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Eco-Friendly Synthesis and Characterization of Reduced Graphene Oxide

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Abstract. Graphene is a single sheet of sp^2 bonded carbon having a two-dimensional (2D) layer. It has remarkable electronic, mechanical and thermal properties. In this paper, the graphene oxide (GO) was reduced by reducing chemicals such as ascorbic acid and hydrazine and then characterized by transmission electron microscopy (TEM), Raman spectroscopy and Fourier transform infrared spectroscopy. TEM results of the chemically reduced graphene were showed that the structure consists of a mixture of single and few layers of reduced graphene oxide (rGO).

1. Introduction

Graphene is a hexagonal lattice structure of one atom thick layer and includes σ bond between sp^2 hybridized carbon atoms. Graphene has properties such as outstanding surface area to mass ratio (2,630 m^2/g), high thermal conductivity (5,000 W/mK), optical transparency (~97.7 %) and high electron mobility ($2,5 \times 10^5$ cm^2/Vs) [1-3]. The unique properties of graphene can be employed in a range of applications such as electronic, composite material, batteries and sensor technology. Due to the high demand for graphene, several fabrication methods such as epitaxial growth (SiC) [4], chemical reduction [5], chemical vapour deposition (CVD) [6] and liquid phase exfoliation [7], have been developed in recent years. Among the four methods, chemical synthesis is considered the best since it is easier, inexpensive and yields large quantities. The researchers have applied different types of reducing agents in order to convert graphene oxide to graphene and then confirmed that hydrazine and ascorbic acid had the ability to remove oxygen functionalities of GO [8,9].While the hydrazine is highly toxic, the ascorbic acid is an eco-friendly and non-toxic reducing agent.

2. Experimental

Materials: Natural graphite power, concentrated sulfuric acid (H_2SO_4, 98%), Potassium permanganate ($KMnO_4$), Hydrogen peroxide (H_2O_2,30%), L-(+)- Ascorbic acid, L-trypotophan, Phosphorus pentoxide, hydrazinehyrate, Potassium persulfate aqueous solution were all analytical grade and purchased from Sigma Aldrich.

Preparation: The technique employed in this study is a two-step process. In the first step, graphene oxide is obtained by oxidation of graphite powder and the following step includes the reduction of graphene oxide. Graphene oxide was prepared by the Hummers method [10] (HGO) and modified

Hummers method (MGO) [11]. Subsequently, graphene was synthesized by using reductant chemicals such as hydrazine hydrate [12] (HIGO) and ascorbic acid [13] (VIGO).

Characterization: Graphene oxide, MGO, HIGO and VIGO sample were freeze-dried and then grounded into power. The CTEM images was obtained using Model FEI Tecnai G2 (TWIN) the range from 20-200 kV. The Raman spectra were recorded from 100 to 3500 cm^{-1} on Senterra Bruker Raman Microprobe using a 532 nm/20nW Nd oil laser. The FTIR spectra of graphene oxide, HIGO and VIGO samples were recorded over the range 4000-400 cm^{-1} on a Vertex 70v FTIR spectrometer.

3. Results and Discussion

The surface morphology and crystallinity of the GO and rGO were analyzed using CTEM and Selected Area Electron Diffraction (SAED) pattern as shown in Figure 1. Both GO and rGO showed transparent, surface rough or wrinkled structure under the CTEM. The CTEM result of the samples HGO and MGO shows the sheet like morphology comprised of many layers of graphene oxide. Researchers defined ultrathin silk veil structure with fold and scroll on its edges [14].
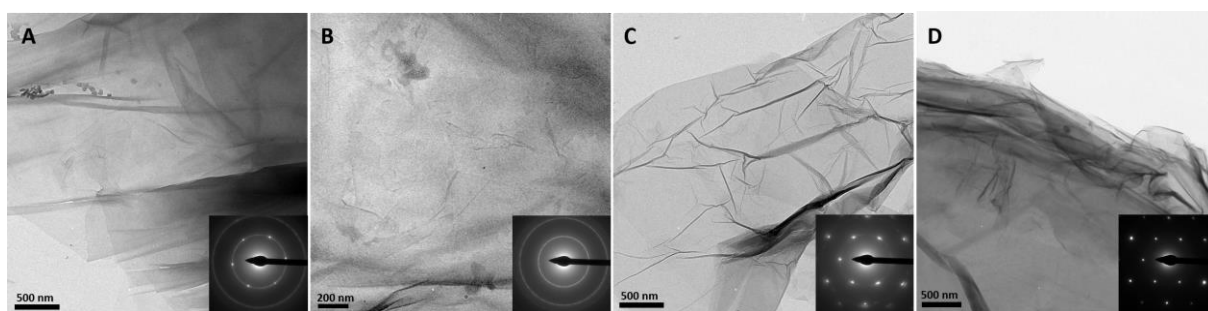

Figure 1. a) CTEM images of HGO, b) CTEM images of MGO, c) CTEM images of HIGO, d) CTEM images of VIGO.

