

Effect of Ascorbic acid Concentration on Electrical Conductivity of reduced Graphene oxide

Kanpichcha Jaroensil, Voranuch Thongpool, and Sumonman Niamlang*

Abstract—The reduction of graphene oxide (GO) by Hummer's methods was investigated using Ascorbic acid. The prepared GO and Ascorbic acid reduced GO (RGO) were characterized by SEM, XRD, Fourier transform infrared, Raman spectroscopy, ultraviolet-visible spectroscopy and electrical conductivity.

Keywords—Graphene oxide; Reduced Graphene oxide; Ascorbic acid; Electrical conductivity.

I. INTRODUCTION

GRAPHENE is a fascinating two dimensional single layered hexagonal lattice of various carbon allotropes with atomic thickness which has been studied extensively in various energy and environmental application.^[1] The preparation of graphene was achieved with various method such as electrochemical methods^[2], chemical reduction of graphene oxide^[3], ion exchange methods^[4], hydrothermal reduction methods^[5] and sol-gel methods^{[6][7]}. Among these, chemical reduction of graphene oxide presents very easier route for the production of good quality graphene. However, chemical reduction of graphene oxide employ hazardous chemicals reducing agents e.g. hydrazine and NaBH₄. Recently, environment-friendly chemical agents, such as glutathione^[8], sugar^[9], clove^[10] and wild carrot root^[11] have been reported to reduced graphene oxide.

Ascorbic acid is a naturally occurring organic compound with antioxidant properties. It is a white solid, but impure samples can appear yellowish. It dissolves well in water to give mildly acidic solutions.

In this paper, The graphene oxide (GO) was produced using simplified Hummer's methods. Ascorbic acid was used as a reducing agent. The reduction graphene oxide (RGO) was characterized by Scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR), UV-VIS spectrophotometer (UV-VIS), Raman spectroscopy (Raman). The electrical conductivity of RGO was also reported.

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II. MATERIAL

Graphite flakes (purity 99%) were obtained from Loba Chemie, Kolkata, India. Concentrated sulphuric acid (98%), hydrogen peroxide (H₂O₂, 30%) and concentrated hydrochloric acid (30%) were purchased from Merck, India and were used as received. Potassium permanganate (KMnO₄) was obtained from Analytical Rasayan, India and was used as an oxidizing agent.

III. PREPARATION OF GRAPHENE OXIDE

GO was synthesized from graphite by a modified Hummer's method^[12]. The 5 g of graphite was mixed with 100 mL of H₂SO₄ in an at temperature 0°C for 15 min. While maintaining magnetic vigorous stirring, a certain amount of KMnO₄ (15 g) was added to the suspension. The mixture was stirred for 15 min at room temperature and 400 mL of H₂O was then slowly added to the mixture. The synthesized GO was obtained. The reaction temperature was rapidly increased to 98°C, and the color changed to light brown. Finally, the mixture was rinsed and filtration with deionized water for several time until pH equal to 7. Synthesized GO was dried in oven at 60 °C for 24 hr.

IV. REDUCTION OF GRAPHENE OXIDE BY ASCORBIC ACID

To reduce GO, 0.30 g of GO was dispersed in 100 ml of water by sonication for 30 min. To study the effect of ascorbic acid on electrical conductivity of RGO, The various amount of ascorbic acid was added into the solution; 100, 300 and 500 mg for 2 hr. After reduction reaction, RGO solution were filtration and rinsed with water for several time to remove the unwanted materials. The RGO were dried in an air oven at 60°C and stored in the air light container for further investigated.

v. ELECTRICAL PROPERTIES MEASUREMENT

The sheet resistivity of the top emitter layer is very easy to measure experimentally using a "four point probe". A current is passed through the outer probes and induces a voltage in the inner voltage probes. The junction between the *n* and *p* -type materials behaves as an insulating layer and the cell must be kept in the dark. A schematic diagram of the test circuit for measuring bar specimen resistivity by the FPP method is presented in Figure 1 A constant current, *I*, was applied to the bar specimen through two outside probes with the help of a DC power source, and then the steady voltage across the other

inside two probes, V was determined. According to the FPP method theory, for a circle specimen of finite thickness, w , the resistivity, ρ , is calculated as

$$\rho = \frac{\pi}{\ln 2} w \left(\frac{V}{I} \right)$$

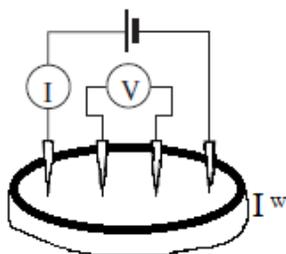


Fig. 1 Schematic diagram of test circuit for measuring specimen resistivity with the four-point probe method

