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Graphene oxide: Synthesis, Characterization and Applications

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Abstract

In this paper, we discuss the different methods for the synthesis of graphene oxide (GO). Besides this various characterization techniques like optical microscopy, fluorescence microscopy, scanning electron microscopy, and atomic force microscopy are discussed. X-ray photoemission spectroscopy and Raman spectroscopy are used for the analysis of chemical, structural, and vibrational properties We have also discussed the fundamental properties which makes GO useful candidate for future applications.

Keywords:- Graphene oxide, Synthesis, Characterization and Applications.

Introduction

In the recent years the scientific community pays more attention towards grapheme oxide (GO) as witnessed by large number of research papers[1-3]. Graphene oxide (GO) consists of sheet of graphite decorated by several oxygenated functional groups on its basal planes and at its edges, resulting in a hybrid structure comprising a mixture of sp^2 and sp^3 hybridized carbon atoms[4]. The outstanding properties of GO arises due to its hybrid electronic structure as it contains both the conducting π states from the sp^2 carbon domains and also the σ states from the sp^3 carbon domains [5]. Theoretical studies have revealed that the properties of GO can be altered by tuning the sp^2/sp^3 ratios of the carbon atoms . The sp^2/sp^3 ratios in GO can be tuned by varying the oxidation degree using suitable chemical reactions. The tunability of the ratio sp^2/sp^3 by reduction chemistry is a powerful way to tune its bandgap and therefore controllably transform GO from an insulator to a semiconductor and to a graphene-like semi-metal. GO with various ratio of sp^2/sp^3 domains may provide novel properties that can be useful for making several improvements in the development of graphene based research applications such as biosensors, supercapacitors, and optoelectronic devices etc. In the present paper we focus on the different methods for Graphere oxide (GO) preparation ,the fundamental characterization of GO and some of the most promising application.

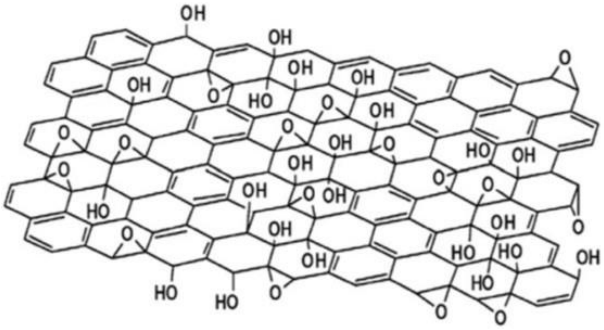

Fig. 1 GO chemical structure based on the Lerf–Klinowski model.

Different methods of Graphene Oxide (GO) Synthesis -

GO is formed by oxidizing graphite. This material is often then exfoliated into mono- and few-layer sheets, depending on the degree of oxidation and postprocessing. The three major methods used to synthesize GO viz. (i) the Brodie method [6], (ii) the Staudenmaier method , and (iii) the Hummers method[7]. Among these methods, most researchers follow the Hummers method which is generally considered to be the best , it has the advantage of non-toxicity compared to the other two methods [3].

The GO particles can be synthesized by a modified Hummers method [7] using expandable graphite powders as the starting material. Briefly, the expandable graphite powders (2 g) was stirred in 98% H_2SO_4 (35 ml) for 2 h. $KMnO_4$ (6 g) was gradually added to this solution while keeping the temperature less than 20 ˚C. The mixture was then stirred at 35–40 ˚C for 30 min, and then at 65–80 ˚C for 45 min. The resulting solution was diluted by adding 46 ml of water and the mixture heated at 90 ˚C for 30 min. The reaction was terminated by addition of 150 ml of distilled water and 30% H_2O_2 solution (10 ml). The mixture was washed by repeated centrifugation with 5% HCl aqueous solution followed by deionized water until the pH of the solution becomes neutral. To obtain GO particles, 160 ml of water was added resulting precipitate and sonicated well to make a uniform suspension for graphene oxide.

The graphene oxide is basically a broad range of disordered oxidized graphene structures where the ratio of functional groups (epoxy, hydroxyl, and carboxyl groups) depends strongly on both the parent material and the processing approach used. Compton and Nguygen recently highlighted this aspect by noting that the carbon to oxygen ratio (C:O) measured in graphite oxide samples ranged from 1.3 to 2.25 depending on the approach used and oxidation time [8].

