A FACILE IMPROVED OXIDATION METHOD FOR ECOLOGICAL PRODUCTION OF GRAPHENE OXIDE

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In recent years, various improvements over different graphene synthesis methods are practiced constantly for safer and functional substitutes. Though graphene extraction through Hummers method is one of the former techniques yet but new advancements are always present. Here, we have compared the properties of graphene oxide prepared through conventional Hummers method and simple room temperature approach and it is concluded that conventional Hummers method can be replaced by simple room temperature approach by replacing sodium nitrate ($NaNO_3$) with phosphoric acid (H_3PO_4) having no change in properties. In comparison to conventional Hummers method, this simple method eliminates need of temperature control and generation of toxic gases. In our case, this one-pot oxidation of graphite powder at room temperature has provided large area production of graphene oxide with 100% conversion.

1. Introduction

Primarily, the synthesis, characterization, exploitation and exploration of nanomaterials are commonly concerned with nanoscience and nanotechnology. Carbon is a most abundant material that naturally have many forms and occurs as an essential component of innumerable substances that are entitled as carbon allotropes [1]. Among these allotropes, a two-dimensional sheet having sp^2-hybridized carbon atoms known as graphene have several properties that tantalize its high thermal and electrical conductivity, lightweight, chemically stable, strong mechanical strength of approx. 1 TPa and highly tunable surface area (up to 2675 m^2 g^{-1})[2-4]. The honey-comb structure of graphene is well thought out as an elementary building block of many imperative allotropes e.g. 3D graphite, 1D nanotubes, 0D fullerenes [5]. The interesting electronic, mechanical and electrochemical properties have fascinated the researchers. Its potential applications in biomedical, energy storage devices, sensors, polymer fillers and energy conversion have attracted very much attention now a day [6-9].

The chemical synthesis of graphene using oxidants and acids is the most common procedure, which is further converted into graphene by reduction. Graphene oxide can be depicted as a planar hexagonal assortment of single layer of carbon atoms which contains functional groups e.g. hydroxyl, carboxylic acid, carbonyl and epoxy groups. Lerf-Klinowski model elucidate that epoxy and hydroxyl group are attached on the basal plane while carboxylic and carbonyl groups are present at the edges of sheet [2].

GO single sheet can be deemed as linked structure of oxygen-containing functional groups, for example C=O, C-O, and -OH that has been sustained on the exterior of a single layer

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graphene. Thus a change in properties and structure of graphene is observed upon addition of oxygen containing functional groups. The structural defects produced by oxidation process shifts the properties of graphene oxide from pure graphene. The oxidation process produces structural defects which shift the physical properties of GO away from that of pure graphene. Fig. 1(a) & (b) displays the single layer graphene and graphene oxide structure respectively. Nevertheless, the existence of oxygen-containing functional groups results in hydrophilic nature of GO, thus making it easily dispersible in numerous solvents as ethanol, acetone, water.
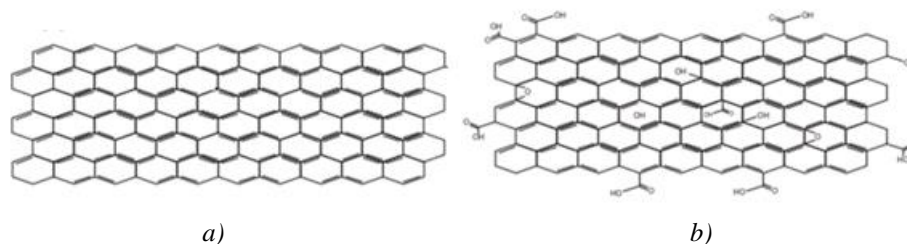

a)   *b)*

Fig. 1. Schematic diagram of (a) single layer graphene (b) graphene oxide.

The commercial level attainment of simple and cost effective synthesis process of GO is the need of hour. Different current chemical oxidation methods for production of GO as Staudeumaier's, Brodie's and Hummer's method involved tiresome and lengthy experimental time. Here, we are not considering the experimental time as the time spent for oxidation of graphite powder but rather it is the time that a researcher expends on experimental working during oxidation process [10].

Here, we have used a simple room temperature oxidation method as comparison of Hummer's method in which we have reduced the extensive hours of mixing, heating or cooling of reactants from 3-6 hours to 10 minutes. In this process, the oxidation of graphite powder was carried out with potassium permanganate ($KMnO_4$) and phosphoric acid under continuous stirring for 3 days at room temperature in order to acquire higher degree of oxidation. The yield of GO is in scalable quantity in both cases. The main advantage of this method is that no temperature control and toxic gases emission is evolved.

