

# Green Synthesis and Characterization of Nanocrystalline Graphene Oxide

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## ABSTRACT

Green reduction of Graphene oxide (GO) using various natural materials including plant extracts has drawn significant attention among the scientist community. These methods are sustainable, cost effective and more ecofriendly than other standard methods of reduction of nanoparticles. In the present work, Graphene oxide (GO) was prepared using predefined Modified Hummer's method. Reduced Graphene oxide (RGO) is obtained using aqueous leaf extract of *Lantana camara* (Tantani) and aqueous peel extract of *Citrus limeta* (Sweet lime) using cold maceration, sonication and refluxing methods. Structural and Optical characterization of graphene and reduced graphene oxide was carried out using XRD, UV-visible, FTIR, SEM and EDX. UV-visible spectroscopy was used to monitor the formation of reduced Graphene oxide. The crystalline size of Graphene nanoparticles was confirmed by XRD analysis. FTIR analysis showed the green reduction of Graphene oxide using phytochemicals. The morphology and elemental composition of synthesized Graphene was studied by SEM and EDX analysis. The production of graphene using phytoextracts as reducing agent emphasizes on facile method and future green technology for various applications such as water purifiers, super capacitors, biosensors, solar cells etc.

**Keywords:** green synthesis, graphene oxide, reduced graphene oxide, phytoextracts

## INTRODUCTION

Nanoscience and nanotechnology mainly deal with the synthesis, characterization, study and use of non-material. Graphene is the world's thinnest, strongest, and stiffest material, as well as being an excellent conductor of heat and electricity. It is the basic building block of other important allotropes. Graphene oxide (GO) is of great interest due to its low cost, easy access, and extensive ability to convert to graphene. Graphene, a two dimensional mono atomic thick building block of a carbon allotrope has received world-wide attention due to its extraordinary thermal, optical, mechanical and transport properties. Recent progress has shown that the graphene-based materials can have a profound impact on electronic and optoelectronic devices, chemical sensors, biosensors, nanocomposites, and energy storage [1-3]. Researchers are taking into consideration two primary methods for the fabrication of graphene: a top-down (TD) and a bottom-up (BU) approach. In TD approach, there are reported methods on the production of graphene such as micromechanical cleavage, graphitization of SiC and solution exfoliation of graphite in organic solvents. However, these methods turn out a poor yield of graphene layers. Chemical reduction of graphite oxide colloidal suspensions has been considered as an effective route to synthesize graphene sheets due to its simplicity, reliability, ability for large-scale production and exceptionally low price. A number of reducing agents such as dimethyl hydrazine, hydroquinone, aluminum powder, sodium borohydride, sulfur containing compounds, hexamethylenetetramine, poly-electrolyte, Ethylene diamine (EDA), sodium citrate, carbon monoxide and norepinephrine have been experimented on and were found to have performed under various conditions i.e., acid/alkali, thermal treatment and others treatments such as laser, plasmas, microwave, sonochemical, electrochemical, two-step reduction and so on. These different reduction methods result in graphene with different properties. Even with the distinct advantages of chemical route for reduction of GO, the reduced GO (RGO) tends to form irreversible aggregation due to strong van der Waals attractive forces among the graphene planes which creates bottle neck and confines its process ability [4-6]. However, this can be eliminated by chemical modification of graphene using small

organic molecules, biomolecules etc. One more negative aspect of the chemical reduction method is the high toxic nature of the reducing agents (hydrazine, dimethyl hydrazine, sodium borohydride, hydroquinone, etc). The existence of such toxic agents could have harmful effect, particularly in cases of biorelated applications such as catalysis and drug delivery. Even in the case of metal/hydrochloric acid reduction of GO, particles/traces of metals may stay behind as impurities. In this context, use of green nanotechnology which reports on the reduction of GO to overcome the above problem by using reducing agents such as biomolecules, microbes and phytoextracts reduction has become extremely crucial. Green nanotechnology in which biomolecules, microbes and plant extracts are used as both reducing and capping agent has been widely explored in the synthesis of metal nanoparticles This method helps in bio-reduction of GO to graphene [7-9]. It has been discovered that various phytochemicals obtained from different parts of plants like leaves, peel, root etc. which mostly contains biomolecules including proteins, vitamins, amino acids, saccharides, alkaloids, pectin's, alcoholic compounds, flavonoids and enzymes have the potential to serve as reducing and capping agents in the bio-reduction and formation of functional graphene from GO. Apart from use of less toxic chemicals, other Salient feature of green technology is that most operates at mild conditions; room temperature & atmospheric pressure making it affordable & cost effective [10-12].

