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Physical and Metallic Based Evaluation of Chemical Treatment of Graphene Oxide to Achieve Reduced Graphene Oxide and Industrial Significance

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Abstract

In the recent research work, synthesis of Graphene oxide was done by treating graphite powder with KMnO4 and a mixture of H2SO4/H3PO4 and then reduced with ascorbic acid to produce graphene oxide. A method that was approved for this purpose was Tour method. X-ray Diffraction (XRD), Raman Spectroscopy and Scanning Electron Microscopy (SEM) were used for the characterization of the obtained samples. Structural analysis was determined with the help of X-ray diffraction (XRD) using CuKα radiation (λ=0.15405nm). Raman Spectroscopy was used for chemical analysis. Surface characterization was done with the help of Scanning electron microscopy. XRD pattern obtained through (SEM) shows that GO and RGO were successfully synthesized at 9.2° and 25.1° peaks respectively. Results from GO and RGO Raman spectra samples indicate that oxidation was effective and there was not a complete elimination of oxygenated group in the RGO sample. In SEM images, RGO exhibits wrinkled and agglomerated structures. Needle like structures were visible at higher magnification.

Keywords: Graphene oxide, Reduced Graphene oxide, Chemical reduction, XRD, Raman Spectroscopy, SEM.

INTRODUCTION

Graphene is the allotropic form of carbon having thick building block in mono atomic layer of atoms [1]. Carbon has been in focused due to its number of applications in electronic industry carbon is the most suitable material known. Discovery of bucky balls in carbon nano structures lead to many researches on carbon material [2]. In 2003, graphene was awarded a noble prize by Andre and Geim and Konstantin Novoselov [3]. It was introduced as winning material due to its huge applications introduced in the field of electronics and many fruitful efforts were made to introduce graphene into electronic structure. In 2004, graphene research entered into a golden rush as GO became center of carbon nano materials research and a number of research paper started to publish about its structure, properties and applications. In 1859, Brodie was the first who came across Graphene oxide [4]. After many researches, chemical procedures were introduced to extract graphene from graphene oxide. Graphene oxide is considered to be appropriate way to extract graphene. Graphene holds its worth more from scientific point of view as it is the basic form of carbon which is oxidized. As graphene does not occur naturally so in the first step Brodie prepared graphene oxide [5]. After 40 years, Staudenmaier introduced different method to prepare graphene oxide [6, 7]. After the Staudenmaier's work in 1958, Hummers and Offeman prepared graphene oxide with the help of strong oxidants for the oxidation of graphite [8]. New techniques were introduced for the preparation of graphene oxide. After this all methods, preparation techniques were modified form of Hummers method after this in 2010 Tour method was known for the production of graphene oxide [9].

2010 Professor James Tour along with his team at Rice University introduced a new method for GO production. Further inventory shows Tang-Lau method for the production of graphene oxide using sucrose and glucose.

In the previous view decades to enhance the chemical structure of graphene oxide numbers of researches have been made [10, 11]. Graphene Oxide edges are associated to some extent with carboxylic, hydroxyl, lactol, ketone and lectone groups. In spite of

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all these researches GO is still under investigation with respect to the positioning and allocation of these groups. A few years ago, NMR analysis shows C13 indicate that the regions of grapheneshow sp2-hyberdization and are powerfully disrupted as they contain covalently bonded hydroxyl and epoxide groups with few carboxylic groups that exist on the outside surface of graphite oxide [12]. Thus, because of these experimental results it's very difficult to find accurate proposed model of GO.

In present time GO is known for its applications in electronic industry such as supercapacitors [13], sensors [14], electrodes [15] and composite materials [16, 17] still it is not easy to work with it as graphene sheets are not produced on large scale. Various methods can be applied to obtain graphene that include epitaxial growth [18], chemical vapor deposition [19, 20], mechanical exfoliation [21, 22], liquid phase exfoliation of graphite [23, 24], in all these methods chemical reduction of GO is the effective way to produce graphene in large quantities. Chemical reduction is introduced to produce graphene oxide on large scale.

