Determination of Crystallite Size, Number of Graphene Layers and Defect density of Graphene Oxide (GO) and Reduced Graphene Oxide (RGO)

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Abstract. Determination of crystallite size, number of graphene layers, interlayer spacing, and defect density with the use of X-ray diffraction and Raman spectroscopic technique. GO was synthesized by using Simple Hummer's method and was subjected to chemical reduction by using tri-sodium citrate. Particularly, the above parameters have presented by some mathematical equation usage. The shrinkage in the dimensions of crystallite upon reduction leads to decrease in number of graphene layers in each domain and clearly increase the defect density. XRD and Raman stated the formation of GO and its reduction to the formation of RGO.

INTRODUCTION

Graphite is one of the allotrope of carbon, that can provide great potential in many areas such as in functional nanocomposites and electronics applications [1]. Graphite and graphene both have unique properties especially when assorted with polar polymer matrices [2]. Several different methods were reported to synthesize graphene oxide including chemical vapour deposition , epitaxial growth [3] , micromechanical exfoliation of graphite, and graphene oxide reduction (RGO) [4]. Generally, the reduction of GO is a low-cost practical approach to the bulk-scale graphene materials, and it is conducted by some chemical methods using hydrazine as the reducing agent[5]. Such parameters like crystallite size, number of graphene layers and defect density of GO and RGO play a critical role to find out the purity of graphene based materials [6]. The reduction of GO is a key topic and different reduction processes used to reduce the graphene oxide [7].

EXPERIMENTAL DETAILS

Materials. Graphite powder (Merk, India),), Potassium Permanganate (Merk, India), Sulphuric acid (RFCL, India), Sodium Nitrate (Fisher Scientific, India), Hydrogen peroxide (Merk, India), tri-Sodium Citrate (Fisher Scientific, India)

Procedures (a) Synthesis of GO.GO was synthesized by simple hummer's method by oxidizing the graphite powder. In this synthesis 3.2 g of graphite powder was added to the mixture of 70 ml of 98% of sulphuric acid (H_2SO_4) and 3g of sodium nitrate ($NaNO_3$) and mixture was magnetically stirred. After 1 h, 8 g of 99.9% of potassium permanganate ($KMnO_4$) was added gently to the reaction and kept the mixture at the ice bath to keep the temperature beneath 20°C and stir continuously at room temperature for 8 hrs. Add 650ml of DI water to the mixture. Allow the mixture to be stirred for 1 hr. 12 ml of 30% of hydrogen peroxide (H_2O_2) is added dropwise. Divide the mixture for cleaning using deionized water (DI) and centrifuge it for each step of washing in 15 minutes at 5000 rpm. The ending product was dried for 24 hrs at 60°C.

(b) Synthesis of RGO. Mix 1g of GO with 100 ml of DI water. Stir the mixture for ½ hr for GO dispersion. Next, add 5g of tri-Sodium Citrate ($Na_3C_6H_5O_7.2H_2O$) into the dispersed product. Heat the mixture at 80°C and stir continuously till 72 hrs. Now, add 120ml of deionized water to the mixture. Divide the mixture for cleaning

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using deionized water (DI) and centrifuge it at 5000 rpm per step of washing in 15 minutes. Dry the sample at 80°C for 6 hrs.

RESULTS AND DISCUSSION

X-Ray Diffraction. For graphite, at 2θ = 26.34° one sharp peak has observed. This peak established the fine arrangement of the layered structure with 0.334809 nm d-spacing) along with the orientation at (002) and (FWHM = 0.34368).

For GO, the 2θ shifted to 10.24°, which specified the full oxidization of graphite into GO. Additionally, with 0.863 nm d-spacing and (001) orientation, the interlayer distance of GO was increased.

Calculated using equation:-

$$2d \sin\theta = n\lambda \quad (1)$$

Where d= Interlayer spacing, θ= Diffraction angle and λ= Wavelength of X-ray source.

The occurrence of wide peak for RGO at 2θ = 24.10 implied the arrangement of crystal phase at (002). The removal of oxygen-containing functional groups reduced the d-spacing of RGO. Another less intense peak showed the band of disordered carbon materials that can be seen at 2θ =42.60° with (100) orientation.

The average crystallite width (D), within the graphene maintenance is given by Debye-Scherer equation:-

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

Where β= Full peak width of the diffraction peak at half maximum height (FWHM), θ= Half diffraction angle and K=0.89 (that is a constant related to crystallite shape) for spherical crystals with cubic unit cells. Likewise, in-plane crystallite size (L) can be expressed as:-

$$L = \frac{1.84\lambda}{\beta \cos\theta} \quad (3)$$

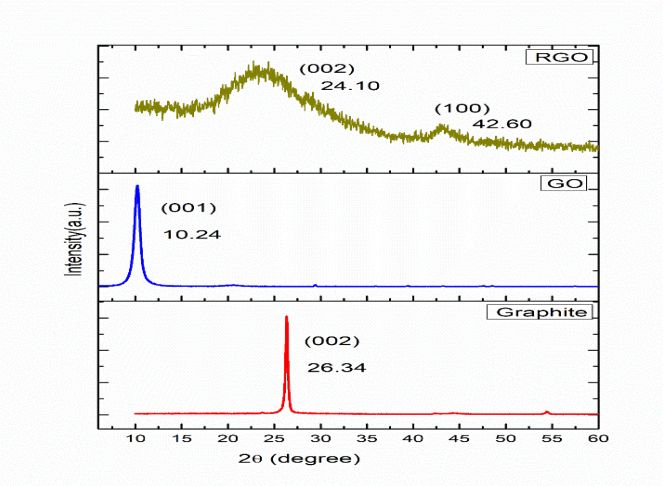

Figure. 1 XRD pattern of Graphite, GO, RGO

The reduction of average crystallite size in RGO relative to GO (D ~ 118 Å; L ~ 301.3 Å) has noticed. That showed the shrinkage of graphene regions and foundation of more lateral defects, which was due to the exclusion of graphene layers upon reduction. The average number of graphene layers (n) per region can be calculated from the broadening of peak by XRD using the grouping of Debye-Scherer and Bragg's equations (1) and (2) that gives the expression for n as :-

Table 1:- Several physical parameters gotten from X-ray diffraction and Raman spectroscopy.

