Reduced graphene oxide synthesis by dry planetary ball milling technique under hydrogen atmosphere

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Abstract: This study reports a new, versatile and eco-friendly approach to produce high quality and high purity reduced graphene oxide (graphene) from natural graphite by dry planetary ball milling technique under hydrogen atmosphere. The morphology, structure and composition of high purity graphite (HPG), graphene oxide (GO) and reduced graphene oxide (RGO)/graphene have been characterized using various analytical techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM) with selected area electron diffraction (SAED) and X-ray photoelectron spectroscopy (XPS). XRD and XPS studies reveal the successful reduction of oxygen content from GO to prepare RGO. The RGO product analyzed by XRD and SAED show the efficient restoration of the hexagonal graphitic structure. From XPS result it is evident that the RGO has a C/O ratio of 17.51 which is among the best RGOs prepared with green reducing agents. TEM further provides clear support of the formation of graphene sheets in RGO.

1. INTRODUCTION

Graphene is a popular material having many attractive properties to its name. It possesses a number of outstanding mechanical, electrical, thermal, optical and electronic properties [1-6]. Therefore, graphene finds wider application in many technological fields such as sensors, single electron transistors, capacitors, solar cells, super capacitors, transparent conductive films, etc. [1-9]. It is a single layer of $sp^2$ carbon atoms closed packed into honeycomb two dimensional lattices. One of the greatest challenges is production of graphene at large scale with high quality at low cost and in a reproducible manner. The miracle material graphene starts from B. Bordin in 1949 [10] and it gives a Nobel award to A. K. Geim and K. S. Novosolve on 2010 [11]. The production process for large scale mostly depends on the chemical method i.e., Hummer’s method top to bottom and bottom to top approach. More precisely, one can fully study the behavior of graphene by two routes which can be up scalable for the mass production. Two main routes are: large-scale growth or large-scale exfoliation [12, 13]. For obtaining high yield and high quality graphene, there are many flaws in the large scale production. Different processes such as scotch tape method, exfoliation, mechanical delamination, synthesis on silicon carbide (SiC), chemical vapor deposition (CVD), microwave treatment and chemically oxidation and reduction method have been explored by many researchers [12-15]. However, above methods have both advantages and disadvantages depending on its applications.

In case of large-scale chemical exfoliation method, the production of graphene by reducing graphene oxide is one of the best alternate methods. It is observed that in case of reducing of graphene oxide (GO) into reduced graphene oxide (RGO) using hydrazine and annealing at high temperature, the restoration of own crystalline structure of graphene is uncertain [8, 9, 16]. Reducing agents used in chemical reduction of graphene oxide are hydrazine hydrate, sodium borohydride (NaBH₄), lithium
aluminum hydride (LiAlH₄), pyrrole, ascorbic acid, hydroquinone, hot strong alkaline solutions and gaseous hydrogen [8, 13, 17]. Based on these reported methods, however, critical reaction conditions are employed including high reaction time, temperature for reduction and strong reducing agents for the complete conversion of graphene oxide into reduced graphene oxide.

In our present study for the first time we report a newly developed, low costs and eco-friendly approach to produce high quality and high purity RGO from natural graphite via oxidation followed by reduction process using H₂ instead of conventional chemical reductants. From natural graphite, first high pure graphite (HPG) was produced by combination of physical and chemical beneficiation processes. In the present research work, we studied the micro structural and spectroscopic properties of HPG, GO and RGO samples by using characterization techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM) with selected area electron diffraction (SAED) and X-ray photoelectron spectroscopy (XPS).

2. MATERIALS AND METHODS

2.1 Oxidation process
HPG (carbon: 94–95%) was treated in the mixture of H₂SO₄ and H₃PO₄. The concentrate of H₂SO₄ and H₃PO₄ in the mixture was maintained of 9:1. KMnO₄ added slowly to the solution at 0 °C with continuous stirring. After 2 hours of reaction, hot water was mixed at 98 °C. Then, hydrogen peroxide H₂O₂ was added for the reaction to be reduced to produce synthesized graphene oxide. The synthesized graphene oxide was filtered and then dispersed in distilled water. 10% HCl solution was used to wash the residual salts from the graphene oxide. Then it was allowed to wash thoroughly by distilled water to for achieving pH around 7. Then wash sample filtered and taken for drying at temperature of 110 °C to eliminate the surface adsorbed moisture.

