



# Structural changes in graphene oxide thin film by electron-beam irradiation



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## ABSTRACT

Although we have a whole class of 2D materials, graphene has drawn much attention for its excellent electronic, optical, thermal and mechanical properties. Recent researches have shown its large scale production by the reduction of graphene oxide either thermally, chemically or electrochemically. Although the structure of graphene oxide is inhomogeneous and hence complicated due to the presence of organic moieties e.g. epoxy, carboxylic acid, hydroxyl groups etc., its properties can be tuned by reduction according to desired application. The aim of this work is to synthesize continuous thin film of graphene oxide using commercially available graphene oxide solution and to study its reduction by 25 keV electron beam irradiation at fluences varying from  $2 \times 10^{11}$  to  $2 \times 10^{13}$  e<sup>-</sup>/cm<sup>2</sup>. Our studies using X-ray diffraction, Raman microscopy and UV-Vis spectroscopy showed that electron-beam irradiation is an effective tool for reduction of graphene oxide and for tuning its band gap.

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## 1. Introduction

With the emergence of wide class of 2D materials in nature, one of the carbon allotropes, graphene [1], has grasped a special attention for its unique properties like ballistic transport, high mechanical strength [2], high transparency and good thermal conductivity [3]. These properties make it an irreplaceable candidate for applications in the area of electronics. Nowadays, its oxidized form, graphene oxide (GO), is also being investigated for its properties. GO can be considered as a single layer of graphite oxide. It can be produced by oxidation of graphite, with subsequent dispersion and exfoliation in water or suitable organic solvents. Many researchers are working for years for determining the structure of graphite oxide and have proposed different models. Its widely accepted model is given by Lerf and Klinowski [4]. According to their model, GO has chemically reactive oxygen functionalities, such as carboxylic acid groups at their edges, and epoxy and hydroxyl groups on the basal planes. However, the exact atomic structure is still uncertain and under debate. Stoichiometric ratio of C: O depends on the synthesis method and degree of oxidation [4] and the parameters for a stoichiometric composition are not yet standardized. Due to its oxygen containing functional groups, it exhibits both sp<sup>2</sup> and sp<sup>3</sup> hybridization [5]. The sp<sup>3</sup> hybridization makes it an insulator which hinders its use as a conductor [3]. Different

functional groups attached with GO help it in dispersing in water, alcohol and other organic solvents [6]. It can be easily deposited on a substrate to work as an electrode which increases its surface-to-volume ratio, and thereby improves the transport properties of electrode by providing a large number of active sites thus enhancing electro-catalytic property [7]. So, there is a large scope for GO in the field of electrochemical sensors and electro analysis [8].

GO can also be used as a precursor for graphene synthesis by its reduction, which is more economical method. Reduced graphene oxide (rGO) is similar in properties to pristine graphene but the difference lies in the presence of some oxygen containing functional groups in rGO, even after reduction [6]. Reduction of GO can be achieved through chemical, thermal [9] or electrochemical method [10]. There are problems associated with the reduction of graphene oxide while going through chemical route of reduction. Chemical methods of reduction lead to the addition of impurities in sample. These impurities can react with active sites of graphene oxide and lead to the formation of other by-products which can change the desired properties of graphene oxide [11]. Thermal route of reduction leads to the damage of graphene oxide platelets. This leads to some loss of graphene oxide mass and also some defects are created. These defects can change the property of reduced graphene oxide [12]. Electrochemical reduction necessitates the use of a conducting substrate (e.g. ITO) as an electrode. So, researchers are looking for other means of reduction which are more precise and can be controlled. Irradiation of graphene oxide can be one of the alternatives.

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There are several reports on effect of radiation on graphene but behavior of graphene oxide on irradiation is not well studied. Lei Chen et al. [13] have shown that reduction of GO can be achieved by electron-beam irradiation. They used electron beam of energy 5 MeV with an adsorbed dose of 500 kGy and a beam current of 200  $\mu\text{A}$  in ambient temperature in air by an industrial electron accelerator and showed a decrease in inter-layer spacing using X-ray diffraction. Amount of oxygen containing functional groups was found to be altered and percentage of C–C bonds was increased from 32.82% to 35.95%. These results were confirmed using X-ray photoelectron spectroscopy (XPS) technique. The disorder, as indicated by  $I_D/I_G$  ratio in Raman spectra slightly increased after electron-beam irradiation.

In the present work, our aim is to study whether reduction of graphene oxide and tuning of energy band gap is possible in low energy regime (keV). We irradiated GO by electron beam of energy 25 keV with beam current of 420 pA at different fluences and observed structural changes using X-ray diffraction. Also, change in optical energy band gap was observed by UV–Vis spectroscopy in reflectance mode. To observe the change in morphology, Scanning Electron Microscopy of the sample was done before and after irradiation.

## 2. Experimental procedure

### 2.1. Synthesis

Commercially procured GO solutions (from Graphene Laboratories Inc. USA) of high concentration (5 g/L) and low concentration (500 mg/L) were used to prepare film of graphene oxide. 5 parts (by volume) of low concentration GO solution and 1 part (by volume) of high concentration GO solution were mixed in a test tube and 20 micro liters of this solution was used to prepare thin film of GO on  $\text{Si}/\text{SiO}_2$  (285 nm) substrate, using drop casting technique. Both the solutions were mixed to obtain uniform, continuous and optimized thickness of film.

