Preparation of graphene oxide by dry planetary ball milling technique under oxygen atmosphere

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Abstract: The work explores the preparation of graphene oxide (GO) from natural graphite by dry planetary ball milling technique under oxygen atmosphere. The ball milling was carried out between 4 and 8 hrs. The structure and composition were studied by various advanced characterization techniques. X-ray diffraction (XRD) confirms the successful formation of graphene oxide showing C(001) peak. X-ray photoelectron spectroscopy (XPS) agrees with XRD result exhibiting various oxygenated functional groups along with matrix of carbon. The increasing oxidation behaviour was confirmed from Raman study with increasing trend of I₂D/I_G ratio. The sample prepared by 8 hr ball milling exhibits BET surface area of 454 m²/g. The sheet type and folded morphology confirm the high quality formation of graphene oxide. The GO-8 hr shows a high O/C ratio (58.87). Purity of typical GO sample was confirmed from EDS analysis exhibiting only presence of carbon and oxygen.

1. INTRODUCTION

Graphene and its derivatives like graphene oxide (GO) show excellent behaviour including excellent mechanical, electrical and thermal properties [1-9]. The graphene has Young’s modulus of 1.0 TPa, high electron mobility of 15000 cm² V⁻¹ S⁻¹, 100 times stronger than steel and high electrical (less resistivity than silver). These properties make it one of the wonder material of 21st century. This 2-dimensional (2D) material has high surface area compared to graphite. Therefore, graphene finds wider application in many technological fields such as sensors, single electron transistors, capacitors, solar cells, super capacitors, transparent conductive films, etc. [1-13]. GO can be considered for many applications including polymer composites, corrosion proof coatings, energy related materials, and also have shown potential candidature for the processing of high quality graphene. The miracle material graphene gives novel award to A. K. Geim and K. S. Novosolve on 2010 [14]. Various techniques such as scotch tape method, exfoliation, mechanical delamination, chemical vapour deposition (CVD), and chemically oxidation and reduction method have been used by many researchers for preparation of graphene [15-16].

For the first time, we reveal a newly developed, and ecological technique to produce high quality graphene oxide from natural graphite by using horizontal high energy dry planetary ball milling process under oxygen atmospHERE. High purity graphite (HPG) was prepared from natural graphite by combination of physical and chemical beneficiation processes. HPG contains more than 99 % of carbon value. In the present research work, well-organized attempt has been performed to evaluate the properties of HPG and GO samples by using different advanced characterization techniques like X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), micro Raman spectroscopy and Brunauer-Emmett-


2. EXPERIMENTAL

The high purity graphite is prepared from natural graphite by following to the patented work [17] to achieve more than 99 % fixed carbon. Here natural graphite is treated with sodium hydroxide (NaOH) solution in the ratio of 1:1. The ultra fine quartz particles convert to sodium silicate by reaction with sodium hydroxide (NaOH), and then come to the aqueous state. After treatment with NaOH, solution was then allowed to filter and washed with dilute HCl to neutralize the pH. During treatment with dilute HCl, impurities like calcium, magnesium, sodium and iron phase minerals found to be dissolved and come to the aqueous stage. Then the concentrate solution was floated in flotation cell. Then liberated and unliberated quartz particles separated to achieve high purity graphite with more than 99 % carbon value in the concentrate.

Different advanced characterization techniques were used to analyse the properties of HPG and GO samples. Samples were characterized by XRD using PANalytical X’Pert Pro diffractometer supplied with Cu Kα radiation (λ=0.15406 nm). The microstructures of samples were observed by using TEM (model: TECNAI G2 (200 kV), FEI (Netherland)). Energy dispersive spectroscopy (EDS) was carried out during TEM analysis. Micro Raman spectra were taken in a dispersive type micro-Raman spectrometer (Renishaw in Via Reflex, UK) using 514 nm line of an Ar⁺ ion laser. XPS (S/N:10001, Prevac, Poland) spectra were taken with AlKα (hν=1486.6eV) radiation and a VG Scienta-R3000 hemispherical energy analyzer. An instrument base pressure 9 x 10⁻¹⁰ mbar was maintained during data acquisition. Specific surface area was determined by BET method (model: ASAP 2020, micrometrics, USA) using N₂ adsorption-desorption technique.

3. RESULTS AND DISCUSSION

3.1 Identification of structure and phase by XRD

X-ray diffraction (XRD) (figure 1) was taken to understand crystalline and phase grown in the sample. HPG sample shows a peak of C (002) at around 2θ = 26.9° with inter layer distance of ~ 0.334 nm. But the HPG taken for ball milling under oxygen atmosphere exhibits different type of patterns. After oxidation, characteristic peak of C (002) at 2θ = 26.9° was found completely missing. The 4 hr and 8 hr ball milled samples show peak at around 2θ = 11.7° of d-spacing ~ 0.82 nm, which can be attributed to the formation graphene oxide (GO) in the ball milled sample. This changes in structure is developed because of lattice expansion of graphite sample by reducing relative Van der Walls forces between adjacent graphene sheets through chemical reaction and intercalation of oxygen molecules because of oxidation. During oxidation various oxygen-containing functional groups such as hydroxyl, epoxy and carboxyl developed on the graphite lattice. Further growth of oxygen-containing functional groups in GO is also confirmed from XPS measurement (infra). The lattice expansion of high purity graphite sample in GO is also marked in TEM and micro Raman studies (infra).
Figure 1. XRD patterns taken for high purity graphite (HPG) and GO samples

In GO sample, besides the major peak at around $2\theta = 11.70$, there is also another small peaks of C such as C (004) is clearly seen which is relating to other diffraction lines associated with hexagonal structure (h-graphite) as shown in the figure 1. The above results indicate better crystalline nature with proper Bernal stacking of the graphene layers in GO.