2.2 Reduction Process
The as prepared graphene oxide was treated under H₂ atmosphere (used as reducing agent) for 8 hrs during ball milling in a dual-drive planetary ball mill. Purging of H₂ was done in the jar available in ball mill at each 2 hrs interval of milling. The typical parts of dual -drive planetary ball mill are (i) gyratory shaft of 590 mm (rotated at speed 250 rpm) , (ii) two cylindrical jars of 200 mm diameter each (made in steel rotated at speed 160 rpm). The ball mill gives impact energy to the charge which enhances the kinetics of grinding, which results ultrafine powder samples. The ball milling was carried out for 8 hrs at a constant frequency of 30 Hz. After ball milling over, samples were allowed to attain room temperature. Then the samples are unloaded from the jars to carry out different characterizations.

2.3 Characterizations
HPG, GO and RGO samples were characterized by various techniques. Samples were analyzed by XRD employing PANalytical X’Pert Pro diffractometer (Cu Kα radiation source, λ=0.15406 nm). Morphology of samples were studied by TEM (model: TECNAI G² (200 kV), FEI (Netherland)). The SAED patterns were taken during TEM analysis. XPS (S/N:10001, Prevac, Poland) spectra was taken by AlKα (hν=1486.6eV) radiation and a VG Scienta-R3000 hemispherical energy analyzer. An instrument pressure of 7 x 10⁻¹⁰ mbar was maintained for XPS study. Origin 8.5 software is used for de-convolution (Gaussian-Lorentzian fitted) of high-resolution spectra to find and assign the different binding energy (B.E.) states in a specific region.

3. RESULTS AND DISCUSSION

3.1 XRD study
To understand atomic structures, crystalline nature, phase purity and interlayer spacing of the high purity graphite (HPG), GO and RGO samples, X-ray diffraction (XRD) was carried out and the results
are shown in Figure 1. Phases and planes are identified by comparing the observed \( d \)-values with the \( d \)-values of standard powder diffraction data file, C (graphite-2H): 00-041-1487 supplied in JCPDS-ICDD PDF-2 (2004). Figure 1 shows the XRD patterns of the samples in 2 theta range of 5\(^{\circ}\)-75\(^{\circ}\). HPG sample shows a peak of C (002) at 2 theta =26.8\(^{\circ}\) with \( d \)-spacing of \( \sim\) 0.337 nm. With chemical oxidation, characteristic peak of C (002) at 2 theta =26.8\(^{\circ}\) is completely disappeared and a strong diffraction peak of C (001) at around 2 theta=11.8\(^{\circ}\) of \( d \)-spacing \( \sim\) 0.74 nm is obtained from GO. The is caused due to exfoliation and lattice expansion of graphite by weakening the van der Walls forces of adjacent graphene sheets through chemical reaction and intercalation of oxygen molecules because of oxidation (formation of oxygen-containing functional groups such as hydroxyl, epoxy and carboxyl attached to the graphite lattice). After advanced environmental-friendly reduction process by dry planetary ball milling under H\(_2\) atmosphere, the peak at around 2 theta=11.8\(^{\circ}\) in RGO disappeared (indicating the removal of oxygen-containing functional groups) and a strong peak of C (002) at around 2 theta =26.4\(^{\circ}\) (corresponding \( d \)-spacing \( \sim\) 0.339 nm) has been found to be developed in RGO due to its retrieving ordered structure.

![XRD patterns observed for high purity graphite (HPG), GO and RGO samples](image)

**Figure 1.** XRD patterns observed for high purity graphite (HPG), GO and RGO samples

This shows that graphene oxide has been effectively reduced to RGO, and restoring and restacking of graphene layers take place in RGO. Further evidence of the formation of oxygen-containing functional groups in GO and their removal in RGO respectively are confirmed from their XPS measurements (infra).