2. Experimental details

2.1. Materials

The most common procedure for synthesis is conventional Hummer's method. The synthesis schemes can be diverse by various oxidizing agents used for exfoliation of graphite powder. Here, we have narrated two synthesis procedures; one is conventional Hummer's method and the other is simple room temperature method. For this purpose, graphite powder, Sulfuric Acid (H_2SO_4), Phosphoric Acid (H_3PO_4), Sodium Nitrate ($NaNO_3$), Hydrogen Peroxide (H_2O_2) (30%), Potassium Permanganate ($KMnO_4$) and Hydrochloric Acid (HCl) were purchased from Sigma-Aldrich. All chemicals were of analytical grades and used as collected, with no further purification. DI water was used to prepare all aqueous solutions.

2.2. Synthesis of GO by Modified Hummer's method (GO-1):

Graphene oxide was synthesized from natural graphite flakes by modified Hummers method. First, graphite flakes (5g) and $NaNO_3$ (2.5g) were dissolved into 97% concentrated H_2SO_4 (116ml) by continuous stirring for 45 min. Then, place it in an ice bath which is maintained at less than 5°C temp. Afterward, 15g of potassium permanganate ($KMnO_4$) was gradually added in 2 hours, followed by maintenance of temperature at 20°C. Then remove the ice bath and stir the mixture for half an hour, this will give an increase in temp up to 35°-40°C. Now, add 230ml DI water drop wise at least in 2 hours. This will elevate the temp up to 60°-70°C. 700ml of DI water was gradually added into the mixture so as to eradicate the reaction. Then, addition of 50ml 30% H_2O_2 will turn the color of solution from deep brown to bright yellow. To attain the neutral PH,

wash the mixture several times with 1M HCL and DI water. In order to get rid of precipitates, after washing, centrifuge the mixture for 15min at 6000rpm. The required graphite oxide will be obtained in the form of dried transparent sheets and then re-disperse this supernatant in water to get graphene oxide solution (1mg/1ml).

### 2.3. Synthesis of GO by Simple Room Temperature method (GO-2)

In this simple room temp method, the oxidation of graphite powder was carried out by H_3PO_4 instead of $NaNO_3$. The H_2SO_4 and H_3PO_4 were mixed with graphite powder (4g) in a ratio of (160:40 ml) and then $KMnO_4$ (9 g) was slowly added using a magnetic stirrer. After slowly addition of all materials, the mixture was allowed to stir for 4 days continuously for complete oxidation of graphite. During stirring, the mixture got dark brown color from dark purplish green. By adding H_2O_2, the mixture changed its color to bright yellow, confirming the high oxidation of graphite. To obtain the PH of 4-5, the prepared graphite oxide was washed with 1MHCL and DI water through centrifugation with a centrifugation force of 6000g. During washing process, the graphite oxide experienced exfoliation of graphite oxide which resulted in formation of GO gel.

2.4. Characterizations

X-ray diffraction (XRD) was performed on a Panalytical X'pert pro Diffractometer using Cu Kα radiation (k = 0.15416 nm, Bruker, Germany). The morphology of graphene oxide was studied by Scanning Electron Microscope (JEOL JSM-6480 LV, Japan) and TEM (Tecnai F20, 200KV). UV-visible spectra were performed by using (Perkin Elmer, Singapore) UV-Visible Spectrometer. Raman spectra were taken out on a Renishaw Raman spectrometer (UK) with a 514 nm laser. The samples used for SEM, UV and Raman characterizations were deposited on glass substrate. Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded on a Fourier Transform Infrared Spectrometer (FT/IR-4100type-a, Jasco).

