

Research Article

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Synthesis of Graphene Oxide Through Ultrasonic Assisted Electrochemical Exfoliation

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Abstract: We report a ‘green’, simple and efficient approach for the production of graphene oxide (GO) by ultrasonic assisted electrochemical exfoliation of graphite rods, and by using Improved Hummers’ graphene oxide (IGO) as an electrolyte. The effects of applied bias, electrolyte concentration and the duration of the electrochemical exfoliation on the quality of the GO nanosheets were investigated. The produced graphene oxide with a high yield (> 48%), and the lowest defect was obtained in the ultrasonic assisted electrochemical exfoliation performed at 0.05% IGO mass percent in DI water and 50 V applied bias for 1 hour at room temperature. The structural, morphological and physical properties of the obtained nanostructures were analyzed by XRD, Raman, FESEM, STEM techniques and thermal conductivity analysis, respectively. The characteristic Raman bands were observed at 1354 cm^{-1} and 1590 cm^{-1} for the prepared GO nanosheets. The produced graphene oxides exhibited a lateral dimension of $3\text{--}7\text{ }\mu\text{m}$ revealed by field emission scanning electron microscopy (FESEM). It was observed that the thermal conductivity enhancement of 14.95% was obtained for GO, which was higher than the other IGO nanofluid (7.64%) with respect to DI water at 20°C .

Keywords: Graphene oxide (GO); Electrochemical exfoliation; Ultrasonic Energy; Graphene; Graphite rod.

PACS: 81.05.ue Graphene, 82.45.Hk Electrolysis

1 Introduction

Graphene is a two-dimensional (2D) sheet formed from sp^2 bonded regular carbon atoms in a hexagonal crystal lattice. Graphene has a major potential in commercial applications and numerous applications in supercapacitors, solar cells and sensors due to its extraordinary properties including an ultra-high specific surface area, high carrier mobility, unique thermal conductivity, chemical stability and elasticity [1-2]. Therefore, scientists are pursuing the development of a wide variety of technologies for synthesizing high-quality low-cost graphene in large quantities. Graphite oxide or aggregated graphene oxide is an oxygenated graphene lattice with the functional groups on their basal planes and edges and is mostly used as a precursor in the production of graphene [3-4]. Although Hummers’ or Improved Hummers’ method is widely used to synthesize GO sheets, because of the usage of strong acids and oxidizing mixtures, it may cause impurities/defects in the final products [5]. Among the other methods, the electrochemical exfoliation method has many advantages, such as being a fast, simple instrumentation and cost-effective due to avoiding complex and expensive organic compounds [1].

In the literature, an electrochemical exfoliating method using KCl solution as an electrolyte has been reported for preparing GO layers from graphite, but this process requires a pretreatment of graphite foil by immersing the graphite in a concentrated sulphuric acid and takes a long exfoliation time as 10 hours [3]. In the electrochemical production of graphite oxide, graphite anode is electrochemically oxidized in deionized water (DI water) rather than sulphuric acid, ammonia solution or other oxidants. Although graphite oxide is produced in an environmentally friendly medium, the separation process needs several steps with the yield of 0.04 wt% after 7 days reaction also with the synthesis of mellitic acid as a co-product [6]. By using pure water as an electrolyte the production of graphene oxide is reported by applying a high oxidation voltage ($\sim 150\text{ V}$) at the graphite electrode. While the proposed method offers a short processing

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time (<1 hour) and a highly pure product, the electrolytic graphene oxide film is obtained on graphite substrates and is not proper for large scale production and they have many pores and defects as a result of the applied high voltage [7].

As the DI water has an insulating property, we added little mass percent of IGO in DI water to improve the conductivity, so we overcame the needs of high oxidation voltage and harsh-expensive and toxic electrolytes. For the production of GO from the exfoliation of graphite rods by using IGO as an electrolyte, the usage of the synergistic effects of ultrasound energy and electrochemical exfoliation has not been reported yet.