### 3.2. XPS analysis

The XPS is a powerful techniques which is employed for HPG, GO and RGO samples to gain information about their composition, the chemical states of carbon (C) and oxygen (O), the degree of oxidation, the kind of oxygen species present and degree of reduction of oxygen function groups after ball milling under H\(_2\) atmosphere. XPS survey spectra of HPG, GO and RGO samples are presented in Figure 2. 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 atomic concentration of C1s, O1s and their ratios for all samples is presented in Table 1. The carbon to oxygen ratio (C/O) of starting graphite is 89.90. The observed lower C/O ratio i.e. 0.746 for GO than that of HPG clearly indicates that GO contains more oxygen-rich functionalities than HPG and RGO. As the GO is undergone reduction under H\(_2\) atmosphere, it is revealed that the C/O ratio increased from 0.746 in GO to 17.51 in RGO. The results indicate the removal of oxygen containing functional groups in the RGO. The C/O ratio of RGO is found higher to that using hydrazine monohydrate (C/O of 10.3) [18], and much higher than those using tannin acid (C/O of 2.44) [19]. The de-convoluted high resolution C1s core level spectra of RGO sample is shown in Figure 3. RGO shows less intense C-OH, C-O-C and
C=O/COOH peaks accompanied by an increase of the sp² carbon peak, revealing that a large number of oxygen-containing functional groups were removed and the majority of the sp² carbon networks were reduced. These results combined with XRD analyses confirm the effective reduction of the GO.

![Figure 2. XPS full survey spectra of HPG, GO and RGO samples](image)

![Figure 3. De-convoluted C1s core level XPS spectra of RGO sample](image)

| Sample ID | Elements (in at %) | C/O ratio |
|-----------|-------------------|-----------|
|           | C1s               | O1s       |           |
| HPG       | 98.90             | 1.10      | 89.90     |
| GO        | 42.74             | 57.26     | 0.746     |
| RGO       | 94.60             | 5.40      | 17.51     |

### 3.3. Morphological characterization by TEM and SAED

The morphological and micro-structural studies of HPG, GO and RGO samples were monitored by transmission electron microscopy (TEM). Figure 4a shows TEM microstructure of HPG. Figure 4b and figure 4c depict typical TEM images for RGO at lower and higher magnifications respectively. As can be seen from figure 4b wrinkled paper-like and sheet like morphological characteristic of RGO.
is observed. The transparency of these layers confirms the successful exfoliation of graphene sheets which indicates that each layer is composed of a few individual graphene sheets. TEM image of RGO at higher magnification Figure 4b shows a large single sheet which appears transparent with low contrast and found folded at the edges. TEM image (Figure 4b & 4c) of RGO overall exhibits typical transparent, thin nanosheets with typical flat graphene films, wrinkled and scrolled structures. The nanosheets in RGO are found to irregular and folding. The corresponding selected area electron diffraction (SAED) pattern taken on TEM microstructure (Figure 4c) is presented in Figure 4d. It shows a hexagonal structure with crystalline nature of RGO. This result confirms about the graphitic AB stacking order is maintained in the lattice of RGO. Taking the results of XRD, XPS, TEM and SAED into account, it is clearly observed that graphite structure has been well restored in RGO sample. Hence, in this research work we developed a new, simple, quick and eco-friendly method of exfoliating graphite to produce high quality and low costs graphene / RGO. The highly efficient reduction of graphene oxide by H\textsubscript{2} treatment during ball milling condition may be employed for the mass production of reduced graphene oxide in the industry. It can satisfy the large scale up in the market of graphene and opens up new possibilities for producing graphene for large scale applications.

![Image](image_url)

**Figure 4.** (a) TEM microstructure of HPG; (b) and (c) TEM micrographs of RGO; (d) SAED pattern of RGO taken on TEM (c)

4. **CONCLUSION**

In this work, we have introduced a novel, fast, facile and eco-friendly approach to efficiently produce high quality and low costs graphene / RGO from natural graphite by oxidation (GO was prepared by well known Hummers process) followed by reduction process by purging H\textsubscript{2} gas as reducing agent in the jar during the planetary ball mill process. The reduction of GO into RGO by removing oxygen containing functional groups are confirmed from XRD and XPS studies. XRD and SAED results demonstrate that the applied reducing process is an efficient approach for the preparation of RGO/graphene with retaining its hexagonal structure. TEM analysis of RGO overall exhibits typical transparent, thin nanosheets with typical flat graphene films, wrinkled and scrolled structures and provide a clear evidence of the formation of few-layered graphene sheets in RGO. Thus, finally it may be considered that the newly introduced low cost reducing method is a promising and potential approach which may open the door towards easy production of high quality and high purity graphene sheets on a commercial scale. We are certain that the prepared RGO can be used in many
applications, e.g., sensors, super capacitors, batteries, catalyst, etc.

