



International Journal Of
**Recent Scientific
Research**

ISSN: 0976-3031
Volume: 7(4) April -2016

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Robin Gamit and Ramanujam B.T.S



THE OFFICIAL PUBLICATION OF
INTERNATIONAL JOURNAL OF RECENT SCIENTIFIC RESEARCH (IJRSR)
<http://www.recentscientific.com/> recentscientific@gmail.com



ISSN: 0976-3031

Available Online at <http://www.recentscientific.com>

International Journal of Recent Scientific Research
Vol. 7, Issue, 4, pp. 10621-10624, April, 2016

International Journal of
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Research Article

COMPARISON OF VOLUME EXPANSION OF NATURAL GRAPHITE WITH SYNTHESIS ROUTES

Robin Gamit¹ and Ramanujam B.T.S^{2*}

^{1,2}School of Science and Engineering, Navrachana University, Vadodara, Gujarat

ARTICLE INFO

Article History:

Received 15th January, 2016
Received in revised form 21st
February, 2016
Accepted 06th March, 2016
Published online 28th
April, 2016

Keywords:

Expanded graphite, Heat treatment,
X-ray diffraction, Scanning electron
microscope, Microwave irradiation

ABSTRACT

Expanded graphite was synthesized by three different routes to produce graphite nanosheets. The synthesis routes were compared with volume expansion of graphite after high temperature heat treatment or microwave irradiation. It was experimentally observed that the volume expansion of graphite, after mixing only with con. sulfuric acid / con. nitric acid mixture and subsequent heat treatment at 930 °C, observed to be maximum (~80%). Optical microscope picture proved the porous structure of acid treated graphite followed by high temperature heat treatment or microwave irradiation. XRD analysis supported crystallite size reduction in treated graphite. FESEM picture proved the formation of graphite nanosheets after high temperature heat treatment.

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INTRODUCTION

Graphene which is a monolayer of graphite formed by sp^2 hybridized carbon atoms is intensively probed due to its exceptional mechanical, electrical and thermal properties [1-2]. Graphene can be synthesized either by top down approach or bottom up approach. High purity graphene can be obtained by CVD process [3]. However CVD process is more expensive and involves more careful fabrication of graphene and hence the mass production of the same may not be possible with that technique. Graphene can also be produced by peeling of graphite layers with scotch tape. However this physical process also cannot be used for large scale synthesis. The synthesis of graphite oxide is known for more than 100 years and it was Hummers who synthesized graphite oxide as reported elsewhere [4]. Since then, the method has been modified and graphite oxide has been synthesized. In all these processes, graphite is treated with oxidizing agents such as potassium permanganate, sodium nitrate etc. to facilitate intercalation of foreign molecules. A large number of oxygen containing functional groups would be introduced onto the basal plane of graphite [5] during oxidation process. However there has to be controlled oxidation in case the graphitic nature needs to be preserved. Complete oxidation of graphite will lead to insulating graphite oxide. The level of oxidation can be varied

on the basis of the method, reaction conditions and the precursor graphite used. Although several models have been proposed regarding oxidation of graphite, those models are subjected to debate till date.

Graphite intercalation compounds (GIC) are made from natural graphite which has hexagonal structure with the lattice parameters $a=b=2.46 \text{ \AA}$, $c= 6.71 \text{ \AA}$. The graphite unit cell is shown below in figure 1.

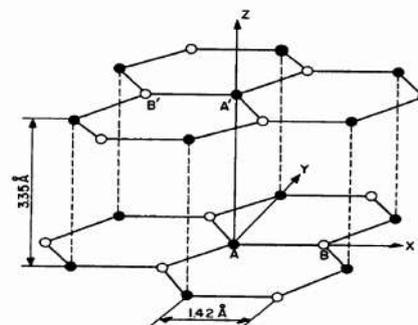


Figure 1 Graphite crystal structure

The layers in graphite are held together by van der Waals forces. Though these are weak forces, π electrons interaction is more and hence cleaving the layers by simple process becomes difficult. Even if the layers are cleaved, stabilization of those

*Corresponding author: Ramanujam B.T.S

School of Science and Engineering, Navrachana University, Vadodara, Gujarat

layers is a challenge as eventually agglomeration leads to three dimensional structure. Not only the interplanar space is available for intercalation of foreign molecules, there exists intergallery space which also serves as the space for insertion of foreign molecule. When these layers are properly cleaved, a single layer obtained is known as graphene sheet. The expansion volume not only depends on concentrations of intercalant and oxidizing agents but also on the particle size of graphite used. In each of those processes, either the reaction time is more or stringent conditions are imposed on the reaction. Hence for a given grade and particle size of graphite, the concentrations of reagents and reaction conditions should be optimized as a preliminary step which will help in mass production of graphite nanosheets. Hence our preliminary results are presented below.