3. Results and discussion

Fig. 2 shows the SEM & TEM images of graphene oxide (GO-1 & GO-2). In both samples, graphene oxide shows a sheet like form resembling to a paper. Also, the graphene nanosheets are wrinkled and transparent in nature. This crumpled nature of graphene oxide is highly advantageous in large surface area applications since these sheets cannot easily collapse back to graphitic structure. [13-15]. As shown in images 2 (a-f), these sheets have large amount of wrinkles or corrugations on their surface which are not point defects rather these are extended surface defects created due to twisting or folding of graphene sheets .These wrinkles can produce digression from the sp^2-planar nature expected for graphene. [11-13].
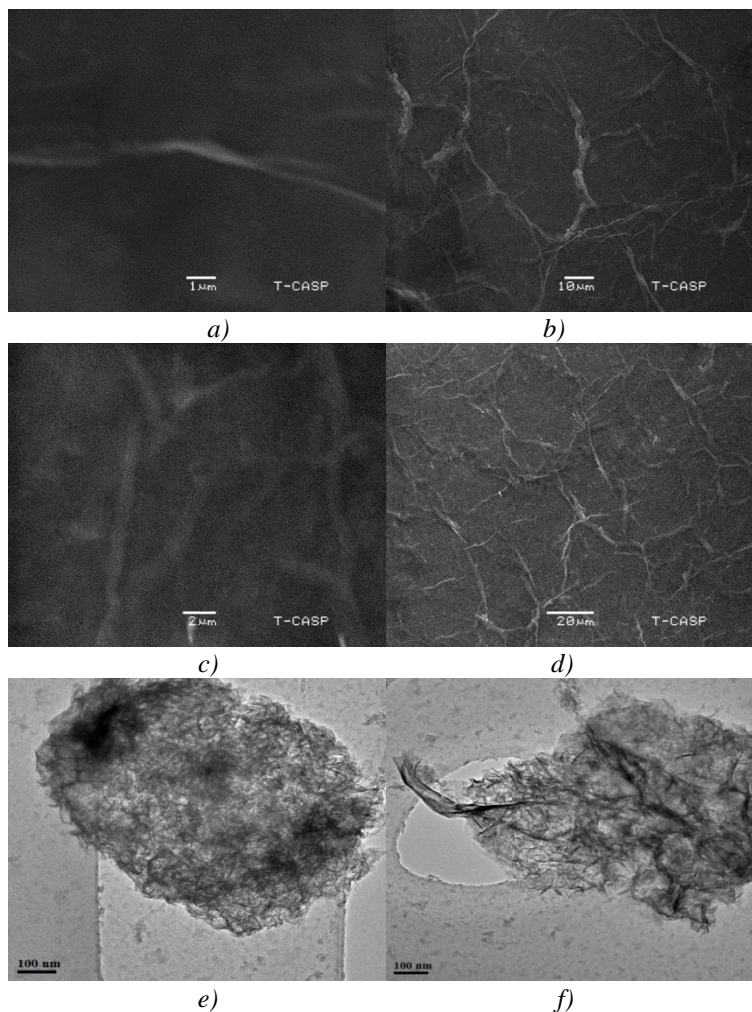
Fig. 2. SEM micrographs of graphene oxide (a, b) GO-1(c, d) GO-2 (e) TEM micrographs of graphene oxide GO-1 (f) TEM micrographs of GO-2.

The crystalline structure of graphene oxide was determined by XRD analysis. Fig. 3(a) illustrates the XRD pattern related to graphene oxide material, which approaches as active oxidation route of graphite showing a very strong peak at $2\theta=11.2^{\circ}$. Initially, the XRD results authenticate the successful synthesis of graphene oxide [14, 15]. To examine the degree of oxidation of graphite powder, Ultraviolet Visible Spectroscopy measurements were performed and presented in figure 3(b). The maximum absorption peak for both samples (GO-1 & GO-2) was found at 230nm which is attributed for $\pi \rightarrow \pi^*$ transitions for C=C bonding. Also, there is a shoulder peak observed for sample GO-1 which is at 300 nm attributable to $n \rightarrow \pi^*$ transitions of carbonyl group. No shoulder peak is observed in GO-2 which might be due to thick layer GO [10, 16, 17].
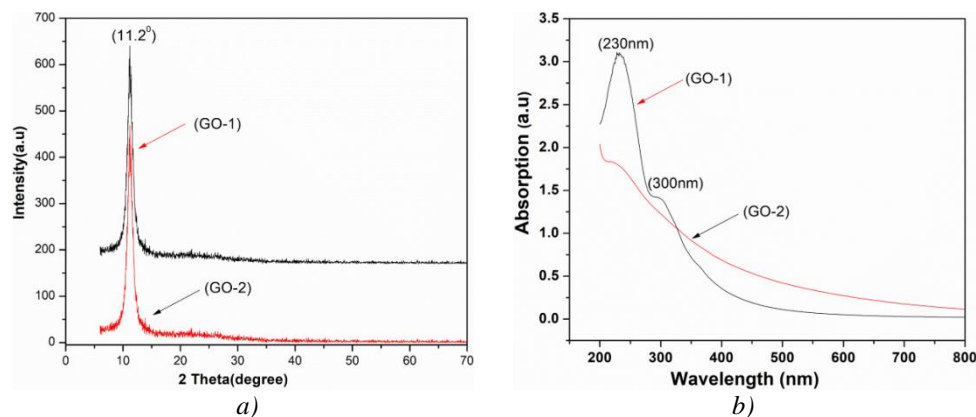
*Fig. 3. (a) XRD spectra of graphene oxide GO-1 & GO-2 (b) UV-Visible spectra
of graphene oxide GO-1 & GO-2.*