VI. RESULTS AND DISCUSSION

A. The morphology of Graphite, GO and Ascorbic acid-RGO

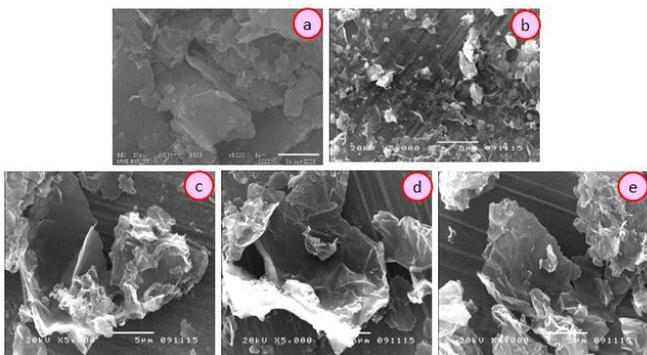


Fig. 2 SEM images of (a) Graphite (b) GO (c) Ascorbic acid (100 mg) RGO (d) Ascorbic acid (300 mg) RGO (e) Ascorbic acid (500 mg) RGO

Figure 2(a) showed a multilayered, wavy, folded flakes graphite. Figure 2(b) showed GO, GO were smooth with folded shapes at the edges, thin sheet and transparent and Reduced GO by 100,300 and 500 mg of ascorbic acid respectively images revealed that the reduced GO material consisted of several layers stacked on top of one another like sheets of paper, with silky, wrinkled, thin morphology were showed in Figure2 (c, d and e) respectively.

B. The crystal structures

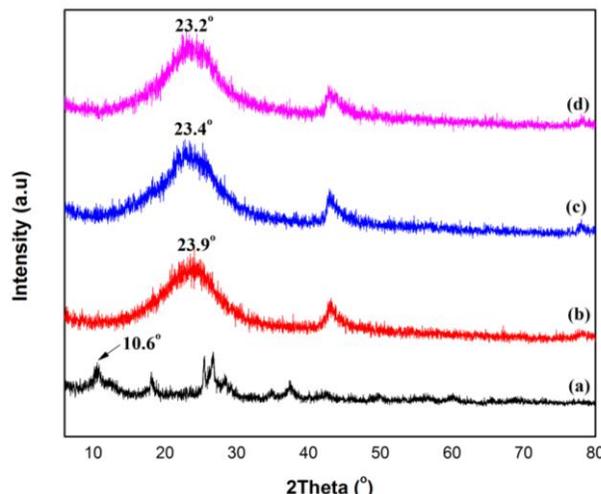


Fig. 3 XRD pattern of (a) GO (b) Ascorbic acid (100 mg) RGO (c) Ascorbic acid (300 mg) RGO (d) Ascorbic acid (500 mg) RGO

Suman Thakur et al, reported XRD patterns of graphite, GO, RGO are Pristine graphite exhibits a basal reflection peak at $2\theta = 26.6^\circ$. Upon oxidation of pristine graphite, the reflection peak shifts to the lower angle at $2\theta = 9.75^\circ$, (d spacing= 0.906 nm). The increase in d spacing is due to the intercalation of water molecules and the formation of oxygen containing functional groups between the layers of the graphite. In contrast to GO, all RGO have a broad peak centered at $2\theta = 25^\circ$ [7]. The crystal structures of GO and Ascorbic acid-RGO were confirmed using XRD analysis. Figure 3 shows the XRD spectrum of GO. The characteristic peak of GO appeared at $2\theta = 10.6^\circ$ which cures. The Ascorbic acid-RGO 100,300 and 500 mg respectively shows peaks at $2\theta = 23.9^\circ, 23.4^\circ$ and 23.2° .