Experimental

MATERIALS

Natural graphite better than 100 mesh has been procured from carbon enterprises, Pune. Concentrated sulfuric acid (H_2SO_4) (98%) (LR grade), Concentrated nitric acid (HNO_3) (72%) (LR grade) and potassium permanganate ($KMNO_4$) are obtained from SDFCL, Mumbai.

Synthesis of expandable graphite

Through three different ways, expandable graphite was prepared. In route-1, 2 gm of natural graphite was taken in 100 ml beaker, to which first 15 ml, 0.1 N $KMNO_4$ was added. The beaker was kept inside an aluminum bowl filled with water in order to remove the heat produced during the exothermic process. The mixture was stirred for five minutes and then the mixture of 40 ml concentrated sulfuric acid and 10 ml concentrated nitric acid (4:1 v/v) were added and then the mixture was stirred for two hours and left overnight. The mixture was repeatedly washed with distilled water till the pH was found to be around 6 to 6.5. After that the mixture was dried in air at 120 °C for three hours in oven and the resultant black powder was used for microwave irradiation for 5 minutes or high temperature heat treatment at 930 °C in a muffle furnace.

In a similar fashion in route-2, 2 gm natural graphite, 40 ml of H_2SO_4 and 15 ml 1N $KMNO_4$ were added and the reaction conditions were maintained the same as mentioned before. First $KMNO_4$ was added and then the other reagents were added.

In route-3, to 2 gm of natural graphite, 40 ml Con. H_2SO_4 and 10 ml Con. HNO_3 were added and stirred for two hours and other procedures stand the same mentioned in reaction carried out in route-1.

Characterization of treated graphite

X-ray diffraction analysis was carried out on as obtained natural graphite, synthesized expanded graphite in X-pert pro x-ray diffractometer from panalytical. CuK_{α} radiation is used as the source.

Optical microscope image of synthesized expanded graphite and natural graphite were taken in Leica optical microscope from Germany.

Scanning electron microscope image of sonicated expanded graphite was taken in FESEM (model FEG 200 quanta FESEM). Haier microwave oven (model: HSC 1770EG) has been used.

RESULTS AND DISCUSSION

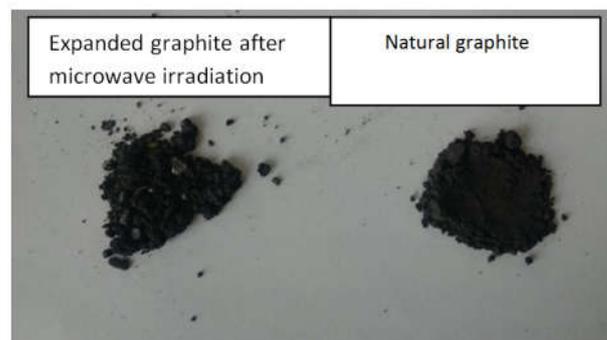


Figure 2 Comparison of appearances of synthesized expanded graphite and natural graphite



Figure 2a Spongy structure of expanded graphite after heat treatment

Figures 2 and 2a represent the appearance of expanded graphite synthesized by route-1 as discussed in experimental section. It can be clearly seen that after acid treatment along with oxidising agents and microwave irradiation for five minutes or high temperature heat treatment at 930 °C for the same time, graphite layers are expanded and more fluffy structure is realized. This can be easily seen in figure 2. In fact at 930 °C few seconds of heat treatment results in expansion of graphite planes.

The porous structure resulted due to the expansion of graphite layers is vivid from the optical microscope image of the microwave irradiated expandable graphite synthesized through route-1 as depicted in Figure 3 below.

Expanded portion of graphite layers after microwave irradiation of expandable graphite is very clearly visible even in optical microscope. The FESEM picture of expanded graphite after heat treatment at 930 °C as shown in Figure 3a clearly proves the formation of graphite nanosheets. The above results clearly demonstrate that graphite layers can be expanded by the synthesis routes employed in this work.

XRD Analysis

In order to make expanded graphite, in all routes, concentrated sulfuric and nitric acid mixture has been used. The carbon

atoms in the graphite planes are oxidized and the oxidized carbon atom can have interaction with the bisulfate anion.