In this study, GO nanosheets were successfully produced by the ultrasonic energy assisted electrochemical exfoliation method. The properties of the obtained GO were analyzed and compared with IGO nanosheets using XRD, Raman, FESEM, STEM and Thermal conductivity analysis.

2 Experimental

Graphite rods (cylindrical, 6 mm dia. x 30 cm long, with 5 ppm or less purity, Bay Carbon Inc., USA) were used as anode and cathode electrodes. A different mass percentage of IGO (0.075%, 0.05%, 0.025%, 0.01%) in 250 ml DI water was used as electrolytes. According to the dynamic structural model (DSM), graphene oxide generates C-C bond cleavage, the formation of vinylogous carboxylic acids and protons after the interaction with water and considered a weak acid [8]. The area immersed into the electrolyte of the cathode graphite rod was about 5 times larger than that of the anode graphite, and the distance between them was set to 2 cm. The electrodes and electrolyte were placed in an ultrasonic bath, and the electrodes were connected to a DC power supply. The exfoliations started at 5 different constant biases (10 V, 25 V, 50 V, 75 V and 100 V) for 3 different times (30 min, 1 h and 3 h) at room temperature. The solution temperature in the beaker was maintained at 70-80°C. When a DC voltage of 10 V and higher was applied to a graphite electrode, the graphite flakes began to exfoliate and disperse in the electrolyte solution. With the applied higher voltage above 50 V, electrochemical oxidation reactions were initiated by the hydrogen gases generated from the hydrolysis of water, conversion of GO flakes into humic acid like structures and the generation of hydrogen cations (protons) at the surface of the electrodes [8-9]. The external force provided by the ultrasonic force

overcame the van der Waals forces between the graphite's adjacent sheets; and thus the exfoliation of the expanded/fractured sheets to the graphene/graphene oxides. The colloidal graphene/graphene oxide sheets were collected and centrifuged for 5 minutes at 20 000 rpm which was repeated 6 times to remove large agglomerates, then they filtered out the decant portions, and the final product was dried at 60°C for 24 hours under a vacuum.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

The amount (%) of each type of graphene (graphene, graphene oxide), the interlayer distance and the crystallite of the GO sizes were calculated from the XRD patterns and expressed as the ratio of the fitted peak area to the total area of the diffractogram. An optimum GO sample was selected from the experiments, by calculating the average number of layers and the amount of (%) of each type of graphene by varying the electrochemical parameters (applied bias, electrolyte concentration and time) [10]. First, to study the effect of the applied potential on the products obtained by ultrasonic assisted electrochemical exfoliation, the effect of the potential applied in the range of 10-100 V was studied while the other conditions were kept constant (0.05% GO-DI water, 1hour reaction time). It has been observed that the potential below 10 V were not sufficient for the exfoliation due to the low conductivity of the graphene oxide-DI water electrolyte solution. Contrary, the graphite rods used in exfoliations performed at a higher voltage above 100 V, were damaged in a short time and were difficult to separate due to the aggregation of the GO nanoparticles in the resulting dispersion. Surface investigations carried out with FESEM also showed the damages, cracks and voids on the graphene oxide nanostructures with the application of high oxidation voltage. Therefore, the study used 10V-25V-50V-75V and 100 V voltages. Second, to obtain the most suitable electrolyte concentration, the applied potential and time for the electrochemical exfoliation was fixed (50 V and 1 hour), and different % electrolyte mass ratios were compared. The experiments that were carried out at a 0.05% IGO mass percentage electrolyte concentration, gave the highest amount of graphene oxide. However, it was indicated that the exfoliation time was proportional to the amount of the obtained exfoliated material [10]. Also, the composition and the morphology of the products could be easily controlled by adjusting the