C. FTIR Characterization of GO and Ascorbic acid-RGO

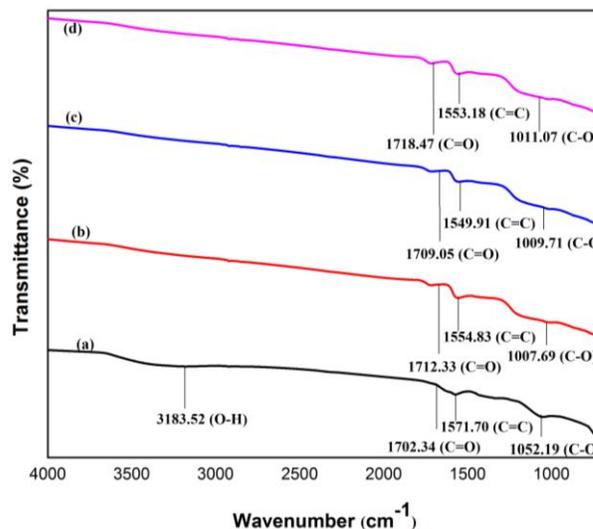


Fig. 4 FTIR spectrum of (a) GO (b) Ascorbic acid (100 mg) RGO (c) Ascorbic acid (300 mg) RGO (d) Ascorbic acid (500 mg) RGO

Fourier transform infrared (FTIR) study was performed over the wavenumber, range of $4000 - 400 \text{ cm}^{-1}$. Figure 4 shows FTIR spectra of the GO. Strong absorption peaks were

observed at 3183.52 cm^{-1} . Due to the vibration and deformation bands of O–H and C=O stretching vibrations from carbonyl groups C=C configurable vibrations from the aromatics C–OH stretching vibrations C–O vibrations from epoxy groups, and C–O vibrations from alkoxy groups respectively. However, most of the peaks related to the oxygen-containing functional groups were removed in the FTIR spectrum of Ascorbic acid (100 mg) RGO Ascorbic acid (300 mg) RGO and Ascorbic acid (500 mg) RGO suggesting that these oxygen containing functional groups were removed in the process of reduction using Ascorbic acid. Interestingly, some new peaks also appeared in the spectra of Ascorbic acid-RGO at $1007\text{--}1012\text{ cm}^{-1}$, $1548\text{--}1560\text{ cm}^{-1}$ and $1700\text{--}1720\text{ cm}^{-1}$ attributed to the skeletal vibration of the graphene sheets. In the Ascorbic acid-RGO sample the intensities of the bands associated with the oxygen functional groups were significantly decreased.

D. Raman Characterization of GO and Ascorbic acid-RGO

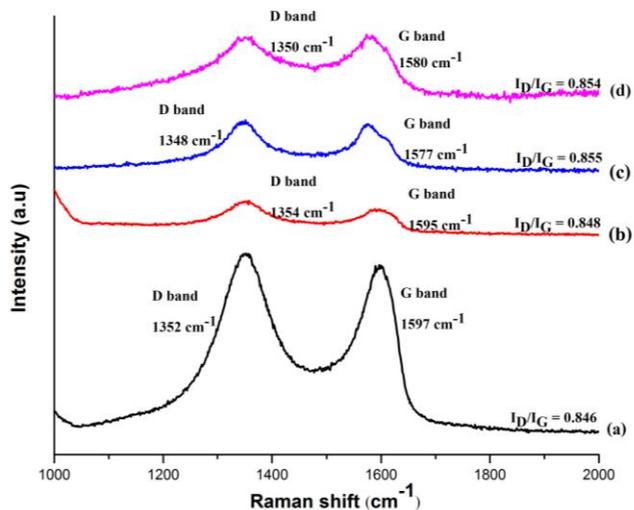


Fig. 5 Raman spectrum of (a) GO (b) Ascorbic acid (100 mg) RGO (c) Ascorbic acid (300 mg) RGO (d) Ascorbic acid (500 mg) RGO

Raman spectra of the GO and Ascorbic acid-RGO show the existence of D-band and G-bands in Figure 5. The D-band is attributed to sp^3 carbon atoms of disordered graphite, and G-band is related to the in plane vibration of sp^2 carbon atoms. The G-band of the GO located at 1597 cm^{-1} , ascorbic acid shifted to $1575\text{--}1595\text{ cm}^{-1}$ for the RGO, which is close to the value of the pristine graphite and confirms the efficient reduction of GO. However, the G-band of RGO showed a longer wave number $1345\text{--}1355\text{ cm}^{-1}$, compared to that of raw graphite 1352 cm^{-1} , possibly due to the interaction between the ascorbic acid and microorganisms.