The carbon based materials are widely characterized by Raman spectroscopy for structural information. The D and G peaks are main characteristics peaks of carbon-based materials in Raman spectra. The Raman Spectra of GO-1 and GO-2 depicted in Fig. 4(a) show a D-peak at 1354 cm^{-1} and a G-peak at 1601 cm^{-1}. These peaks arise from the vibration of sp^2 carbon atoms. The breathing mode of aromatic rings is usually represented by D peak which comes up due to the defects in the sample while G peak corresponds to optical E_{2g} phonons at Brillion zone center ensuing from bond stretching of sp^2 carbon pairs. The 2D peak around 2680cm^{-1} gives rise to production of two phonons with differing momentum due to twofold resonance transitions. Also a (D+G) peak is present at 2950cm^{-1} which is also called defect activated peak [14, 16, 18, 19]. The ratio of intensity of D/G peaks is a measure of the defects present in carbon nanomaterials structure. Here, we have also calculated I_D/I_G ratio for GO-1 and GO-2 which is approximately same i-e 0.98 for GO-1 and 0.97 for GO-2 indicating that same number of defects are introduced in both samples which is in consistent with FTIR spectra. The different oxygen-containing functional groups in graphene oxide are generally determined by Fourier Transform Infrared Spectroscopy. Also, an unknown sample can also be quantitatively analyzed through this technique. Fig. 4(b) shows a peak at 3380cm^{-1}ascribed the stretching mode of an O-H bond, exposes the loads of hydroxyl groups in graphene oxide. The absorption peak at 2065cm^{-1} is assigned to the alkyne C≡C functional group in graphene oxide. A peak at 1634cm^{-1} is allocated to the stretching vibration C=C of carboxylic acid at the edge of graphene oxide which also shows that C=C bond still remained after oxidation process. Also, a peak at 1267cm^{-1} is attributed to the stretching vibration of the epoxy group C-O-C [1, 13, 17, 20, 21].
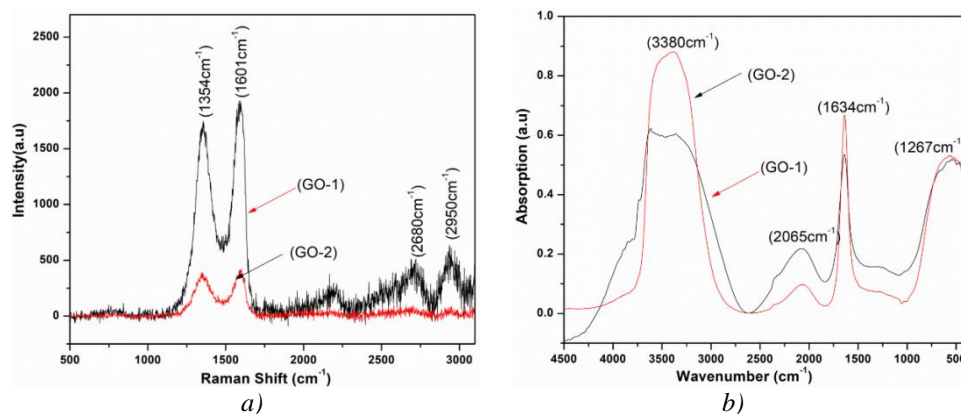

*Fig. 4. (a) Raman spectra of graphene oxide GO-1 & GO-2 (b) FTIR spectra
of graphene oxide GO-1 & GO-2.*

4. Conclusion

We developed a simple room temperature method with H_3PO_4 as an oxidizing agent instead of $NaNO_3$ for graphene oxide synthesis. This simple method eradicates the production of toxic gases and makes the procedure easier that does not involve any temperature control, thus makes GO synthesis simple and cost effective. The GO products prepared by both simple room temperature and Hummers method are nearly identical in their thickness, dispersibility, lateral dimensions and chemical structures.

The simple room temperature method explained here can be used to prepare graphene oxide on large scale and it is one-step towards the graphene and its derivative's synthesis through environmental friendly approach. This graphene oxide can be further used for many applications which include sensors, conductive films, membranes, composite materials, fuel cells, supercapacitors and batteries.

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