### 2.2. Characterization

Pristine film was characterized using X-ray diffraction technique (Cu  $K_{\alpha}$  at 1.54  $\text{\AA}$  wavelength), Raman microscopy (using 514 nm Argon laser excitation of power 5 mW) and UV–Vis spectroscopy. Fig. 1 shows the XRD spectra of pristine GO which gives the characteristic peak at  $9.70^\circ$ . Fig. 2 shows the Raman spectra of

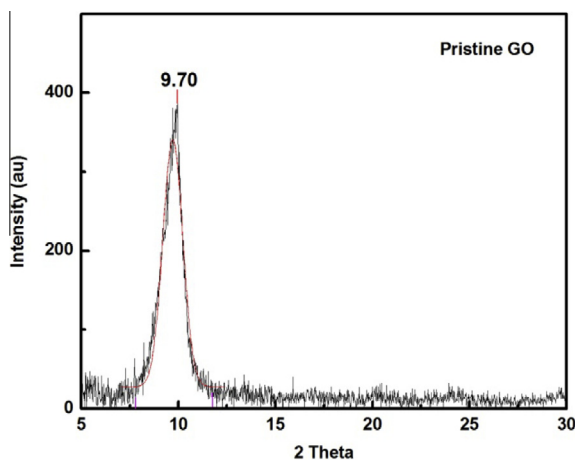


Fig. 1. XRD spectra of pristine graphene oxide film showing the characteristic peak at  $9.70^\circ$ .

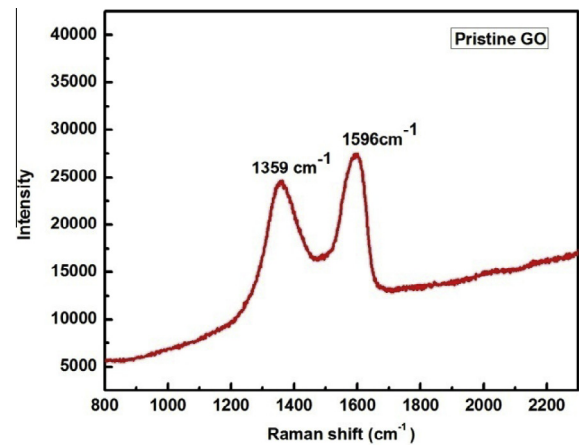


Fig. 2. Raman spectra of pristine graphene oxide showing the characteristics D and G modes at  $1359$  and  $1596\text{ cm}^{-1}$ .

pristine GO which shows the bands at  $1359$  and  $1596\text{ cm}^{-1}$  which corresponds to D and G modes respectively.

Nearly  $0.5\text{ cm}^2$  area of film was irradiated under Scanning Electron Microscope (SEM) with electron-beam of energy 25 keV and beam current of 420 pA. The irradiation fluences used:  $2 \times 10^{11}$ ,  $2 \times 10^{12}$  and  $2 \times 10^{13}\text{ e}^-/\text{cm}^2$ . After every fluence irradiation, X-ray diffraction and UV–Vis reflection measurements were done for both pristine and irradiated samples. Scanning Electron Microscopy was done before and after irradiation to observe morphological changes.

## 3. Results and discussion

X-ray diffraction plots obtained at different fluences are shown in Fig. 3. GO has its characteristic  $2\theta$  peak at  $9.70^\circ$ . Broadening of XRD peak indicates the presence of nanocrystallites. It is observed that peak position shifts towards higher side from  $9.70^\circ$  for pristine sample up to  $10.38^\circ$  for fluence  $2 \times 10^{13}\text{ e}^-/\text{cm}^2$ , indicating a decrease in inter-planar spacing [13] from 0.90 nm to 0.86 nm as calculated from Bragg's law:  $n \times \lambda = 2 \times d \times \sin\theta$ .

Where,

$d$  is the inter-planar distance,

$n$  is the order and

$\lambda$  is the wavelength of X-rays

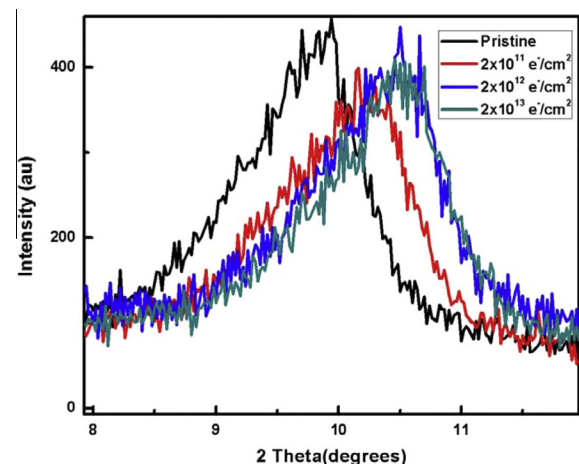


Fig. 3. XRD plots for pristine and electron beam irradiated GO for different fluences showing reduction of GO.

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