

Synthesis of Graphite Oxide from Kahatagaha Vein Graphite using a Localized Improved Hummers Method

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Introduction

In modern world, materials, - regardless of their make, whether natural or synthetic – play a huge role. From all these materials, Graphite is taking a wide consideration of scientists as they are naturally occurring, cheap material with very interesting physical, chemical and mechanical properties. Within the range of applications of Graphite, Graphite Oxide (GO) and Graphene are more important as they are having many applications and very good potential in Nano scale materials and Nano Technology. GO has attracted much interest recently as a possible route for the large scale production and manipulation of Graphene, a material with extraordinary electrical properties. Sri Lanka has two major natural vein graphite deposits in Kahatagaha-Kolongaha and Bogala. Of the two Kahatagaha vein graphite has the highest purity that can be upgraded up to 99.97% Carbon by HCl leaching (Amaraweera et al, 2013). No researches and experiments have been conducted on Kahatagaha vein graphite which has been upgraded up to 99.97% Carbon in nano scale. The potential for value addition to Kahatagaha graphite has not yet been adequately explored. This study aims at synthesizing GO using a localized version of the Improved Hummers Method and characterization of GO to confirm the oxidation.

Methodology

Graphite sample, KNPG (Kahatagaha Needle-Platy Graphite) was first crushed using a hammer to obtain +10 mm chips and then the sample was milled in a disc mill for 15 minutes. The milled sample was sieved using a sieve shaker and <53 microns portion was taken for further treatments.

675 ml of 5% HCl was added to 50 g of graphite in 1000 ml beaker and it was vigorously stirred for 1.5 hours at 60°C. The solution was vacuum filtered and washed with distilled water (500 ml) and the same procedure was repeated once. Finally purified graphite was washed until the pH become neutral. KNPG achieved purity level of 99.97% Carbon.

9: 1 mixture of conc. H₂SO₄ (96% 360 ml) and conc. H₃PO₄ (85% 40 ml) were added to a mixture of 3 g of purified KNPG and 18 g of KMnO₄. The mixture was stirred for 6 hours at 50°C. Then the solution was poured on to ice (200 ml) with 30% H₂O₂ 3 ml and then vacuum filtered through Fisherbrand filter paper. The brown product left on the filter paper was collected and washed with water (200 ml x 3) and left in a vacuum drier at 105°C for 2 hours. The hard black solid taken out from the vacuum drier was crushed using an agate mortar and pestle to obtain finer particles of 6.86 g of GO.

A pellet for electrical conductivity measurements was made using 1g of GO and FTIR Spectrum for GO was taken. A tape was casted using GO for sheet resistance measurements and XRD spectrum was obtained for characterization of GO.

Results and Discussion

The FTIR spectrum of GO (Figure 1) has more prominent indication of attached –OH, C-O-C and –COOH groups than raw graphite. The overall absorbance of the GO has significantly increased. The proposed structure for GO (He et al, 1998) can be supported with the obtained FTIR data for GO, hence the localization of Improved Hummers method has shown the expected results.

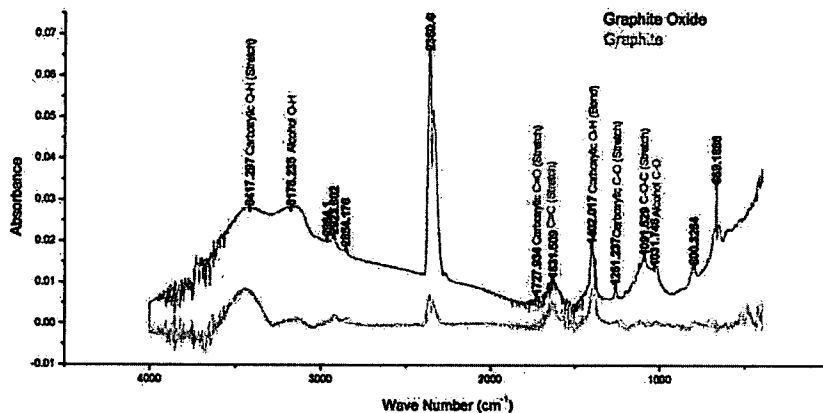


Figure 1. Comparison of FTIR spectrum between Graphite (Green) and Graphite Oxide (Blue)

Electrical Conductivity of Graphite and GO was calculated using the four-probe method.

Electrical Conductivity (σ)

For Graphite = $8.23 \Omega^{-1}\text{cm}^{-1}$

For GO = $9.74 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$

The electrical conductivity of graphite and GO has a significant difference in order of 10^{-4} . In theory due to GO formation, hydroxyl groups, carboxylic groups and epoxy bridges, the electrical conductivity of GO is considerably lower than that of the graphite (Stankovich et al, 2007). As the conductivity calculated for GO is much lower than that of graphite, we can conclude that the oxidation process done using the localized improved Hummers method is effective.

Sheet resistance of GO (R_s) = $5.15 \times 10^{-4} \Omega/\text{sq}$.

The reported sheet resistance for few layer graphite is $200 \Omega/\text{sq}$. (Cai et al, 2009). The casted tape of GO has much more thickness ($\sim 0.5 \text{ mm}$) than the few layer graphite in the reported work ($\sim 50 \text{ nm}$). That should be the reason for the very low sheet resistance shown for GO tape. To compare the sheet resistance the tape's thickness should be maintained at the same order of magnitude at least.