Figure 3 Optical microscope image of expanded graphite (route-I) under 50X magnification

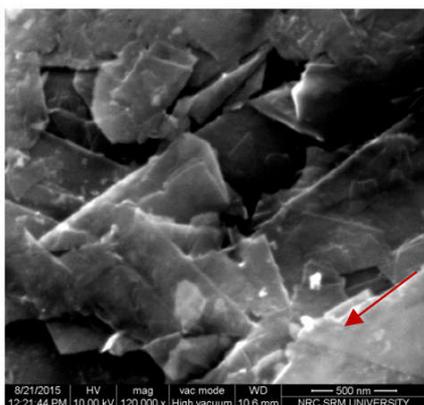


Figure 3a FESEM image of expanded graphite after heat treatment

This results in easy penetration of sulfuric acid into the graphite planes whose interplanar distance is 3.35 Å. When high temperature heat treatment or microwave irradiation has been carried out the acid can burst and push the graphite layers causing expanded graphite. Figure 4 shows the X-ray diffractogram of natural graphite and acid treated graphite. Graphite has hexagonal structure and the most prominent reflection comes from 002 plane.

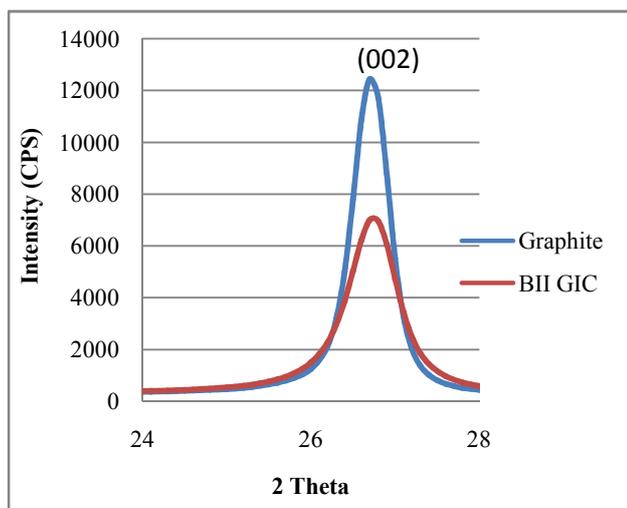


Figure 4 XRD pattern of natural graphite and treated graphite

It is clear from the figure that the intensity of treated graphite (BII GIC inside the plot) is reduced and also the full width at half maximum (FWHM) is increased. The crystallite size is inversely related to FWHM. Hence after acid treatment, the crystallite size is reduced due to penetration of acids into the gallery space of graphite and eventually results in decrease in the particle size. This trend is observed for treated graphite when prepared by other routes as well.

Measurement of expansion volume

The same amount of natural graphite and expanded graphite synthesized by different routes are taken and volume occupied by them after gently tapping in a graduated cylinder is measured and given in Table 1.

Table 1 Volume expansion of graphite obtained in different synthesis routes of expanded graphite

Route/Batch	Volume of material cc/g		% volume enhancement
	ExGr	Natural graphite	
I (graphite +conc.HNO ₃ + conc. H ₂ SO ₄ +0.1N KMnO ₄)	1.5	1.0	50
II(natural graphite + conc.HNO ₃ +conc. H ₂ SO ₄ + 1N KMnO ₄)	1.3	1.0	30
III (graphite +conc.HNO ₃ + conc. H ₂ SO ₄)	1.8	1.0	80

The above tabulation shows that when acid mixtures were used in 4:1 ratio (Con.H₂SO₄/Con.HNO₃), the expansion ratio obtained was maximum. It should be mentioned that in our route only two hours of stirring of natural graphite has been carried out.

CONCLUSIONS

Expanded graphite has been synthesized by three different routes designated as route 1, route 2 and route 3. All three synthesis routes result in expansion of graphite layers. Maximum expansion of graphite layer was obtained when concentrated H₂SO₄ and HNO₃ mixture with 4:1 volume ratio was mixed with graphite. The fluffy expanded graphite can be seen visually as well through optical microscope. Formation of graphite nanosheet has been proved through FESEM picture.

Acknowledgement

The authors sincerely thank the Head, Nanotechnology Research Center, SRM University, Chennai for taking FESEM pictures. The authors thank Navrachana University, Vadodara, to support this work. The authors would like to thank Ganesh Industries, Mumbai for providing commercial expanded graphite free of cost.

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How to cite this article:

Robin Gamit and Ramanujam B.T.S.2016, Comparison of Volume Expansion of Natural Graphite With Synthesis Routes. *Int J Recent Sci Res*. 7(4), pp. 10621-10624.

T.SSN 0976-3031



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