Since many years the structure of GO has been the subject of considerable debate. There are so many reasons for this, but the foremost contributors are the complexity of the material (including sample to sample variability) due to its amorphous, berthollide character (i.e nonstoichiometric atomic composition) and the lack of precise analytical techniques for characterizing such materials. Inspite of these hurdles, considerable effort has been directed toward understanding the structure of GO, much of it with great success. The most recent models of GO have rejected the lattice based model and have focused on a nonstoichiometric, amorphous alternative. The model given by Lerf and Klinowski [9] is widely accepted by scientific community . According to this model, GO is built of non oxidized aromatic patches of variable size, which are separated from each other by aliphatic 6- membered rings containing hydroxil groups, epoxide groups, and double bonds (Fig. 1). In this model the basal plane contains the O functional groups both above and below it , which gives rise to the polar nature and hydrophilic behavior of GO.

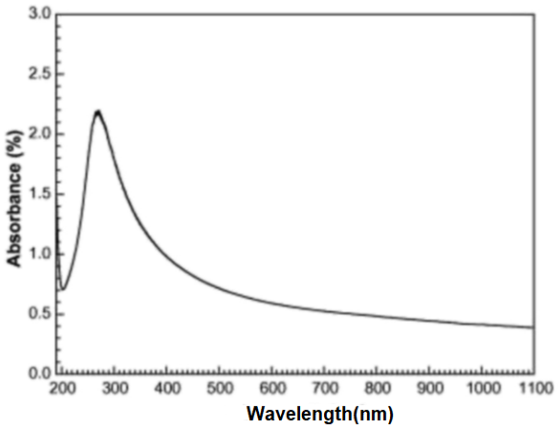

Fig. 2a UV-Vis spectrum of graphene nanosheet dispersion in water (Ref. 11)

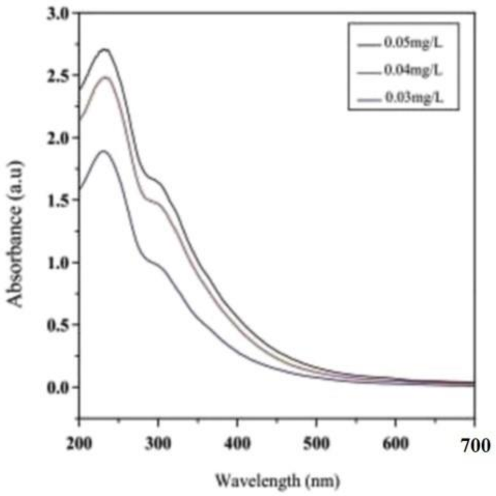

Fig. 2b UV-Vis of GO diluent at different concentrations(Ref.13).

Characterization techniques

There are several methods given in literature to characterize GO. This section describes the different methods to characterize GO: -

Ultraviolet -visible spectroscopy (UV-Vis)

UV-Vis has been used to measure the optical absorption properties of GO sheets [10]. A UV-Vis absorption peak at 265 nm for graphene nanosheets (Fig. 2a) indicates a graphitic structure [11], and is generally regarded as the excitation of the π-plasmon of the graphitic structure [12]. It is known that the UV-Vis absorption spectrum of GO has two characteristic features (Fig.2b) [13], which are used as a means of identification, i.e., a maximum at 231 nm corresponding to the $\pi \rightarrow \pi^*$ transitions of aromatic C=C bonds, and a shoulder at ~300 nm attributed to $n \rightarrow \pi^*$ transitions of C=O bonds [14, 15].

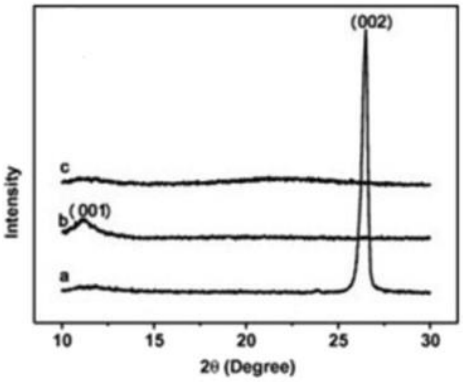

Fig. 3 XRD patterns of graphite (a), GO (b), and rGO (c) (Ref. 18).