REFERENCES

[1] Zhu B Y, Murali S, Cai W, Li X, Suk J W, Potts J R and Ruoff R S 2010 Graphene and graphene oxide, synthesis, properties and applications. Advanced Materials vol 22 pp 3906-24K

[2] Dash P, Dash T, Rout T K, Sahu A K, Biswal S K and Mishra B K 2016 Preparation of graphene oxide by dry planetary ball milling process from natural graphite. RSC Advances vol 6 pp 12657–68

[3] Sun Y, Wu Q and Shi G 2011 Graphene based new energy materials. Energy & Environmental Science vol 4 pp 1113-1132

[4] Allen MJ, Tung VC and Kaner RB 2010 Honey comb carbon: A review of graphene. Chemical Reviews vol 110 pp 132-145

[5] Nieto A, Bisht A, Lahiri D, Zhang C and Agarwal A 2017 Graphene reinforced metal and ceramic matrix composites: a review International Materials Reviews vol 62 pp 241-302

[6] Wang J, Ma F and Sun M 2017 Graphene hexagonal boron nitride and their hetero structures: properties and applications. RSC Advances vol 7 pp 16801-16822

[7] Drewniak S, Muzyka R, Stolarczyk A, Pustelny T, Morańska M and Setkiewicz M 2016 Studies of reduced graphene oxide and graphite oxide in the aspect of their possible application in gas sensors. Sensors vol 16 pp 1-16

[8] Xu M, Chai J, Hu N, Huang D, Wang Y, Huang X, Wei H, Yang Z and Zhang Y 2014 Facile synthesis of soluble functional graphene by reduction of graphene oxide via acetylacetonate and its adsorption of heavy metal ions. Nanotechnology vol 25 pp 1-9

[9] Chen L Y, Konishi H, Feihrebacher A, Ma C, Xu J Q, Choi H, Xu H F, Pfefferkorn F E and Li X C 2012 Novel nanoprocessing route for bulk graphene nanoplatelets reinforced metal matrix nanocomposites. Scripta Materialia vol 67 pp 29-32

[10] Brodie B C 1860 Sur le poids atomique du grafite. Annales de Chimie et de Physique vol 59 pp 466–72

[11] Geim A K and Novoselov K S 2007 The rise of graphene. Nature material vol 6 pp 183-191.

[12] Bae S, Kim H, Lee Y, Xu X, Park J S, Zheng Y, Balakrishnan J, Lei T, Kim HR, Song YI, Kim YJ, Kim K S, Ozylmaz B, Ahn J H, Hong B H and Iijima S 2010 Roll-to-roll production of 30 inch graphene films for transparent electrodes. Sensors vol 16 pp 574-578

[13] Cisewski M, Mianowski A and Nawrat G 2013 Preparation of electrochemical properties of sodium-reduced graphene oxide. Journal of Material Science: Materials in Electronics vol 24 pp 3382-3386

[14] Jeon IY, Choi HJ, Jung SM, Seo JM, Kim MJ, Dai L and Baek JB 2013 Large scale production of edge-selectively functionalized graphene nanoplates via ball milling and their use as metal-free electrocatalysts for oxygen reduction reaction. Journal of the American Chemical Society vol 135 pp 1386-1393

[15] Park S and Ruoff RS 2009 Chemical methods for the production of graphenes. Nature Nanotechnology vol 4 pp 217-224

[16] Amiri A, Shanbedi M, Ahmadi G, Eshghi H, Kazi S N, Chew B T, Savari M and Zubir M N M, 2016 of highly-porous graphene for high-performance supercapacitors. Scientific Reports vol 6 pp 32686: 1-11.

[17] Cui P, Le J, Hwang E and Lee H, 2011 One-pot reduction of graphene oxide at subzero temperatures. Chemical Communication vol 47 pp 12370-12372.

[18] Stankovich S, Dikin DA, Piner RD, Kohlhaas K A, Kleinhammes A, Jia Y, Wu Y, Nguyen ST and Ruoff RS 2007 synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. Carbon 45 1558-1565.

[19] Lei Y D, Tang Z H, Liao R J and Guo B C 2011 Hydrolysable tannin as environmentally friendly reducer and stabilizer for graphene oxide. Green chemistry vol 13 pp 1655-1658