

SYNTHESIS AND CHARACTERIZATION OF NANO-GRAPHENE PLANES VIA LOW TEMPERATURE THERMAL EXFOLIATION.

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Introduction

Graphene is the latest addition to family of carbon materials having attracted focus of researchers from various disciplines of Science and Technology because of its promising electrical, thermal and mechanical properties. Fabrication of Graphene reinforced composite demands large scale production of Graphene. This has necessitated research in different routes to develop grapheme^[1-4]. Various methods being tried to develop sufficient amount of Graphene for fabrication of composites. It mainly involves thermal exfoliation^[2] planetary ball-milling^[3] and solution technique or colloidal dispersion technique.^[4] In this work we tried to exfoliate graphite at low temperature ($\approx 220^{\circ}\text{C}$) as compared to conventional exfoliation temperature ($800\text{-}1000^{\circ}\text{C}$). Objective behind this research was to develop technique which can give high throughput with minimum defects caused by exfoliation temperature.

Experimental

Natural Graphite flakes having mean flake size of approx. $400\ \mu\text{m}$ were taken as starting material. Natural Graphite flakes were oxidized by Modified Hummer's method.^[5] Bright golden color suspended graphite flakes were observed. Above suspension was washed by centrifugation and decantation cycles until neutral pH observed. Obtained slurry type product was abbreviated as GO slurry. Drying of GO Slurry was carried out in ambient conditions. Reddish brown film obtained after drying stage was collected and abbreviated as GO-Dried. $0.2\ \text{g}$ GO-Dried film folded and inserted in preheated oven at 220°C for 5 min. Black fluffy powder obtained by exfoliation was collected and abbreviated as EGD.

XRD analysis at each step of reaction was carried out by powder diffraction method on Philips X'pert, Holland (with Cu K α radiation) to evaluate d spacing of graphitic structure. FTIR analysis was carried out to get idea about type and degree of functionality. DSC analysis was performed on DSC 20, Mettler with standard aluminum crucible from room temperature to 300°C at heating rate of 10°C per minute. TEM analysis was performed on Philips-Technai 20, Netherlands with accelerating voltage 200 kV. Sample for GO was prepared by drying diluted GO slurry droplet on copper TEM grid covered with amorphous carbon film in ambient condition. In the case of EGD 2mg sample was dispersed in 100 ml Dimethyl Formamide in 100 ml beaker by using bath ultrasonicator for 10 minutes. Drop of above dispersion dried

in ambient condition on Cu TEM grid with thin amorphous carbon film. SAED photographs were taken during TEM analysis. Natural Graphite Flakes were characterized by EDAX analysis (XL 30, Philips, Netherlands) to determine oxygen content present in starting material.

Results and Discussion

Modified Hummer's method was followed to introduce more functionality (mainly $-\text{OH}$, epoxy and carboxylic acid groups) into graphitic planer structure. It is necessary to produce sufficient volatiles for total disruption of planar stacking structure. Increase in functionality was confirmed by FTIR analysis. Starting material Natural Graphite Flakes (GF-ARC) contains some functionality as shown in Fig. 1(a). These are naturally present functional groups in Natural Graphite. EDAX analysis was carried out to determine oxygen content present in starting material. Results show approximate 18.5wt% oxygen atoms present in graphite flakes. FTIR analysis reports that most of oxygen is attached in the form of hydroxyl group showing broad peak at $\approx 3447\ \text{cm}^{-1}$. It also shows sharp peak at $\approx 1625\ \text{cm}^{-1}$ corresponds to the skeletal vibrations of basal plane itself. FTIR graph of natural graphite shows no peak at $\approx 1735\ \text{cm}^{-1}$ indicating more over absence of carboxylic groups. Peak at $\approx 3425\ \text{cm}^{-1}$ gets broadened after pre-Oxidation stage. It also shows small peak at $\approx 1735\ \text{cm}^{-1}$ indicating presence of carboxylic groups.

Pre-Oxidation stage reduces crystallite size from the actual size of starting material. XRD results show dramatic decrease in intensity and broadening of characteristic peak of graphite at $2\theta = 26^{\circ}$ as shown in Fig. 1(b). These evidences show partial disruption of crystallites but still presence of planer stacking. FTIR analysis shows peak at $\approx 1625\ \text{cm}^{-1}$ conforming that skeletal structure has not been disrupted.