3.2. Micro Raman and BET analysis

Raman spectroscopy was used to specify the structure and quality of carbon materials, and also to explore the defects and ordered and disordered structure of graphene. Micro Raman spectra of HPG and GO samples are presented in figure 2. The spectra show G, D and 2D bands at 1345-1350, 1578-1582 and 2740-2750 cm$^{-1}$ correspond to the first-order scattering of the $E_{2g}$ phonon from sp$^2$ carbon (graphite lattice), 1$^st$ order disorder in graphite lattice and second order disorder in graphite lattice [1, 18]. The intensity ratios of D to G peak i.e. $I_D/I_G$ and $I_{2D}/I_G$ for HPG, GO and RGO is calculated and presented in Table 1. From the figure it is evident that the intensity ratio of D and G bands ($I_D/I_G$) increases with enhancing ball milling time from 4 to 8 hr. The result indicates about structural distortion (oxidation of graphite introduces structural imperfections/disorder created by the hydroxyl, carboxyl and epoxide groups at the basal plane and also at the edges) and decreasing size of the inplane sp$^2$ domain (diminishing of randomly-located crystallite size). As $I_D/I_G$ ratio increases , which is also a feasible reason behind the increased fraction of graphene edges. The emergence of oxygen functional groups in GO increases disorder of turbostratically aligned graphene layers. From the $I_{2D}/I_G$ ratio calculation it is that graphene developed in 8 hr ball milled is bi-layer in nature. From the observation it is concluded that oxygen purging with optimized ball milling condition helps in exfoliation in layers of graphene. To better understand the structure of GO, XPS, TEM and BET information are comprised and the results additionally confirm that the GO is successfully formed.

The average crystallite size of the sp$^2$ domains ($L_a$(nm)) is calculated for HPG and GO samples by succeeding the equation given by Lucchese, et al. [19] by relating the $I_D/I_G$ ratio to the fourth power of laser line wavelength ($\lambda_l$ in nm units). This equation can be written as

$$L_a$(nm)=$(2.4\times10^{-10})\lambda_l^4(I_D/I_G)^{-1}$  \hspace{1cm} (Eq. 1)

The calculated $L_a$(nm) values for HPG, GO- 4hr and GO -8 hr ball milled samples are 85.8, 40, 22.8 nm respectively. Thus, it is observed that the average crystallite size of GO decreases as ball milling time increases under oxygen atmosphere. The BET surface area of for HPG, GO- 4hr and GO -8 hr ball milled samples were determined to be 47, 377 and 454 m$^2$/g. The decrease of crystallite size of
RGO is found to be supported by its high surface area value.

| Sample ID | D peak, (cm\(^{-1}\)) | G peak (cm\(^{-1}\)) | 2D peak (cm\(^{-1}\)) | I\(_D\)/I\(_G\) |
|-----------|-----------------------|---------------------|----------------------|----------------|
| HPG       | 1350                  | 1582                | 2750                 | 0.2            |
| GO-4 hr   | 1348                  | 1580                | 2745                 | 0.655          |
| GO-8 hr   | 1345                  | 1578                | 2740                 | 0.788          |

**Figure. 2** Comparison of micro Raman spectra for HPG and GO samples

3.3. **XPS study**

The XPS is one of dynamic techniques which is implemented for HPG and GO samples to yield information about their composition and the degree of oxidation. XPS survey spectra of HPG and GO samples are presented in figure 3. Survey spectra show the peaks only due to C1s and O1s. The presence of minor peak of O1s in the HPG sample is due to physically absorbed oxygen. The carbon to oxygen ratio (O/C) of high purity graphite is 1.08. O/C ratio for 4 hr and 8 hr ball milled specimens was found to be 40.8 and 58.87 respectively indicate that GO contains more oxygen-rich functionalities than the HPG.

**Figure. 3** XPS survey spectra for HPG and GO samples
3.4. Morphological characterization by TEM and EDS

The morphological and elemental analysis micro-structural studies of GO sample prepared by 8 hr of milling under oxygen atmosphere is shown in figure 4 and figure 5 respectively. It can be seen from figure 4 that GO has sheet like morphological characteristic of graphene. The transparency of these layers confirms the successful exfoliation of graphene sheets by ball milling route and indicates that each layer is comprised a few individual graphene sheets. The nanosheets in GO are found to random and folding in nature. The corresponding EDS spectra taken on TEM image shows major peaks of O and C. Taking the results of XRD, TEM and EDS into account, it is clearly observed that graphite structure has been well restored in ball milled GO sample. Hence, in this research work we developed a new, simple, quick and ecologically friendly technique of exfoliating graphite to produce high quality and low costs GO.

![Figure 4 TEM micrograph of GO sample prepared by 8 hr of milling](image1)

**Figure 4** TEM micrograph of GO sample prepared by 8 hr of milling

![Figure 5 EDS result of GO sample prepared by 8 hr of milling](image2)

**Figure 5** EDS result of GO sample prepared by 8 hr of milling

4. CONCLUSION

In this work, we have introduced a novel and ecologically friendly approach to efficiently produce
high quality GO from high purity natural graphite by ball milling route under oxygen atmosphere. The GO formation was confirmed from XRD, XPS, micro Raman and EDS studies. The GO-8 hr has been proved to have a high O/C ratio (58.87). The G, D and 2D Raman peaks change in shape, position and relative intensity further confirm the formation of few layers of graphene in GO. TEM analysis of GO provide a clear evidence of the formation of few-layered graphene sheets in GO. EDS analysis of the GO sample shows presence of oxygen and carbon without any other unwanted impurities. Thus, finally it may be considered that the newly introduced method is a promising and potential approach which may open the door towards easy production of high quality and high purity graphene sheets for a commercial scale.

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