of considerable amounts of antioxidant phytochemicals in spinach, it may act as good reducing agent for the reduction of GO. Therefore, an attempt has been made for the first time to reduce GO using spinach leaves.

2. Experimental

AR grade conc. Hydrochloric acid, conc. Sulfuric acid, Hydrogen peroxide, Potassium permanganate and Sodium nitrate were procured from S. D. Fine Chemicals Company, Mumbai, India and used without further purification. Graphite flakes were from SigmaAldrich Company (Catalog no.—332461, $>90\%$ purity). Fresh leaves of spinach were purchased from local market, thoroughly washed in distilled water, chopped in to small pieces and grinded well with water to obtain homogeneous juice.

2.1. Preparation of GO

Graphite (5 g) and Sodium nitrate (2.5 g) were thoroughly mixed and treated with 120 mL of H_2SO_4 (95%) [16]. The mixture was vigorously stirred (Remi 1 MLH magnetic stirrer) for 30 min under ice cold condition. Potassium permanganate (15 g) was added with continued vigorous stirring and the temperature was maintained below 20 °C. After overnight stirring, 150 mL of distilled water was slowly added with continued vigorous stirring. The reaction temperature was rapidly increased to 98 °C and 50 mL of 30% Hydrogen peroxide was added. The product was allowed to cool and washed with 5% Hydrochloric acid, then with distilled water and dried [17].

2.2. Reduction of GO

GO (80 mg) was added to 50 mL of distilled water and subjected to sonication (40 min) (Elma Ultrasonic bath, 3 l capacity) for uniform dispersion. The suspension was uniformly mixed with spinach juice in a round bottomed flask and refluxed for 30 min. The resulting product settled at the bottom was separated and rinsed with distilled water and centrifuged (Remi swing out centrifuge) until colorless, clear supernatant was obtained. The rGO was dried and stored in an airtight container until further use.

2.3. Characterization

The obtained GO and rGO were subjected for characterization using powder X-ray diffractometer (Shimadzu – 7000 with monochromatized CuKα radiation), UV–visible Spectrophotometer (Thermo Evolution—220) and TEM (TECNAIF-30).

2.4. Dye elimination activity

20 mg of rGO was mixed with 100 mL of 5 ppm MB and MG separately and stirred under dark condition. Known volume of the reaction mixture was drawn at specific intervals of time and absorbance was recorded (663 and 617 nm for MB and MG respectively). The percentage of absorption of the dye was determined using the formula

$$\%\ \text{of absorption} = \frac{C_i - C_f}{C_i} \times 100$$

where C_i and C_f are initial and final dye concentrations respectively.

2.5. Antioxidant activity

DPPH (oxidized form) is a stable free radical with purple color. In the presence of an antioxidant which can donate an electron to DPPH radical decays, and the change in absorbance at 520 nm is followed which can be measured spectrophotometrically [18]. 39.4 mg of DPPH was dissolved in 100 mL of methanol to get concentration of DPPH in the assay which was 0.14 mM. 2360 ul of 50% methanol solutions containing

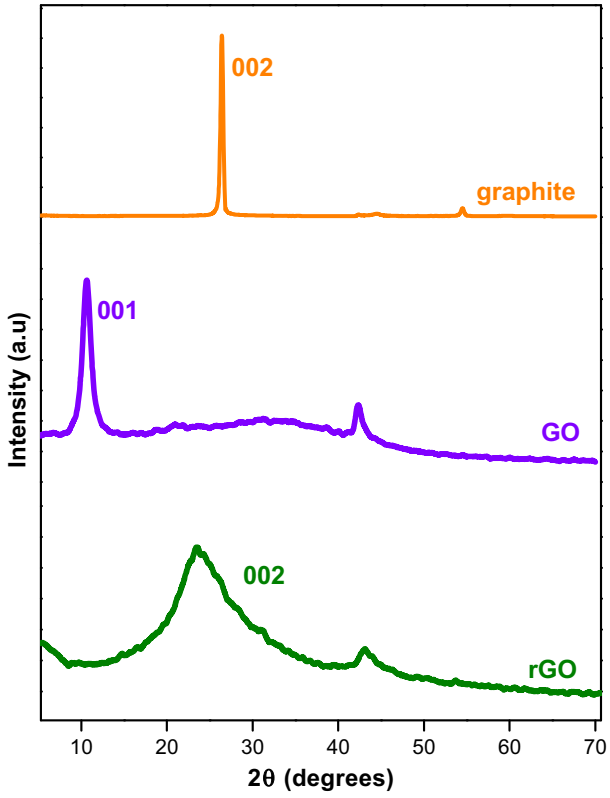

Fig. 1. X-ray diffraction patterns of graphite powder, GO and rGO sheets.