The structure of graphene oxide (GO) is different from reduced graphene oxide (rGO) in SAED analysis. It was observed that the SAED pattern of the rGO has clear diffraction spots with a six-fold pattern that is compatible with the hexagonal lattice. Moreover, for single layer rGO, the intensity of the outer hexagon spot is almost similar to or less than that of the inner one. According to the SAED analysis, the structure consists of a mixture of single and few layers of rGO (VIGO).

Raman spectroscopy is an efficient technique to determine the number of graphene layers and the change of crystal structure of GO and rGO. There are two main bands, the D band and the G band together with weak 2D (also called the G′) band. The D band is related to disorders and defects in graphene. The G band is Raman active for sp^2 hybridized carbon-based material. The 2D (the G′) band is used to determine whether the graphene is single or few layered. Raman spectrum of graphite, GO and rGO are shown in figure 2 and 3.
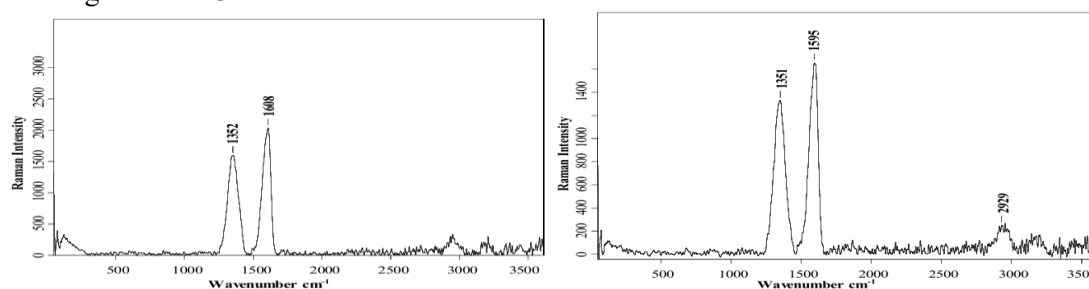

Figure 2. a) Raman spectrum of HGO, b) Raman spectrum of MGO.

The two main bands in the graphite spectrum are known as the G band at ~1582 cm^{-1} and the 2D band at ~2685 cm^{-1}. On the other hand, The Raman spectra of graphene oxide (HGO and MGO) displays a D band at ~1350 cm^{-1} and a broad G band at ~1580 cm^{-1}. The D band of the Raman spectrum of graphene oxide is prominent. This results in the degradation of the in-plane sp^2 domain in graphene oxide owing to the extensive oxidation.
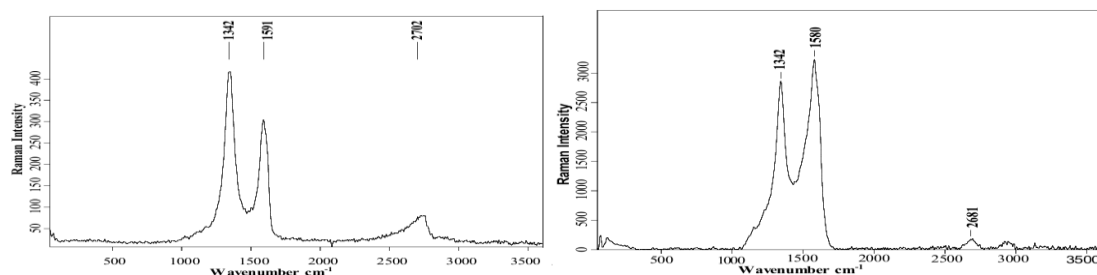

Figure 3. a) Raman spectrum of HIGO, b) Raman spectrum of VIGO.