## METHODOLOGY

### Preparation of Graphene oxide

Graphene oxide powder was prepared by modified Hummer's method [13]. Graphite powder (2 gm), 2 gm  $\text{NaNO}_3$ , 90 ml of conc.  $\text{H}_2\text{SO}_4$  was added in 1000 ml beaker/ volumetric flask in ice bath and stirred continuously for 4 hrs. 12 gm of  $\text{KMnO}_4$  was added very slowly (below  $15^\circ\text{C}$ ) for 30 minutes. The mixture was diluted with 184 ml of DI water and stirred for 2 hrs continuously at  $35^\circ\text{C}$ . Further it is refluxed at  $98^\circ\text{C}$  (10-15 min) till brown color is obtained. The mixture was treated with 40 ml  $\text{H}_2\text{O}_2$  till solution turned to bright yellow color and stirred with double distilled water for 1 hr. The mixture was centrifuged with 10% HCl and DI water. Gel like substance was vacuum dried at  $60^\circ\text{C}$  for 6-7 hrs.

### Preparation of Phytoextracts

Fresh leaves of *Lantana camara* (Tantani), *Citrus limeta* (Sweet lime) fruit peel were collected from local area and washed with DI water to remove the dust particles. They were blended with domestic blender and kept in DI water for cold maceration overnight. The mixture was stirred for 30 min in 50 ml of DI water at 50°C and cooled the filtrate and store at 4°C.

### Synthesis of reduced graphene oxide

60 mg GO was sonicated in DI for 45 min and 10 ml leaf extract of *Lantana camara* (Tantani) was added to it. The mixture was refluxed for 6 hrs at 50 °C, until color changes to brown-black. The mixture was centrifuged with water for several times. The reduction of GO is indicated from the color change of the solution before and after reaction (from yellow, brown to dark brown), which could serve as a piece of evidence for the conversion of GO to graphene. The color change is also due to the large number of hydrophilic functional groups, such as carboxyl, hydroxyl, and epoxy groups, on GO nano sheets. After reduction, a homogeneous yellow-brown GO dispersion was converted to black, indicated the conversion of GO to L-rGO. The process was repeated for the peel extract of *Citrus limeta* (Sweet lime). After reduction, a homogeneous yellow-brown GO dispersion was converted to black, indicated the conversion of GO to C-rGO [14-17].

### Characterization of synthesized GO, L-rGO & C-rGO

#### Optical characterization

UV-Visible absorption spectroscopy, JASCO V-670 spectrophotometer in the operating range 200-800 nm was used. The prepared samples were exposed to UV-Vis radiation and the absorption wavelength was determined from the intensity of the transmitted light.

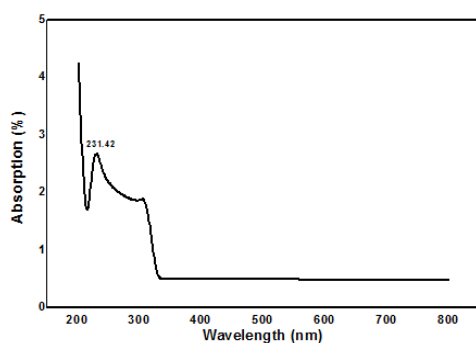


Fig. 1 a) UV-visible spectra of L-rGO

For FTIR study, we have employed FTIR-6100 spectrometer (JASCO) in the transmission (T) mode. Transmissions have taken in the wave number range 400-4000  $\text{cm}^{-1}$ .

### Structural characterization

XRD analysis for the synthesized GO, L-rGO and C-rGO powder was carried out with Bruker D8-Advanced Diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ) with an operating voltage of 40 kV and a current of 30 mA. The grain size measurement is carried out using Scherer formula. The surface morphology and elemental composition of rGO sample were studied with the help of Scanning Electron Microscope (SEM) (JEOL JSM 6360).