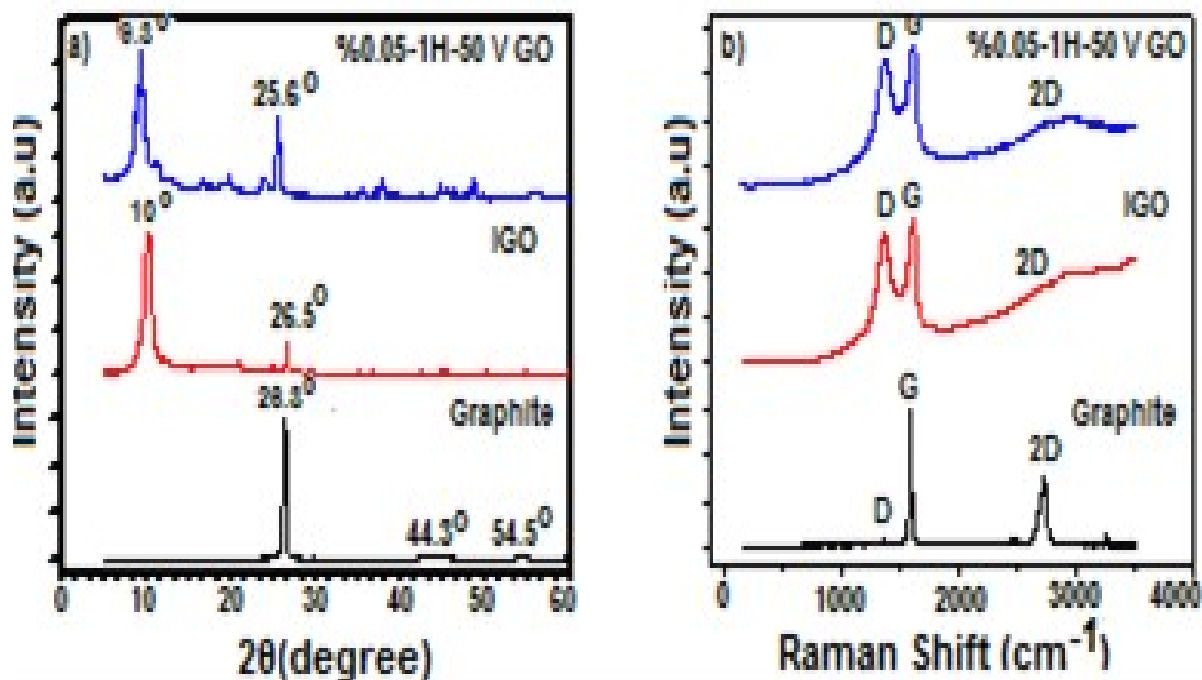


Figure 1: a) XRD patterns and b) Raman spectrum of graphite rods, IGO and 0.05%-1h-50V GO sheets.

applied voltage, electrolyte concentration and exfoliation time and consequently, 0.05-1h-50 V (0.05% IGO mass percent, 1hour reaction time and 50 V applied bias) was selected as the best experimental condition. Moreover, the present method is an environmentally friendly way to prepare graphene oxide because only DI water with a small amount of IGO is used as an electrolyte solution. After the ultrasonic-assisted electrochemical exfoliation, the obtained product was washed with a large amount of DI water by centrifugation to remove the impurities, strong acids and/or oxidants such as manganese peroxide contained in the IGO nanosheets.

X-ray diffraction patterns and the Raman spectrum of graphite rods, IGO and 0.05%-1h-50V GO sheets are presented in Figures 1(a) and (b), respectively. The characteristic diffraction peaks of graphite rods were located at 26.3° as an intensive peak and 44.3° , 54.5° (2θ values) corresponding to 002, 101 and 004 reflections, respectively (ICDD-PDF #411487) and calculated pattern (PDF 75-1621) (Figure 1a) [11, 12]. The strong peaks at $2\theta \approx 10^\circ$ and 9.3° , showing the presence of oxygenation on the basal planes of few layered graphene sheets, are called as GO nanosheets. Consequently, d-spacing values were obtained as 0.898 nm and 0.950 nm for IGO and 0.05%-1h-50V GO sheets, respectively [13].