X-ray diffraction (XRD)

X-ray diffraction (XRD) is the most commonly used technique for characterizing GO. This technique is based on observing the intensity of scattered X-rays as a function of scattering angle [16]. XRD provides information regarding the stacking of graphite and GO, and has been used to quantitatively estimate the degree of exfoliation [17]. XRD patterns of graphite, GO, and reduced graphite oxide (rGO) are shown in (Fig.3) [18]. Graphite has a strong diffraction peak at $2\theta = 26.52°$ (002), representing an interlayer distance (d-spacing) of 0.34 nm as evaluated by the Bragg equation. This peak disappears in GO and a new peak at a smaller 2θ value (greater spacing between sheets) appears. The 2θ value of this GO peak depends on the method of preparation and on the presence or absence of water in the gallery space [19].

Raman spectroscopy

Raman spectroscopy can provide important information regarding the bonding configurations of atoms in carbon structures[20]. Raman spectroscopy of GO can also serve as an effective characterization method elucidating structure-specific vibrational phonon modes. The Raman spectra of graphite and graphite-based materials such as GO have several distinctive features, including D (~1385 cm^{-1}), G (~1580 cm^{-1}) and G′ or 2D (~2700 cm^{-1}) bands[21-23] . The D band originates from a second-order effect involving a phonon and a defect in the sp^2 graphitic structure; thus it is often attributed to disorder in sp^2 carbon material. The G band comes from first-order Raman scattering in graphitic materials involving a single phonon from the E_{2g} mode involving doubly degenerate in-plane optical vibration in sp^2 carbon[20]. The G′, often called 2D, band originates from the two-phonon process involving phonons with opposite momenta and depends strongly (inversely) on the number of graphene layers.

The G band describes the sp^2 graphitic structure and the D band is associated with defects in that structure. The G band peak becomes broader and also experiences a blue shift to roughly 1,593 cm^{-1}. Upon transforming graphite oxide to reduced graphite, the G band peak returns to the original graphite frequency, indicating that the presence of oxygen could be related to the observed blue shift.

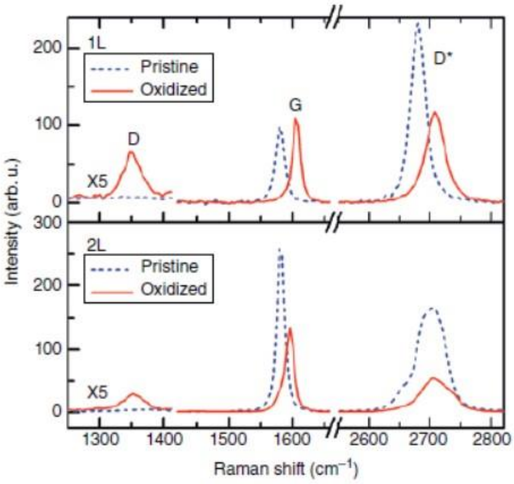

Fig.4 Raman spectra of single-layer (top) and double-layer (bottom) pristine and oxidized graphene(Ref. 23)

X-ray photoemission spectroscopy

XPS is an excellent technique to study the chemical composition of GO. It is possible through XPS analysis to identify the functional groups which are present in GO by deconvolving the C 1s and O 1s core level spectra into components, each one assigned to a specific functional group[24, 25]. In some literature reports the C1s peak of GO is deconvoluted into five components: sp^2carbons from graphite (~284.6eV), C atoms bonded to hydroxyl groups (~285.7eV), epoxy/ether groups (~286.7 eV) [26], carbonyls (~288.0 eV) and carboxylic acid groups (~289.1 eV) (Fig. 5). Other literature deconvolutes the C1s peak into only four components [27, 28]. The O1s spectra of GO is reported to be composed of two major components: C–O (epoxy and hydroxyl, ~532.5 eV) and C=O (carbonyl and carboxyl, ~531.6 eV), with two minor components arising from quinones (~530.5 eV) and O–H (hydroxyl, ~533.5 eV) [29]. XPS analysis has been used to determine the atomic composition as well as the C/O ratio of GO [30] by dividing the C1s peak area by the area of the O1s peak multiplied by the ratio of the photoionization cross sections.