Samples	2θ (degree)	d (Å)	D (Å)	Lattice Strain (Å)	Number of layers (n) per domain	L (Å)	D-band (cm^{-1})	G-band (cm^{-1})	I_D/I_G ratio	LSp^2 (nm)	L_D (nm)	$nD \times 10^{11}$ (cm^{-2})
Graphite	26.34	3.38	301	0.053	91	589.9	1354	1584	0.27	63.49	24.89	1.07
GO	10.23	8.64	118	0.344	15	231.1	1353	1598	0.99	17.33	13.01	1.93
RGO	24.36	3.65	8.7	1.981	03	17.0	1349	1596	1.16	14.75	12.00	2.50

$$n = \frac{D}{d} + 1 = \frac{2k \tan\theta}{\beta} + 1 \tag{4}$$

Raman Spectroscopy It can be perceived that GO gives two noticeable Raman features at ~1353 $cm^{-1}$and ~1598 cm^{-1} corresponding to D and G bands. G peak contributed by the C-C stretching, which was same in all Sp^2 Carbon systems. The D peak was because of disordered regions having Sp^3 carbons connected with out of plane vibrations. Besides, a higher wavenumber of 2D peak, was seen at ~2686 cm^{-1} for GO. The location of GO confirmed the produced GO was multilayered. The S3 was ascribed to the combination of D and G peaks dignified at 2938 cm^{-1}.

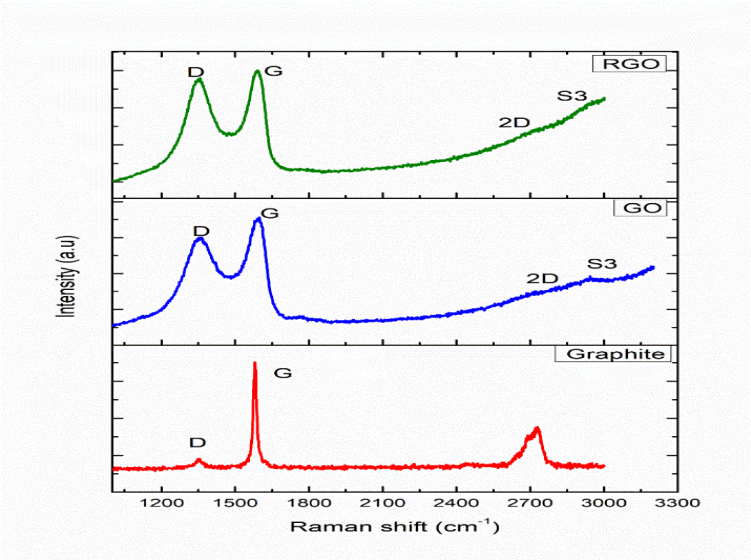

Figure.2 Raman of Graphite, GO, RGO

For RGO the broadening and narrowing of G and D peaks has observed with rise in relative intensity and the fall in width of 2D and S3 peaks. The reduction of GO mains to shifting of D, G, 2D and S3 peaks to ~1349cm^{-1}, ~1596cm^{-1}, ~2714cm^{-1} and ~2947cm^{-1}.

I_D/I_G ratio for GO is increased to 1.16 after reduction due to rebuilding of Sp^2 carbon and decrease in average size of Sp^2 region upon reduction. I_D/I_G ratio is utilize for estimation of in-plane size of sp^2 domains (LSp^2), average defect distance (LD) and defect density (nD, cm^{-2}) using the following equations: -

$$Lsp^2 = \frac{560\, I_G}{E_L^4\, I_D} \tag{5}$$

$$L_D^2(nm^2) = 2.4 \times 10^{-9} \lambda_L^4 \frac{I_G}{I_D} \tag{6}$$

$$nD = \frac{2.4\times^{10^{22}} I_D}{\lambda_L^4 \quad I_G} \tag{7}$$

Where E_L and λ_L are the energy and wavelength of the laser source. The Equations (6) and (7) are legal for intercalants and charge impurities and defects. The observed I_D/I_G ratio and calculated values for both in and out planes the crystallite size (i.e., D and L values) displayed that RGO has more number of sp2 domains formed that are in small size as compared of GO. Accordingly, the calculated defect density (nD) was found huge in RGO that advocated the development of more defects.

CONCLUSION

In the end, both GO and RGO were successfully obtained. The average number of graphene layers and average sp^2 crystallite size (L) both decrease from 15 to 3 and 17.33 nm to 14.75 nm, after reduction of GO to RGO. The increased I_D/I_G ratio displayed the increase in quantity of sp^2 domains with the defect density increment after reduction. Successfully, determine the Crystallite size, Number of graphene layers and Defect density of Graphene Oxide and Reduced Graphene Oxide using XRD and Raman spectroscopy.

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