In Figure 1(b), the characteristic Raman bands of graphite are shown as a weak D band at 1356 cm^{-1} , a

prominent G band is seen around $\sim 1583\text{ cm}^{-1}$ and a broad 2D band at $\sim 2723\text{ cm}^{-1}$. In the Raman spectra of IGO and 0.05%-1h-50V GO, as compared to graphite, the G bands are broadened and shifted to higher wave numbers as 1596 cm^{-1} and 1599 cm^{-1} , respectively. However, the high intensity and also broadened D bands in the Raman spectra of IGO and 0.05%-1h-50V GO, indicate the oxidation between the graphite layers [14].

Figure 2 presents the FESEM micrographs of the the IGO nanosheets and selected samples of the ultrasonic assisted electrochemical exfoliated graphene oxide (UAEGO) nanosheets. 0.05%-1h-50V GO nanosheets show edge-corrugated sheet structures which have a lateral dimension in the range of $3\text{ }\mu\text{m}$ to $7\text{ }\mu\text{m}$ (Figure 2a). For the UAEGO nanosheet samples, relatively thick nanosheets were obtained at an applied low bias (Figure 2d); and with the increase in the applied bias, the exfoliated sheets showed an increment in their domain size with larger platelets and irregular structures (Figure 2e). The FESEM images of the IGO samples clearly show that they have randomly arranged the crumpled nanosheets (Figure 2f).

Figure 3 presents STEM images of the 0.05%-1h-50 V GO and IGO samples. In all figures, the samples reveal a mixture of multi-layer graphene oxides (black areas) with few-layer graphene oxides (more transparent zones). The less transparency of 0.05%-1h-50 V GO samples confirm that they have fewer layers than the IGO samples [15].