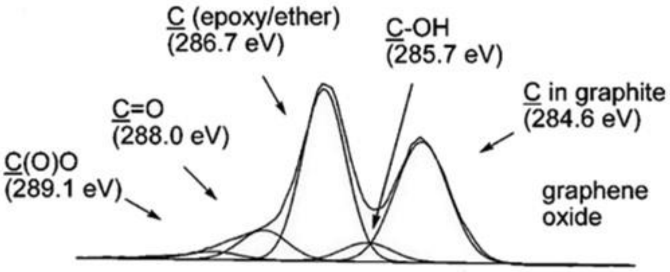

Fig. 5 Deconvoluted XPS spectra in the C1s region of unmodified GO paper (Ref. 26).

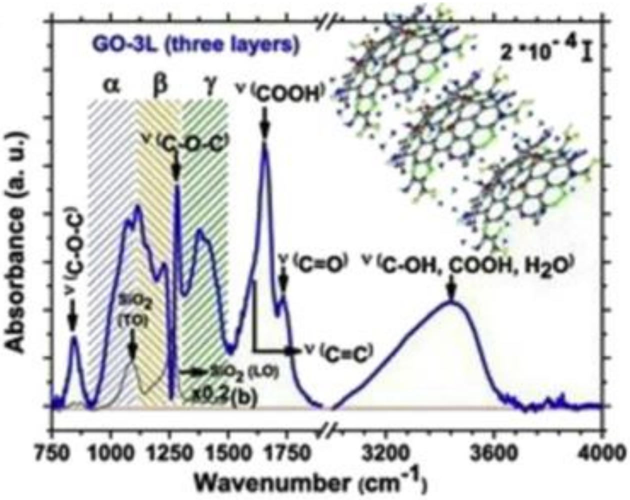

Fig. 6 Infrared absorbance spectrum of GO (three layers) at room temperature (Ref. 32).

FT-IR characterization -

FTIR measures the absorbance or transmittance of light through a sample as a function of wavelength and provides information regarding the identity of functional groups [31]. It is especially useful in identifying the different oxygen functionalities in GO [14].As an example, the FTIR spectra of three-layer GO at room temperature is shown in Fig.6 , revealing the presence of vibrational modes for hydroxyls at 3000-3700 cm^{-1}, carbonyls at 1750-1850 cm^{-1}, carboxyls at 1650-1750 cm^{-1}, sp^2-hybridized C=C (in plane stretching) at 1500-1600 cm^{-1}, and epoxides at 1280-1320 and 800-900 cm^{-1} [32]. For multilayer GO, ketones and/or carboxyls are found within the overlapped frequency range of 700- 1900 cm^{-1}, sp^2 -hybridized C=C (in-plane stretching) is found at ~1550-1650 cm^{-1}, and epoxides are found at approximately 1350 and 800-900 cm^{-1} [33].

Electron microscopy -

Transmission electron microscopy (TEM) is a useful tool for identifying single-layer and few-layer graphene oxide sheets[34]. TEM uses electrons that pass through the sample with contrast resulting from differences in electron density, so multiple sheets appear darker relative to single sheets[35]. TEM images of ultrasonically exfoliated GO exhibits a typical wrinkled morphology[36, 37], with GO exfoliated into single or very few layers [37]. The wrinkles and folds in the sheets of exfoliated GO are a characteristic feature of single-layer sheets [38]. In other studies, TEM has shown GO sheets with a curly morphology[39] or with the sheet edges scrolled and folded slightly [40].

Scanning electron microscopy (SEM) images are the result of secondary electrons emitted by the sample[41]. The topology and lateral dimensions of the sample can be analyzed [42], but it can be difficult to quantify sheet thickness. Typical SEM images of GO show 2D nanosheet morphologies [39] with wrinkled and folded textures [43] with sometimes irregular edges, rough surfaces, and crumpling as a result of the scrolling [44]. SEM has shown GO sheets with lateral dimensions as large as 200 mm and as small as a few microns in the same GO sample[45].