Reduction of graphene oxide is based on several researches that include thermally, electromagnetically, chemically and electrochemically. Chemical reduction is mostly favorable for the production of graphene oxide. Hydrazine [25, 26] acts as reducing agent in many studies. Prof. Rodney Ruoff [27] reported the presence of the material in achieving RGO for the first time.

In the last many years researches have made in finding environment friendly reductants so we can use have the property of good dispersibility in water. According to few researches oxygen functionality of GO can be removed with the help of hydrazine and sodium borohydride. Fernandez-Merino *et al*., [28] found L-ascorbic acid (L-AA) first safe and water-soluble mild reductant as compared to hydrazine for the deoxygenation of GO.

In this paper we have discussed the production of RGO from GO and as reductant L-ascorbic acid (L-AA) was used. In literature reduction of graphene oxide using L-ascorbic acid (L-AA) and their dispersibility water was highlighted so we can have new vision in the field of graphene based composite materials. Knowing the applications of graphene-based materials in the field of energy storage devices and biomedical and study the preparation of GO and RGO for various application is considered in the present time. Different techniques that include X-ray Diffraction (XRD), Raman Spectroscopy and Scanning Electron Microscopy (SEM) were used to characterize prepared Composite.

MATERIALS AND METHODS

Chemical and Reagent

From Sigma –Aldrich, graphite, potassium permanganate, hydrogen per oxide and sulfuric acid were bought and for solution preparation the water from Mili-Q system was used.

Synthesis of Graphene oxide (GO)

The GO was prepared by the Tour Method [29]. In the typical method, two solutions were required for the preparation of graphene oxide. In first solution sulfuric acid (180 mL) and phosphoric acid (20 mL) was required while in second solution mixture of 0.6 g graphite powder and 7.9 g potassium permanganate was placed. Exothermic reaction occurs due to which heat was produced so $KMnO4$ was added slowly in the solution. The two solutions were mixed well and were heated for 12 hours at 50˚C. The solution turns to paste so 200 mL distilled water and $H2O2$ with 30% wt. (20 mL) was added. The mixture turns to bright yellow color. Filtration of solution was carried out using 5% HCL and barium chloride. $BaCl2$ was added to remove metal sulfate ions. The mixture was rotated for 4 hours at 4000 rpm. Distilled water (200 mL) was added with constant stirring and the mixture was added to water bath for 12 hours for heating at 60˚C. Drying process was carried out in the last step and the mixture was heated for 24 hours again at 60˚C.

Chemical reduction of Graphene Oxide (GO)

In the preparation of RGO, 8.8 g Ascorbic acid and distilled water (800 mL) was added to GO powder (800 mg). Magnetic stirrer was used for stirring at 60˚C for 30 minutes. Centrifugation was done at 4000r/s for 40 minutes to remove the supernatant. 30% wt. $H2O2$ was added and stir continuously for 30 minutes at 60˚C. Mixture was washed 3 times with Ethanol and Distilled water. Drying process was carried out. In drying process mixture was heated for 24 hours in oven at 120˚C.

Samples are prepared to obtain the desired materials used in different applications. It is important to know about the specific properties, sample prepared is efficient to be used in different applications. Different techniques that include XRD, Raman spectroscopy and SEM were used for the investigation of the material properties. The prepared composite was characterized by XRD (Bruker D8 advance diffractometer), Raman spectroscopy using T-6400 triple jobin Yyon-Atago/Bussan spectrometer and SEM (ZEISS EVO 10).

RESULTS AND DISCUSSION

GO and RGO XRD pattern gives information about structural approach as shown in figure. The values of "2θ" lies in the range of 5-50 degree. Two peaks were observed in the pattern of graphene oxide. Dominant peak is observed at 2θ=9.2°, which corresponds to 9.61 nm which is an interlayer distance determined by Bragg's equation. RGO was obtained through chemical treatment as a result wide peak is observed at the center of about 25.1°, which corresponds to an interlayer spacing~ 3.54 nm and it is also determined by Bragg's equation. Reduction of GO by hydrazine gives similar interlayer spacing of RGO [30]. Highly reduced graphene oxide was obtained.

