



Reduced graphene oxide synthesis by high energy ball milling



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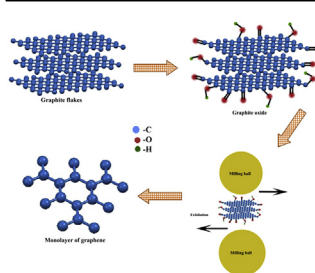
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HIGHLIGHTS

- Graphene oxide is transformed to reduced graphene oxide by high energy ball milling in inert atmosphere.
- Fine tuning the band gap by introducing defects and removing oxygen functional groups.
- Introduction of excess defects leads to amorphization.
- Photoluminescence has been observed in the UV-blue region.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene oxide is transformed to reduced graphene oxide by high energy ball milling in inert atmosphere. The process of ball milling introduces defects and removes oxygen functional groups, thereby creating the possibility of fine tuning the band gap of all intermediate stages of the structural evolution. A limit of the backbone sp^2 network structure has been found which should be able to accommodate defects, before amorphization sets in. The amorphization of graphene oxide is achieved rather quickly in comparison to that of graphite. From thermogravimetric and differential scanning calorimetric analysis along with Fourier transform infrared (FTIR) and Raman spectroscopic studies, it is found that the number of oxygen-containing groups decreases at a faster rate than that of aromatic double bonds with increasing ball milling time with a maximum limit of 3 h. Several characterization techniques (FTIR, Raman, UV–Visible and X-ray photoelectron spectroscopy) have confirmed that the material synthesized is, indeed, reduced graphene oxide.

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1. Introduction

Defects play a very important role in semiconductor technology for device designing and help in tuning the band gap. Although graphene initially attracted attention for the possibility of ultrafast

nanoelectronics due to ballistic transport of electrons, resulting from zero band gap, and several other requirements of electronics could not be achieved because of this characteristic. There was limitation for its use in field effect transistor (FET), for which a controlled band gap was essential. Defects such as oxygen functional groups can fine-tune this band gap. Graphene without any defect is not sensitive to produce any kind of sensors [1]. For building sensors, the FET platform is important and so also is the designing of the functionalization and decoration of the defects to trap specific entities to be sensed. Graphene, with its extraordinary

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electronic [2], mechanical [3] and thermal [4] properties has created excitement in the areas of both basic [5,6] and applied research [7,8]. Initially production of large area single layer graphene sheet with no defect was the aim and was best produced by the so called “peel off” method from highly oriented pyrolytic graphite (HOPG) [2]. As this method was not suitable for large scale production, a number of techniques for producing graphene evolved [9–14]. Graphene produced by these methods, however, differed in terms of defects and functional groups present from those originally prepared by mechanical peeling [15,16].

Graphene exfoliation is achieved by oxidizing graphite followed by chemical reduction of the graphene oxide (GO). By oxygen functionalization, the gap between the graphitic planes is increased and the corresponding van der Waals force between the planes is reduced. As a result, it becomes easy to exfoliate GO planes. A mere ultrasonication can lead to separation of the GO planes and therefore it becomes an interesting monolayer system. GO reduction results into the restoration of graphitic structure. However, complete removal of oxygen functionalization and restoration of defect free graphene structure is difficult. Moreover, due to inter-layer π - π conjugate interaction between the graphene sheets, irreversible particle agglomeration occurs in chemical methods [17], which is a limitation. However, the attraction of this method lies in the fact that oxygen functionalization in a controlled way can tune the band gap of graphene, which is known to have a linear correlation with the molar concentration of oxygen, leading to possible tailoring of the physical properties [15,18,19]. Annealing treatment can restore some degree of sp^2 network [15] when graphene is prepared from GO. Controlled number of defects and their nature can result in further tunable graphene.

There are recent reports of graphene being prepared directly from graphite using ball milling as a technique in the presence of dry ice and melamine [20,21]. In these works, molecular adsorption on the graphene surface is used as a key strategy which leads to compensation of the van der Waals attraction between the graphene sheets [22]. In the first work [20], the basal plane functionalization has been avoided and individual graphene planes got edge functionalized by highly energetic carboxylates ($-\text{COO}-$). This edge-selective functionalization of graphite without the basal plane oxidation by ball milling in the presence of dry ice led to edge-carboxylated graphite which is highly dispersible in various polar solvents to self-exfoliate into graphene monolayers. On the other hand, León et al. [21] synthesized graphene by ball-milling 30 mg of graphite/melamine under different milling conditions, using air or nitrogen atmosphere. It was reported that no covalent bonds were formed during the milling treatment and simple hot water treatment could restore the graphene structure easily.