Applications

Due to its unique chemical composition and flakes size GO finds application in many fields:-

Sensors

GO is inherently a good material for sensing applications due to the large number and diversification of the functional groups decorating its surface, which are potential anchoring sites for several molecules. However, while many works are reported in the literature on the use of graphene for gas sensing and biosensing, [46-50]less attention is given to GO, due to its dielectric nature which prevents from an efficient extraction of the electric signal from the sensor. As a compromise between graphene and GO, chemically and thermally reduced GO has been used with excellent results [51-54]. Xiaohui Leng et al demonstrated GO (graphene oxide)-based sensor with differential structure was designed to detect both humidity and temperature[55]. Two identical units have been fabricated with patterned gold electrodes on which a layer of GO was deposited by drop-casting or spraying coating method. One unit was then covered by a layer of PDMS to modify its response to the temperature and humidity. Using this differential structure, the sensor shows great linearity in a temperature range from 20 °C to 60 °C and a humidity range from RH 25% to RH 95%. The humidity response of the two units varied for three orders of magnitude under the same temperature, which indicates a good sensitivity of the device. They found that the spray coated sensor has a relatively short response and recovery times than the drop-casted one. Yun Chen et al [56]demonstrated a NH_3 detection device at room temperature based on SnO_2- rGO . SnO_2 nanorods randomly oriented grew on the reduced graphene oxide substrate through a hydrothermal method and formed a porous network structure. The as-prepared SnO_2 nanorods size with a uniform diameter of about 10 nm. The gas sensing experiments had shown a highly response to NH_3 at room temperature and less affected by humility. These improved sensing properties at room temperature are favorable for the ammonia detection in practical application. Moreover, the enhanced sensing performance could ascribe to the new structure of SnO_2 coupled on rGO substrate that exhibited a synergic effects superior than either of constituent compounds, which the nanorods structure provided a large specific surface area with pore volume for gas adsorption. In this structure of SnO_2-rGO that rGO provided effective electron transfer and highly response sensitivity at room temperature. This work had demonstrated the gas sensor fabricated by composites of SnO_2-rGO could perform a high sensing property for NH_3 at room temperature.

Energy storage

We cannot use GO directly in supercapacitors due to its intrinsically poor electrical conductivity ,although there have been some investigations that demonstrated feasible usage of GO in SCs [57, 58]. To improve the electrical conductivity of GO and to retain the pseudo-capacitive behavior, partially reduced GO has been widely adopted[59-61]. The residual oxygenated groups on RGO can induce large pseudo-capacitance in SCs [57]. Moreover, the co-contribution of double layer capacitance and pseudo-capacitance from the oxygenated groups were observed in the SCs with water-soluble RGO as the electrode materials [62]. There reduction level of the RGO sheets (especially the variation of oxygen-containing groups) plays a significant role in controlling the intrinsic properties such as the interlayer spacing ,oxygen content ,BET (Brunauer– Emmett–Teller) specific surface area, and thus affects the overall performance of SCs [63].

Organic photovoltaic (OPV) materials have recently garnered significant attention as enablers of high power conversion efficiency (PCE), low-cost, mechanically fexible solar cells.

The utilization of GO thin films as the hole transport and electron blocking layer in organic photovoltaics was demonstrated by Li et al. [64].The incorporation of GO deposited from neutral solutions between the photoactive poly(3-hexylthiophene) (P3HT):phenyl-C61-butyric acid methyl ester (PCBM) layer and the transparent and conducting indium tin oxide led to a decrease in recombination of electrons–holes and leakage currents. This resulted in a dramatic increase in the OPV efficiencies to values that are comparable to devices fabricated with PEDOT:PSS as the hole transport layer. Liu et al. [65]utilized sulfated GO as a layer for high-performance polymer solar cells. Radich et al.[66] reported Cu_2S reduced GO composite for high efficiency quantum dot solar cells. Murray et al.[67] applied electronically tuned GO as an effective interfacial layer (IFL) for templating the optimum donor polymer p-stacking orientation for high efficiency OPVs. In addition to functioning as a solution-processable PEDOT:PSS alternative, GO significantly enhances the durability of fully fabricated devices by increasing the active layer-IFL interfacial stability under thermal and environmental stress.

Conclusion

In this article, the synthesis, characterization and applications of grapheme oxide have been reviewed. Due to its unique structure with several types of oxygen-containing functional groups on the basal plane and the sheet edge allows GO to interact with variety of organic and inorganic materials in non-covalent, covalent and/or ionic manner and gives rise to many functional hybrids and composites with unusual properties.

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