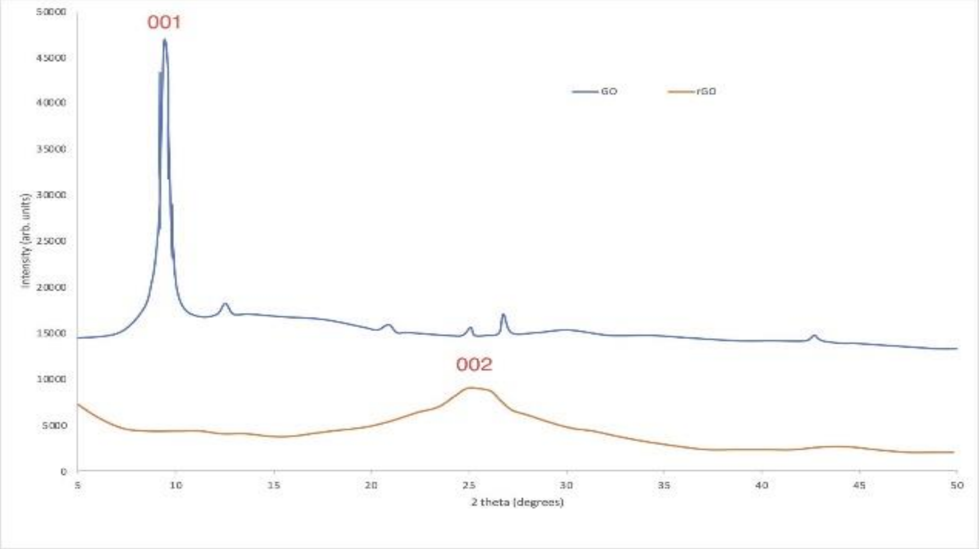

Fig-1: XRD pattern of GO and RGO Composite

Table 1: Interplanar spacing and corresponding hkl values

Sr.#	2θ (deg)	d (Å)	Hkl
1	9.2	9.61	001
2	25.1	3.54	002

Raman spectroscopy was used to study the characterize properties that include structural and electronics properties as the technique was non-destructive and had efficient approach. The table shows the Raman spectra of GO and RGO and the parameters obtained during the analysis.

In the given figure and table, the parameters related to GO and RGO Raman spectra are displayed. One is for GO and other shows RGO. Raman spectra of GO shows two broad band D and G at 1356 per cm and 1612 per cm. D band counters to defects and the failures of translational symmetry whereas in G band first order scattering of graphite is confirmed having sp2 domain. The band D shows strength in comparison to G band based on the disorder amount in the graphene material [31]. Increase in the disorder is observed due to change in intensity and width of the G and D peaks. Disorder continues due to the defects via oxygen containing functional group that lies in Bessel layer [32]. Shifting of peak G towards low frequencies is due to the partial removal of oxygenize group and it is moved from GO to RGO.