## RESULTS AND DISCUSSION

### Optical Characterization

#### UV-Visible Spectroscopy

The UV-visible spectrum for rGO is presented in Fig.1. The characteristic peak of L-rGO appears at 332 nm indicates that the formation of L-rGO. The band gap can be calculated using equation  $E = hc / \lambda$ , the band gap was found to be 5.36 eV. The characteristic peak of C-rGO appear at 332 nm indicates that the formation of C-rGO. The band gap was found to be 3.73 eV.

#### FTIR analysis

The stretching and vibrational studies of rGO were carried out using FTIR. Figure 2(a) shows the FTIR spectrum of L-rGO. The characteristic absorption band is observed at 1432.82 and 1094.4  $\text{cm}^{-1}$  which is assigned to C-O stretching due to carboxyl / alkoxy functional groups. The band at 1734.65  $\text{cm}^{-1}$  shows

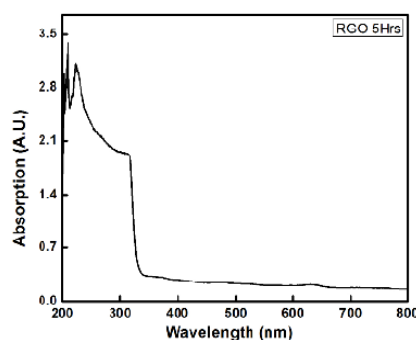


Fig 1. b) UV-visible spectra of C-rGO

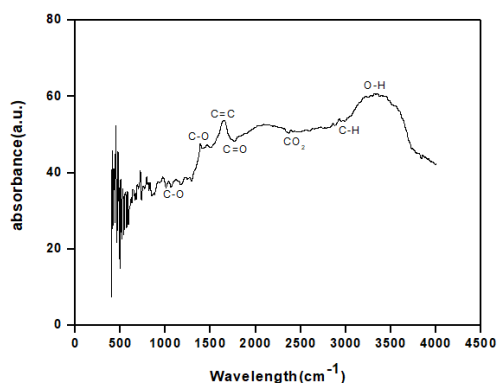


Figure 2 (a) FTIR spectrum of L-rGO

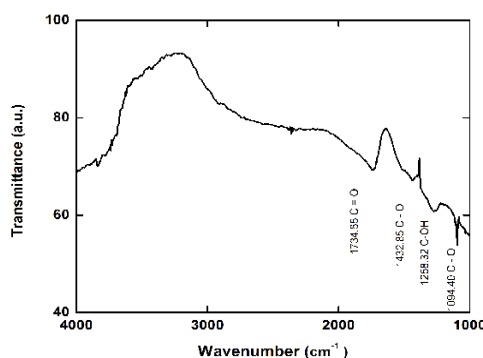


Figure 2 (b) FTIR spectrum of C-rGO

C=O (carbonyl/carboxyl functional group) stretching. The band observed at 1258.32 $\text{cm}^{-1}$  shows C-OH stretching (epoxy functional group). Figure 4.4(b) shows the FTIR spectrum of C-rGO. The characteristic absorption band is observed at 1432.82 and 1094.4  $\text{cm}^{-1}$  which is assigned to C-O stretching due to carboxyl / alkoxy functional groups. The band at 1734.65  $\text{cm}^{-1}$  shows C=O (carbonyl/carboxyl functional group) stretching. The band observed at 1258.32 $\text{cm}^{-1}$  shows C-OH stretching (epoxy functional group).