Raman spectra of the VIGO are observed in the D band at approximately 1340 cm^{-1} and the G band at 1580 cm^{-1} together with a weak 2D band around 2700 cm^{-1} [15]. Structurally, the D band and G band of the rGO are sharper and more intense as against those of graphene oxide. Moreover, the intensity ratio of D band and G band (I_D/I_G) indicates the oxidation degree and the size of sp^2 ring clusters in a sp^3/sp^2 hybrid network of carbon atoms. The (I_D/I_G) intensity ration chemically reduced graphene is 1,37 which is larger than that of graphene oxide 0,80. This result suggests that more sp^2 domains are formed during the reduction of graphene oxide.
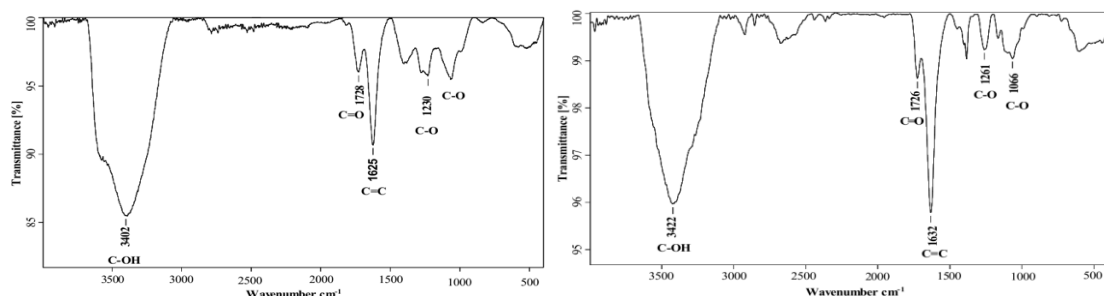

Figure 4. a) FTIR spectra of HGO, b) FTIR spectra of MGO.

To investigate the different types of functional groups formed in the GO and rGO, FT-IR spectroscopy was used. The FT-IR spectra of graphene oxide (HGO and MGO) are shown in figure 4. Firstly, the broad peak at 3000-3500 cm^{-1} originates from stretching vibrations of -OH group, and the peak observed at 1700-1750 cm^{-1} stretching vibrations of carboxyl peaks (C-O). Another aromatic C=C peak appears between the peak at 1600-1650 cm^{-1} and at 1000-1280 cm^{-1} stretching vibrations of epoxy C-O groups. Finally, the peak showed alkoxy stretching vibrating between the peak at 1040-1170 cm^{-1}.
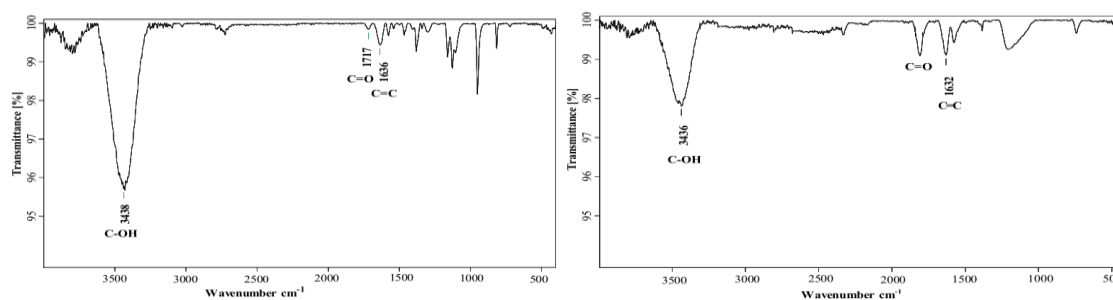
Figure 5. a) FTIR spectra of HIGO, b) FTIR spectra of VIGO.

The FT-IR spectra of rGO in figure 5 shows three peaks, the broad and intense peak at ~3400 cm^{-1} arising from–OH stretching vibration, a peak at ~1720 cm^{-1} due to C=O stretching vibrations of carboxylic groups and sharp C=C band within the range of 1600 cm^{-1}. As can be seen in Figure 5, the absorption peaks containing oxygen such as, epoxy and alkoxy vibration peaks disappeared in HIGO and VIGO. This result confirms that the atomic frame of sp^2 carbon is formed in reduced by graphene oxide.

4. Conclusions

The reduction of graphene oxide by ascorbic acid formed sp^2 structures and was found to increase regular structures in comparison to hydrazine. The chemical reduction of graphene oxide by ascorbic acid is found to be a very promising technique for large scale production of reduced graphene (rGO). The ascorbic acid reduction technique does not contain toxic agents, which provides eco-friendly and high quality graphene when compared to other known techniques. The use of hydrazine hydrate as the reductant has also been revealed not to be biocompatible. Consequently, excellent chemical reduction of graphene oxide by ascorbic acid can be utilized for tissue engineering and other biomedical applications in the future.

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