Grape extract assisted green synthesis of reduced graphene oxide for water treatment application

Ravi Kant Upadhyay [a], Navneet Soin [b], Gourav Bhattacharya [c], Susmita Saha [d], Anjan Barman [d], Susanta Sinha Roy [c,*]

[a] Department of Chemistry, School of Natural Sciences, Shiv Nadar University, Gautam Budh Nagar 201314, Uttar Pradesh, India
[b] Knowledge Centre for Materials Chemistry (KCMC), Institute for Materials Research and Innovation (IMRI), University of Bolton, BL3 5AB, UK
[c] Department of Physics, School of Natural Sciences, Shiv Nadar University, Gautam Budh Nagar 201314, Uttar Pradesh, India
[d] Department of Condensed Matter Physics and Material Sciences, S. N. Bose National Centre, Block JD, Sector III, Salt Lake, Kolkata 700098, India

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ABSTRACT

Grapes (*Vitis vinifera*) extract was explored as a "green reducing agent" for the preparation of reduced graphene oxide (RGO) from graphene oxide (GO). The effect of reduction time on physical, chemical and optical properties of the RGO was also investigated. Synthesized RGO samples exhibited excellent activity as an adsorbent for the removal of organic dye. Proposed synthesis is environmental friendly, cost effective and promising for the large scale production of RGO.

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1. Introduction

Graphene, owing to its exotic physical and electrical properties has led the recent advances in material sciences and is finding its way into various fields including electronics, biomedical, environment and engineering [1]. Chemical reduction of graphene oxide (GO) is one of the highly explored synthesis approaches for the graphene preparation. The synthesis approach involves oxidation of graphite via Hummers method followed by chemical reduction using harsh chemical reducing agents e.g., hydrazine [2] and NaBH$_4$ [3]. The involvement of hazardous chemical reducing agents in the second step is a major drawback and ongoing efforts are there to find environment friendly and safe green reducing agents. Environmentally benign reducing agents such as ascorbic acid [4], sugar [5], amino acids [6] and plant extracts [7,8] have recently been utilized for the reduction of GO to reduced graphene oxide (RGO). Plant extracts are attractive alternatives to the toxic chemical reducing agents as these are easily available, comparatively cheap and environmental friendly.

Grapes (*Vitis vinifera*) extract is a rich source of phytochemicals e.g., polyphenols, flavonoids and catechins, which are capable of reducing gold and silver salts to their metallic form [9]. Apart from preparation of metal nanoparticles, grapes extract has also shown remarkable performance as a reducing agent for the selective reduction of ketone [10] and nitro compounds [11]. These reports confirm that grapes extract holds immense potential as a reducing agent. The phytochemicals present in the grapes extract are of great medicinal value and also environmentally benign, which makes these an attractive alternative to the conventional toxic reducing agents.

2. Experimental

Graphite LR was procured from Alfa Aesar. Fresh grapes were purchased from local market. De-ionized water was used in the preparation of all the solutions.

Graphene oxide was prepared using modified Hummers method [12–14]. Typically, 1 g of graphite and 23 ml of concentrated H$_2$SO$_4$ were taken in a conical flask and the reaction mixture was placed on an ice bath. About 3 g of KMnO$_4$ was slowly added to the reaction mixture under constant stirring at temperatures of 0–5 °C and was further stirred for another 30 min. The flask was then transferred on a hot plate with a preset temperature of 35 °C, and kept for 1 h. After completion of heating period, 46 ml of de-ionized water was added to the reaction mixture followed by vigorous stirring. As obtained reaction mixture was then

* Corresponding author.
  E-mail address: susanta.roy@snu.edu.in (S.S. Roy).

further heated on a boiling water bath for 30 min. 10 ml of 30% H_2O_2 was added to the reaction mixture to stop the reaction, followed by addition of 140 ml of de-ionized water. Yellow color graphene oxide was obtained which was filtered and washed repeatedly using 10% HCl followed by de-ionized water and ethanol.

40 g grapes were crushed and transferred into a round bottom flask containing 100 ml de-ionized water. As prepared reaction mixture was heated up to boiling and allowed to boil for 10 min. After completion of heating the reaction mixture was allowed to cool down to room temperature and filtered to obtain a red color extract. 30 mg GO was added to the 50 ml extract and stirred vigorously in order to disperse the GO uniformly throughout the extract. 180 μl aqueous NH_3 solution was added to the above reaction mixture, which changed the color of it from red to dark green. Reaction mixture was placed on an oil bath and heated at 95 °C for different time intervals (1, 3 and 6 h) with a water condenser to avoid the evaporation of water. After completion of heating periods, the RGO samples were filtered, washed and dried in an air oven at 70 °C.

UV–vis spectra of aqueous dispersion of GO and RGO samples were recorded using UV–vis spectroscopy (Thermo Scientific Evolution 201). X-ray analysis was performed using Rigaku miniflux X-ray diffractometer (XRD). Morphology and structure of RGO was investigated using transmission electron microscope (TEM, TECNAI G220 S-TWIN).