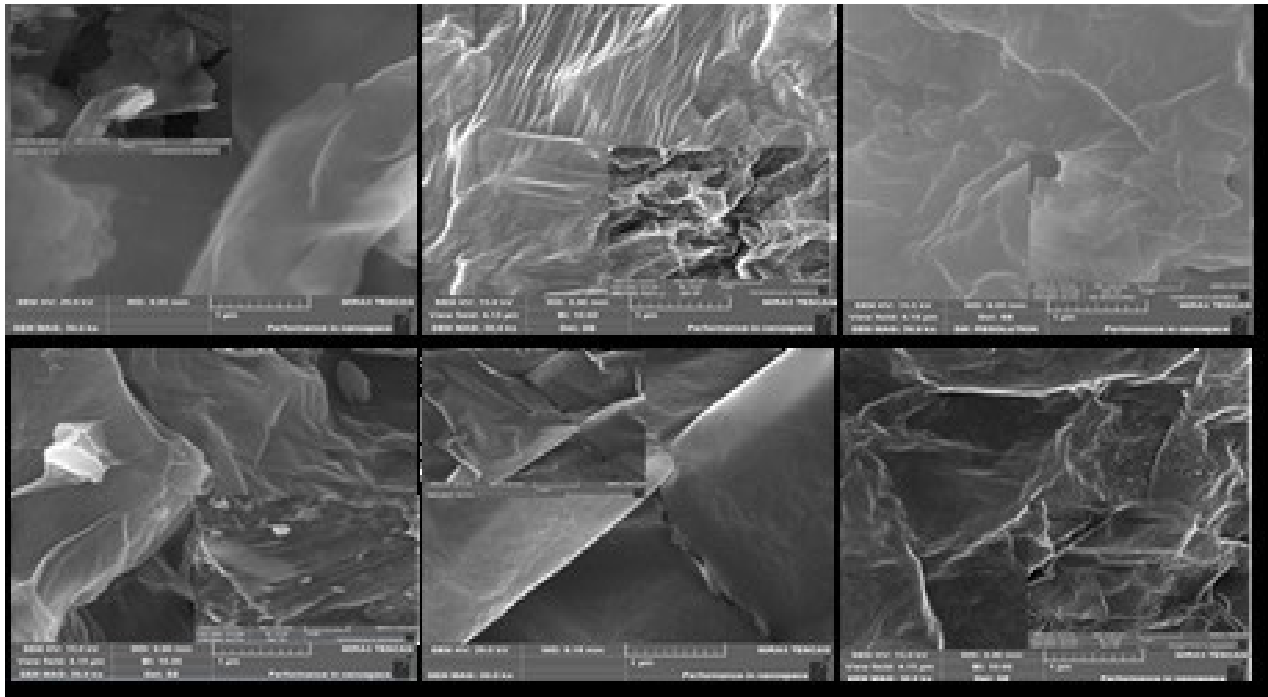


Figure 2: FESEM micrographs of a) 0.05%-1h-50V GO, b) 0.05%-30min-50V GO, c) 0.025%-1h-50V GO, d) 0.025%-1h-25V GO, e) 0.025%-1h-75V GO, f) IGO at 50.00 kx magnification (Inset images at 20.00 kx magnification).

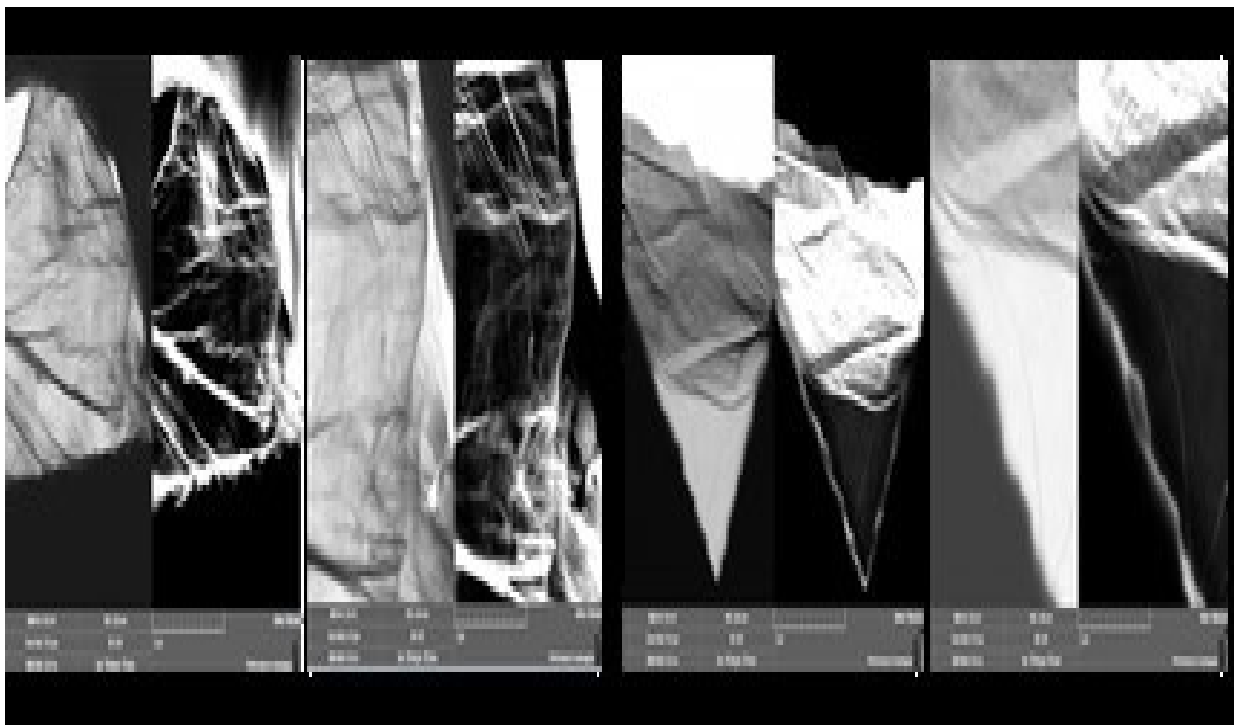


Figure 3: STEM images of 0.05%-1h-50V GO nanosheets at a₁) 20.00 kx, a₂) 50.00 kx magnification, Improved Hummers' GO nanosheets at b₁) 20.00 kx and b₂) 50.00 kx magnification.