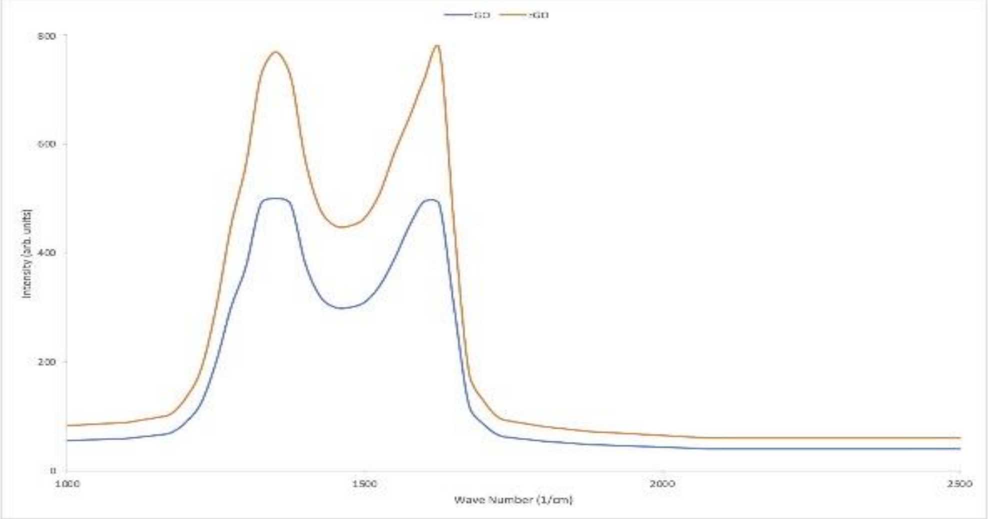

Fig-2: Raman spectra of GO and RGO

Results shows that there was not complete elimination of oxygenize group in the sample of RGO. Sp3 amorphous and untidy carbon corresponds to graphitic carbon that have sp2 proportion that shows quantitative relation of intensities of bands "D" to "G" $(\frac{I_D}{I_G})$ [33, 34]. The relation also shows the structural arrangement. The value of "$\frac{I_D}{I_G}$" ratio for GO is 0.80 and for RGO the values of "$\frac{I_D}{I_G}$" is 0.84. Reduction in the sp3 domains shows size is proposed by the RGO "$\frac{I_D}{I_G}$". Reduction in mean size of sp2 domains was suggested due to high ratio RGO as compared to GO. Chemical treatment was used for elimination of oxygenated functional group as exfoliated GO was reduced. Reduction of GO produces new graphite domain as well as large number of edged that increase the D peak and fragmentation occur throughout the reactive site.

Quantative relation between the intensities is used and then the Koeing and Tuinstra equation that shows the crystal size that are parallel to Basel planes is determined [35, 36].

The Tuinstra and Koeing [35-38] equation is:

$$L_a\,(nm) = (2.4 \times 10^{-4})\lambda_1^4(\frac{I_D}{I_G})^{-1}$$

Where "λ_1 " is the wavelength of excitation and its value is (λ_1=514.5nm)

So, the values of "La" for both GO and RGO is given below higher value of "La" it shows increase in the domain of sp2 in the case of network of carbon.

Table 2: Parameters obtained from Raman spectra.

Samples	**Banda D (cm^{-1})**	**Banda G (cm^{-1})**	$\frac{I_D}{I_G}$	**L_a (nm)**
GO	1356	1612	0.80	21.1
RGO	1352	1625	0.84	20.1

Chemical reduction was used to synthesize microstructure RGO form GO. The synthesis was observed at different magnification of 4.64KX, 21.17KX, 50.71KX and 4.64KX with the help of SEM. The development of graphene/metal oxide nanocomposite-based water treatment technology is a very intriguing but tough challenge for researchers since there still are few issues, such as what the future of these composites will be like, and how environmentally friendly. several unique techniques are highlighted to show the potential of using GO in many applications, with the key to the exceptional functionalities being related to fabrication techniques that are unscalable, expensive, and time-consuming.

CONCLUSION

The sp2 structures are formed due to the reduction of graphene oxide by ascorbic acid and increase in regular structures was found as compared to hydrazine. For large scale production of reduced graphene oxide (RGO) chemical reduction of graphene oxide using ascorbic acid was found to be a very promising technique. Graphene produced as a result of the ascorbic acid reduction does not contain toxic agents, which makes it eco-friendly and high-quality graphene as compared to other techniques. GO and RGO were successfully synthesized. Oxidation of graphite was used for GO while TOUR method was used to prepare RGO through chemical treatment. Results of XRD, Raman and SEM for both GO and RGO showed that the experiments were successful.

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