We have however started from the traditional GO materials resulting from modified Hummers method. Hydroxyl and epoxy groups are usually distributed over the carbon basal plane while carboxyl groups are present mostly at the edge in GO [23,24]. It is also known that edge plane carboxyl groups of GO are highly unstable, whereas the edge plane carbonyls are much more stable [25,26] and surface density of the epoxy species is the key factor to control the lattice damage on the basal plane of graphene. The objective of both the methods reported were to produce graphene in a green way directly from graphite and to keep the defects to a minimum to achieve a graphene comparable to mechanically “peeled off” defect free graphene. However, as the oxygen functionalization played no role in both the works, fine tuning of the band gap was beyond the scope of those investigations.

In this article, we report a very simple method for the production of reduced graphene oxide (rGO) from GO. The method is devoid of any hazardous chemicals that have been used for producing chemically converted graphene (CCG). This brings us to the

possibility of fine tuning of the band gap, starting from a monolayer system such as GO and ending up with rGO. This can create platform for nanoelectronics which can be FET based and therefore can function as sensors.

The fundamental question addressed here is to understand the optimum condition which indicates the capability of graphene structure to accommodate maximum amount of defects, beyond which the structure evolves towards amorphization under ball milling [27]. The ball milling simultaneously removes oxygen functionalized groups due to energy transfer from impact and induces defect formation. By controlling the time and other parameters of ball milling, tuning of the band gap is possible.

2. Experimental section

2.1. Synthesis

The GO was prepared using a modified Hummers method [28]. The GO powder was then ball-milled for different durations with zirconium oxide balls of diameter 5 mm in a FRITSCH Pulverisette 7 planetary ball mill. The ball to mass ratio (BPMR) was kept constant at 20:1 with angular speed 800 rpm in inert (Ar) atmosphere. Although the range of disc and vial rotation was kept in the range of high energy ball milling, the time used for the synthesis of the final product was kept rather low deliberately. The samples will be referred to as BM1, BM2, BM3 and BM4 for 75, 120, 180 and 240 min of ball milling respectively.

2.2. Materials characterization

The synthesized samples were characterized using different techniques. Fourier transform infrared (FTIR) and UV–Vis spectra of the samples were recorded using Shimadzu FTIR 8400S and Varian Cary 5000 UV–Vis–NIR spectrophotometers respectively. The thermal characterization of the samples was carried out using TA Instrument SDT Q600 DSC-TGA and Q2000 DSC. The photoluminescence spectrum was recorded using ELICO SL 174 Spectrofluorimeter. Raman scattering study was performed with 514.5 nm excitation of continuous He/Cd laser and dispersion with 2400 gr/mm grating in the backscattering configuration using Raman spectrometer (inVia Renishaw). A thermoelectric cooled ‘back-thinned’ charged coupled detector was used for the detection of scattered intensity. The morphology of the sample was studied using JEOL 2010 transmission electron microscope (TEM). The X-ray photoelectron spectrum (XPS) of the sample was recorded on Specs (Germany) spectrometer.

3. Results and discussion

3.1. FTIR spectroscopy

The structure of GO is dependent on preparation methodology and is still under debate in the literature [28]. As we followed the modified Hummers method, the expected established structure can be described by the Lerf–Klinowski model [10,29]. The corresponding bending and stretching modes are identified in the FTIR spectrum (Fig. 1(a)). The characteristic peaks are due to $\text{C}=\text{O}$ ($\sim 1725\text{ cm}^{-1}$), $\text{C}=\text{C}$ aromatic bond ($\sim 1634\text{ cm}^{-1}$) and $\text{C}-\text{O}$ ($\sim 1065\text{ cm}^{-1}$). The peaks at 3406, 1390 and 652 cm^{-1} corresponds to stretching, deformation and bending modes of $\text{O}-\text{H}$ group of adsorbed water molecules respectively.

Fig. 1(b) shows the FTIR spectra of the samples BM1, BM2, BM3 and BM4 together and it is apparent that with an increase in ball milling time the amounts of the oxygen-containing functional groups ($\sim 1725\text{ cm}^{-1}$) are decreased. However, in Fig. 1(c) where the

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