### Structural characterization

#### XRD analysis

Pristine graphite exhibits a basal reflection (002) peak at  $2\theta = 24.8^\circ$  ( $d$ -spacing = 0.358 nm). Compared with pristine graphite, the diffraction peak of synthesized GO appears at the lower angle from  $2\theta = 12.3^\circ$  ( $d=0.718$  nm) as shown in Fig. 3 (a). The intense crystalline peak of graphite occurs at  $24.8^\circ$  ( $d$ -spacing = 0.358 nm) was observed for the GO powder. This is the characteristic peak of hexagonal graphite with a  $d$ -spacing of 3.58 Å. Upon conversion of graphite into GO the peak position shifts to  $12.3^\circ$ . The interlayer spacing now increases to 7.18 Å. This increase in  $d$ -spacing is due to the intercalation of OH containing functional groups in between the graphene layers [18]. After reduction by *Lantana camara* leaf extract a broad peak appears, starting from 24 to  $30^\circ$  as shown in Fig. 3 (b). The characteristic XRD peaks appear at position  $2\theta = 24.9^\circ$  ( $d= 3.58\text{Å}$ ) and  $26.6^\circ$  which confirms the formation of L-rGO from GO as seen in Fig 3(b). The average crystallite size was estimated according to the Scherrer equation. The average crystallite size was found to be 2.71 nm. This broad

peak is also suggestive of a loss of the long range order in graphene and the great reduction of GO and formation of few-layer graphene. After reduction by *Citrus limeta* peel extract the  $12.3^\circ$  peak disappears and a broad peak appears. The characteristic XRD peaks appear at position  $2\theta = 24.9^\circ$  which confirms the formation of C-rGO from

GO as seen in Fig 3 (c). The average crystallite size was estimated according to the Scherrer equation  $D = \frac{0.9\lambda}{\beta \cos\theta}$ . The average crystallite size of C-rGO was

found to be  $\approx 17\text{nm}$ .

Table showing calculation of average grain size of L-rGO

Peak no.	$2\theta$ (degree)	$d$ (Å)	D grain size nm
1	12.39	7.13	2.64
2	15.83	5.59	2.84
3	24.75	3.59	3.05
4	26.59	3.34	2.88
5	21.03	2.88	2.47
6	41.45	2.18	3.20
7	52.39	1.74	2.57
8	60.29	1.53	2.64
9	72.49	1.30	2.77

The surface morphology and elemental composition of rGO sample were studied with the help of Scanning Electron Microscope (SEM) (JEOL JSM 6360). Figure 4 (a) shows the SEM images of synthesized L-rGO sample and Fig 4 (b) shows the SEM images of synthesized C-rGO sample. The SEM images clearly show that the multilayered sheets of rGO which conforms the formation of rGO. Number of rGO sheets are layered onto each other results agglomeration of rGO.



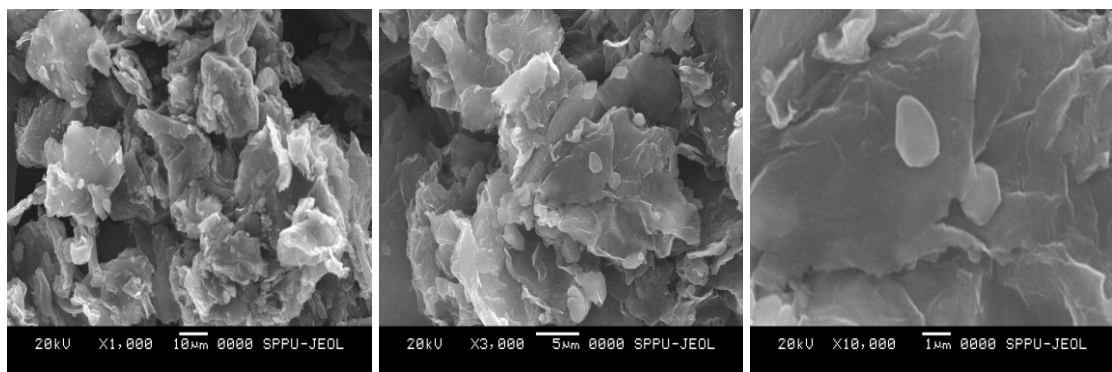
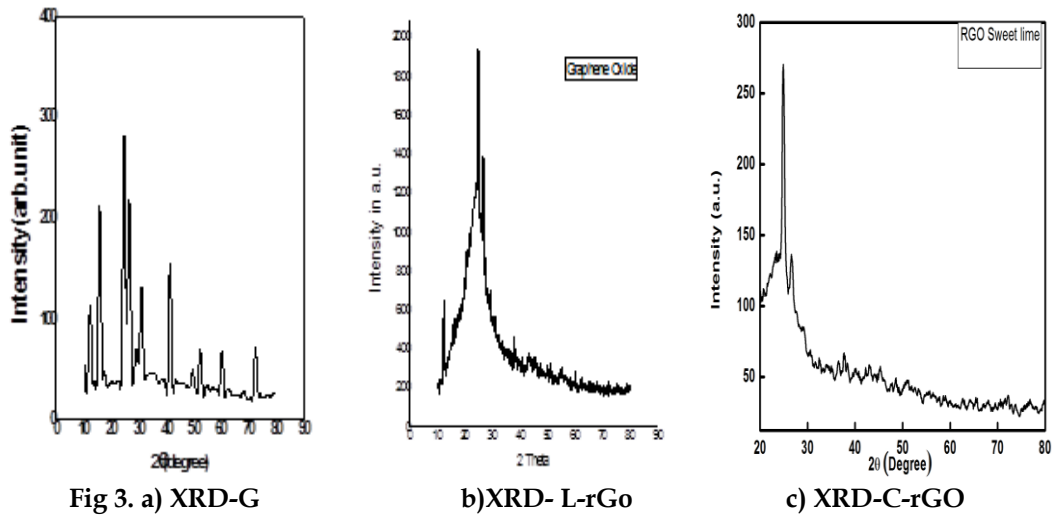