20 mg RGO-6 h was added to the 100 ml malachite green (MG) solution (5 ppm). A fixed volume of the dye solution was taken out after regular time intervals and centrifuged for the removal of RGO. Absorbance for all extracted dye samples was recorded at 617 nm. Removal percentage was estimated by using the following formula [15].

$$\text{Removal percentage} = (A_0 - A_t)/A_0 \times 100 \qquad (1)$$

where A_0 is the initial absorbance of dye and A_t is absorbance after a time interval t. The adsorption amount q_t was calculated using following equation [16]:

$$q_t = [(C_0 - C_t)V]/m \qquad (2)$$

where q_t is the amount of adsorbed dye per gram of the adsorbent (mg/g), C_0 and C_t are the concentrations of the MG solution (mg/L) at the initial and adsorption time t, respectively. V is the volume of the MG solution (L) and m is the mass of the adsorbent (g) used.

3. Results and discussion

The UV–vis spectrum of GO (Fig. 1a) exhibits a peak at 230 nm and a shoulder peak at 300 nm. The peak at 230 nm can be corresponded to π–π^* transitions of aromatic C=C, while the shoulder peak originates from n–π^* transition of the C=O bonds

[17]. The absorption spectra of RGO samples (Fig. 1b) exhibit a single peak around 270 nm. This red shift in the absorption spectrum from 230 to 270 nm points towards the restoration of sp^2 hybridized carbon network due to removal of the oxygen bearing functional groups. An increase in the absorbance around 600 nm on increasing the reduction time from 1 to 6 h has also been observed (Fig. 1b).

The FTIR spectrum of GO (Fig. 1c) comprises of a broad peak at 3180 cm^{-1} and a sharp peak at 1615 cm^{-1}, which can be ascribed to stretching and deformation vibrations, respectively of physically adsorbed water. Peaks at 1715, 1360 and 1040 cm^{-1} can be corresponded to C=O, COO^- and C–O stretching vibrations, respectively. However, with the increase in the reduction time the intensity of these peaks reduced significantly and after 6 h of reaction time, most of the peaks assigned to oxygen containing groups almost disappeared (Fig. 1c), confirming the efficient reduction of GO by the grapes extract.

The X-ray diffraction pattern of graphite exhibits one sharp basal reflection peak at 2θ value of 26° (d-spacing of ~0.357 nm) corresponding to (002) plane (Fig. 2a). Oxidation of graphite to graphene oxide results in a shift in this peak towards lower 2θ value 10.4° (d-spacing ~0.850 nm). This large increase in the d-spacing indicates the intercalation of water molecules as well as formation of oxygen containing functional groups in between the graphite layers. In the case of RGO-6 h sample, the sharp peak at 10.4° disappeared; however, a broad peak at approximately similar 2θ value can still be observed suggesting the presence of residual oxygen functionalities in the sample. Simultaneously, a new broad peak, centered at 23.7°, was also observed indicative of the formation of few layered graphene structure [18,19]. The transmission electron microscopy image of RGO-6 h sample shows that the sample consists of aggregated and wrinkled few layers of graphene (Fig. 2b). These wrinkles and corrugations endow thermodynamic stability to the two-dimensional graphene sheets.

For dye adsorption experiments, 20 mg GO and RGO samples were utilized to treat 100 ml malachite green solution (5 ppm). Fig. 3 shows absorption spectra of dye solution treated with RGO-6 h sample for different time durations. A sharp decrease in the absorbance for the initial 5 min indicates that most of the dye was removed in first 5 min. Graph plotted between removal percentage and time (Fig. 3 inset) shows that for all the samples (GO, RGO-1 h, RGO-3 h and RGO-6 h) most of the dye has been removed in first 10 min, after which the adsorption process achieved equilibrium. The order of removal percentage for all the samples was found to be following:

GO < RGO − 6 h < RGO − 1 h~RGO − 3 h

The removal percentage of the GO was found to be lowest as compared to RGO-1 h, RGO-3 h and RGO-6 h samples. We believe that the reason behind the lowest removal percentage for the GO might be the presence of trace amount of GO which leftover in the
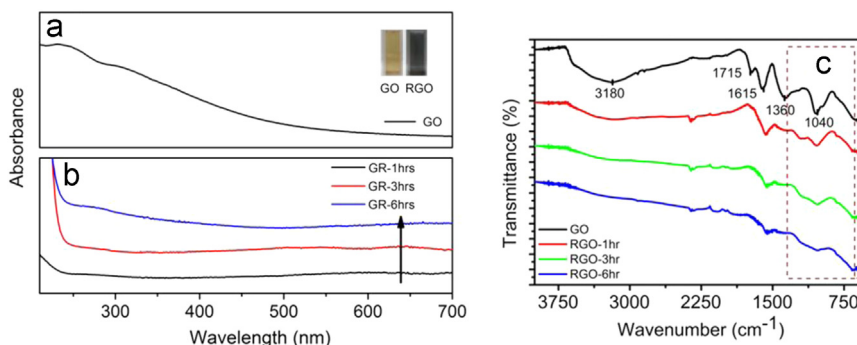

Fig. 1. (a) UV–vis spectrum of GO and real pictures of GO and RGO aqueous suspension (Inset) (b) UV–vis spectra of RGO samples (c) FTIR spectra of GO and RGO samples.