E. UV-Vis spectrum of GO and Ascorbic acid-RGO

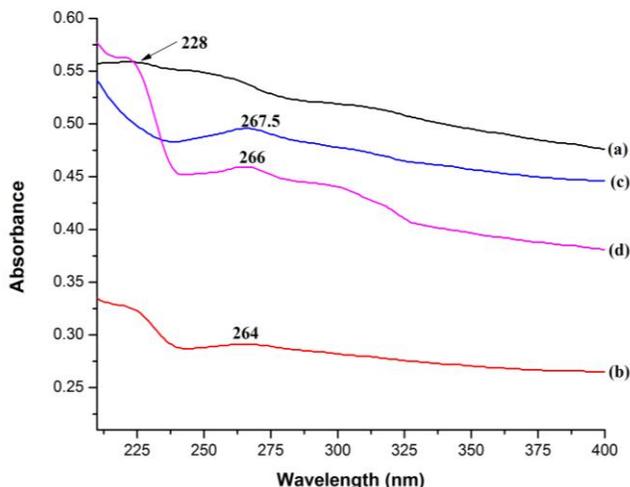


Fig. 6 UV-VIS spectrum of (a) GO (b) Ascorbic acid (100 mg) RGO (c) Ascorbic acid (300 mg) RGO (d) Ascorbic acid (500 mg) RGO

The UV-vis spectrum of GO (Figure 6) exhibits a peak at 230 nm and a shoulder peak at 300 nm. The peak at 228 nm can be corresponded to $\pi\text{--}\pi^*$ transitions of aromatic C=C, while the shoulder peak originates from $n\text{--}\pi^*$ transition of the C=O bonds. The absorptions spectrum of Ascorbic acid-RGO samples exhibit peak around 264, 266 and 267.5 nm. This 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.

F. Electrical conductivity

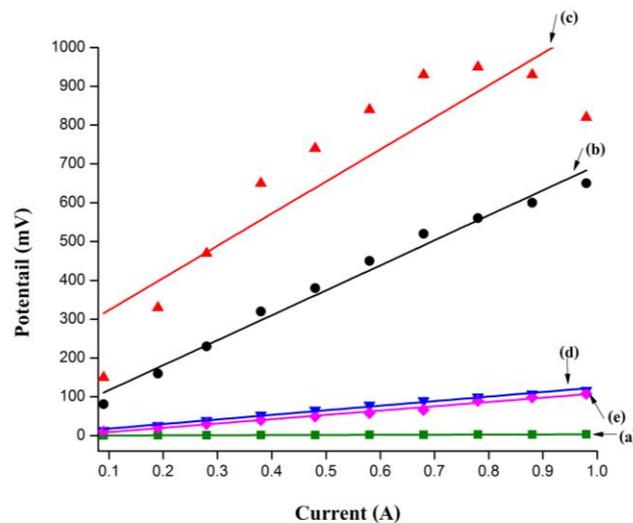


Fig. 7 Electrical conductivity of (a) Graphite (b) GO (c) Ascorbic acid (100 mg) RGO (d) Ascorbic acid (300 mg) RGO (e) Ascorbic acid (500 mg) RGO

The conductivity values obtained from I–V curves were comparable with benzyl alcohol reduced GO (conductivity values 4600 S m^{-1}) as well as vitamin C reduced GO (conductivity values between 2690 and 7700 S m^{-1}) [7]. Figure 7 shows the conductivity values obtained from I–V curves. The analysis of the conductivity data show in Table 1. Graphite show that conductivity values 0.29 S cm^{-1} , GO show

conductivity values at $1.50 \times 10^{-3} \text{S.cm}^{-1}$, ascorbic acid (100 mg) RGO show conductivity values at $9.01 \times 10^{-4} \text{S.cm}^{-1}$, ascorbic acid (300 mg) RGO show conductivity values at $6.32 \times 10^{-3} \text{S.cm}^{-1}$ and ascorbic acid (500 mg) RGO show conductivity values at $6.72 \times 10^{-3} \text{S.cm}^{-1}$.

TABLE I
THE ANALYSIS OF ELECTRICAL CONDUCTIVITY DATA

Sample	Thickness (cm)	Resistivity ($\Omega \cdot \text{cm}$)	Conductivity (S.cm^{-1})
Graphite	0.27	3.48	0.29
Graphene	0.25	665.65	1.50×10^{-3}
Ascorbic acid (100 mg) RGO	0.35	1109.58	9.01×10^{-4}
Ascorbic acid (300 mg) RGO	0.35	158.23	6.32×10^{-3}
Ascorbic acid (500 mg) RGO	0.35	148.74	6.72×10^{-3}

VII. CONCLUSION

Demonstrated that the studied ascorbic acid concentration have tremendous potential to be used as reducing agents for the reduction of GO with an environmental benign synthetic. The most important advantages of the ascorbic acid are their abundance in nature, cost effectiveness and easy. The values of high electrical conductivity are acceptable. Thus this green method can be used for large scale production of RGO.

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