Fig. 4 a. SEM of image of L-rGO

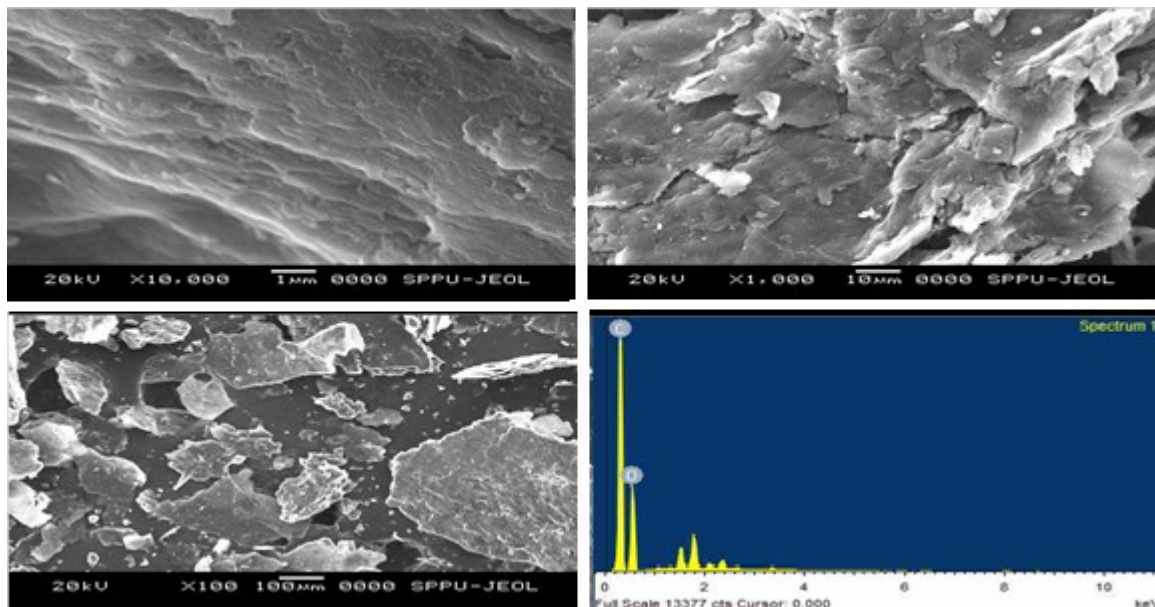


Fig 4 (b) SEM of image of C-rGO

**EDX analysis**

The EDX result also confirms and showing the elemental composition of elements C and O respectively.

**CONCLUSIONS**

*Lantana camara*, *Citrus limeta* can successfully reduce GO and forms graphene sheets which are

dispersible in water. Graphene obtained through such green routes could be of great importance in a countless industrial applications, especially in biologically sensitive areas.

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