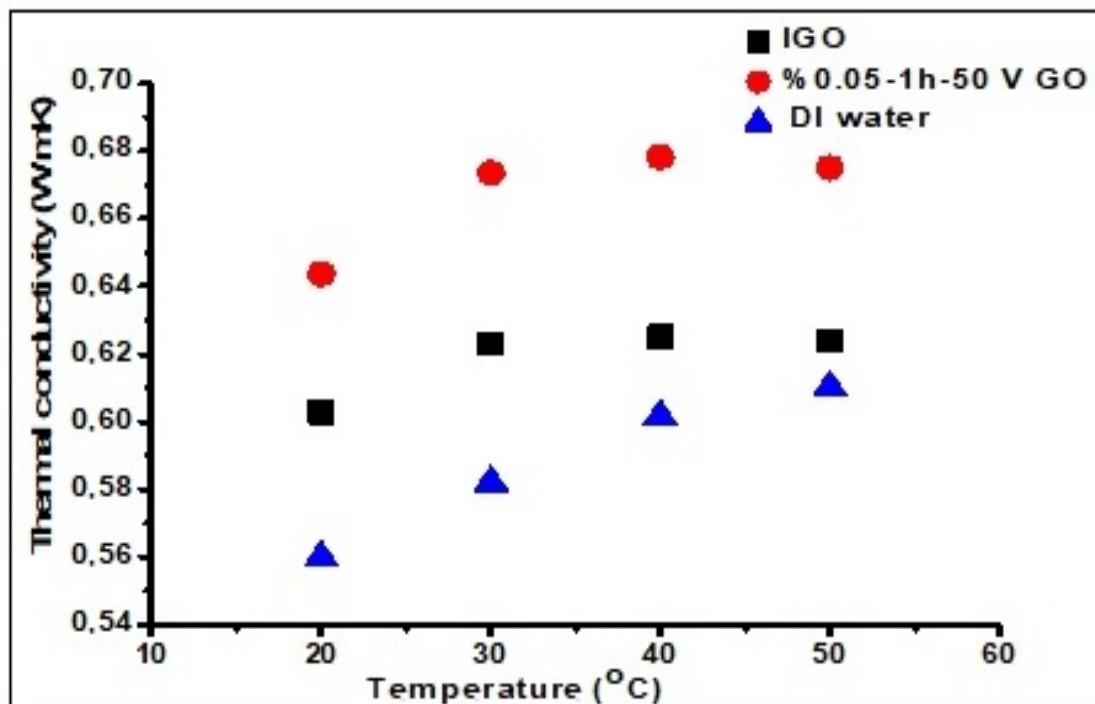


Figure 4: Thermal conductivity of 0.05%-1h-50 V GO and IGO samples.

Thermal conductivity of 0.05%-1h-50V GO and IGO samples at different temperatures was shown in Figure 4. At all the temperatures all graphene oxide nanofluid samples have higher thermal conductivities than the DI water (base fluid) [16]. 0.05%-1h-50V GO and IGO nanofluids showed 14.95% and 7.64% thermal conductivity enhancement with respect to DI water at 20°C, respectively. The thermal conductivity enhancement of IGO is similar to the GO nanofluids prepared by the modified Hummers' method which was 6.78% with respect to DI water at 20°C. The highest thermal conductivity enhancement obtained with 0.05%-1h-50V GO might indicate that, they had more potential as heat transfer fluids than the others [17].

4 Conclusion

Graphene oxide has been successfully prepared through the ultrasonic assisted electrochemical exfoliation method in an environmentally friendly route at 0.05% IGO mass percentage in DI water, 50 V applied bias for 1 hour at room temperature. FESEM micrographs indicated that the high quality and larger flake sized graphene oxides (0.05%-1h-50V GO sheets) with the lowest defects were obtained at a high yield (>48%) in the experimental conditions. It has been proven that the ultrasonic assisted

electrochemical exfoliation method resulted in higher amounts of oxygenated functional groups and a less layered GO structure compared to the Improved Hummers' method by XRD and STEM analyses, respectively. Thus, the present method is very useful for the simple, efficient and environmentally friendly production of GO nanosheets avoiding the usage of complex, organic compounds and strong acids, and therefore will find many application areas.

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