The XRD spectrum of graphite which is shown in Figure 3 has two peaks at 26.73 and 54.84 degrees and the same peaks are shown in the XRD spectrum of GO (Figure 3) are slightly shifted to the left. The previous studies have shown (Wei, 2012) that GO is showing a prominent but somewhat broad peak around 11 degrees and the position can be easily influenced by the oxidation and hydration level of the GO sample. The obtained XRD spectrum for GO (Figure 3) shows a broad, prominent peak at 9.3 degrees (indicated by the red circle in Figure 3) which is

not shown at the XRD spectrum of graphite. As the peaks are slightly shifted to the left side in GO spectrum than graphite spectrum, that may be the indication of oxidation and it may deviated from the obtained results of Wei (2012) due to the level of oxidation and hydration as given in the same reference.

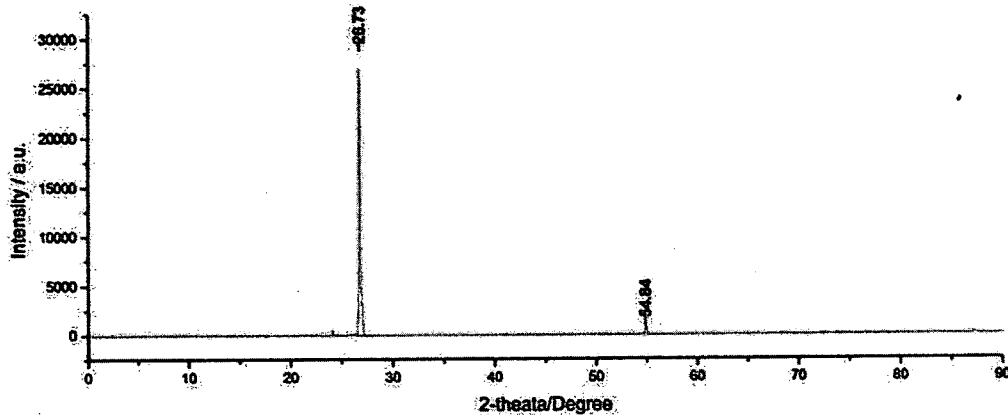


Figure 2: XRD spectrum of graphite (Source: RRUFF.info, RRUFF project at University of Arizona)

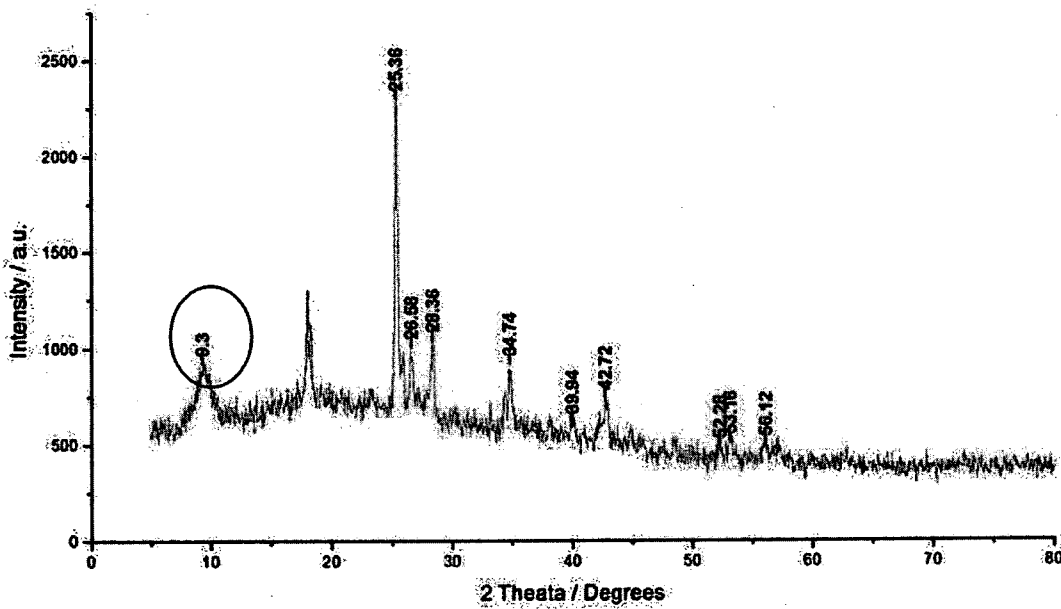


Figure 3. XRD spectrum of GO.

Conclusions

In conclusion, there are evidences of oxidation of graphite and the localized improved Hummers method is effective in GO preparation. Evidence from FTIR Spectroscopy, Conductivity measurements and XRD spectroscopy can support the above statement. The level of oxidation still should be determined using an experimental procedure. Kahatagaha Needle Platy Graphite has a high level of purity and can be easily purified to obtain 99.95+ % carbon purity hence it can be utilized to make GO and other products such as Graphene. A much more effective and a low cost method still should be identified by further experiments.

References

- Amaraweera, T.H.N.G., Balasooriya, N.W.B., Wijayasinghe, H.W.M.A.C., Attanayake, A.N.B., Dissanayake, M.A.K.L., 2013. Purity Enhancement of Sri Lankan Vein Graphite for Lithium - ion Rechargeable Battery Anode., Proceedings of 29th Technical Sessions of Geological Society of Sri Lanka, 101-104.
- He, H., Klinowski, J., Forster, M. Lerf, A.A., 1998. New structural model for graphite oxide. *Chem. Phys. Lett.*, 287, 53–56.
- Sasha S., Dmitriy A., Dikin, R.D., Piner, K.A., Kohlhaas, Alfred, K., Yuanyuan, J., Yue, W., SonBinh, T.N., Rodney, S.R., 2007. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*, 45, 1558–1565.
- Weiwei C., Yanwu, Z., Xuesong, L., Richard, D.P., Rodney, S.R., 2009. Large area few-layer graphene/graphite films as transparent thin conducting electrodes. *Applied physics letters*, 95, 115- 123.
- Wei, G.A.O., 2012. Graphite oxide: structure, reduction and applications; Ph.D. thesis, Rice University, USA.