Final oxidation stage (GO) causes tremendous amount of functionality over graphitic planes that can be conformed by much broadened peak of hydroxyl group at $\approx 3425\ \text{cm}^{-1}$ as compared to natural graphite flakes and pre oxidized flakes. It is also remarkable that peak at $\approx 1734\ \text{cm}^{-1}$ with increased intensity shows more carboxylic groups attached after final oxidation stage. XRD pattern of GO-dried shows total removal of characteristic peak at $2\theta = 26^{\circ}$ corresponding to d spacing $\approx 3.34\ \text{\AA}$. Functional groups attached to graphitic planes increases interlayer spacing, Hence, new peak is observed at $2\theta = 10.4^{\circ}$ corresponding to d spacing $\approx 8.4\ \text{\AA}$ which is higher than reported earlier in the case of Staudenmaier method ($7.1\ \text{\AA}$).^[2] As shown by early researchers pressure required to separate two planes is inversely proportional to cube of distance between two planes.^[2] As inter planer distance increases binding forces decreases facilitating less required pressure for separation of both planes.

GO dried was analyzed by DSC to estimate temperature of exfoliation. DSC graph shows initially endothermic reaction indicating vaporization followed by sharp exothermic peak at $\approx 220^{\circ}\text{C}$ showing decomposition of functional groups causing evolution of gases (mainly CO , CO_2 , H_2O etc).

Reaction plot of exothermic reaction shows more over completion of reaction after two minute at 220 °C.

This data became quit helpful to decide reaction temperature that is 220°C and reaction time 5 minutes to ensure completion of reaction. GO dried was heated separately in oven furnace up to 220°C for 5 minutes to estimate total amount of released gases by gravimetric method. Heating rate was intentionally kept very slow (1 °C/min) to prevent from exfoliation. Result shows 50.7% weight loss with respect to initial weight of GO dried. This is quite higher than previously reported values. Here, two factors that (i) increased inter planer spacing (8.4 Å) in GO dried and (ii) high amount of gas produced (≈50 wt %) during exfoliation lead us to succeed the exfoliation at much lower temperature.

XRD pattern of exfoliated GO dried (EGD) shows total disruption of planer stacking. It can be conformed by absence of characteristic peak at $2\theta = 26^\circ$. As shown in Fig. 1(d) product obtained after exfoliation is fluffy black dull powder having very light weight. It is mainly because of disruption of planer stacking.

In FTIR analysis characteristic peak of graphite skeleton at $\approx 1625\text{ cm}^{-1}$ got broadened and shifts little bit lower value ($\approx 1595\text{ cm}^{-1}$) probably because of disruption in stacking and defects generated in planer structure. Still even after exfoliation certain amount of functionality gets trapped and doesn't get released after completion of reaction.

GO slurry and EGD were also analyzed by TEM. In case of GO slurry TEM micrograph shows bunch of planes as shown in Fig. 2. SAED image shows single crystalline structure showing all possible reflections. While in the case of EGD it shows few or single layer structure of Graphene stacked on each other. SAED image of EGD also confirms disintegration of crystallites and shows no long order stacking.

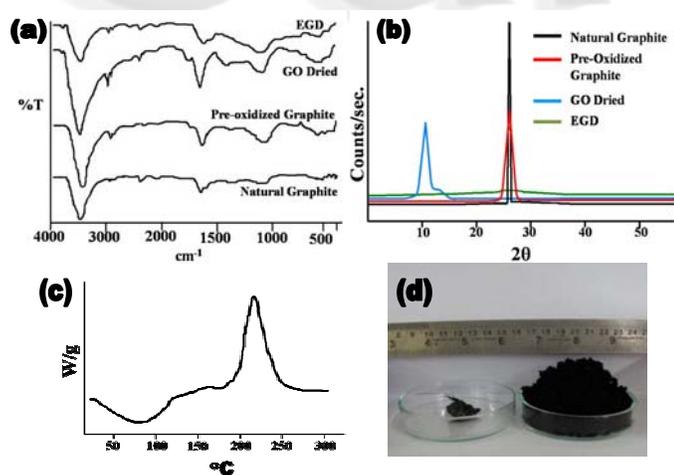


Fig. 1 (a) FTIR spectra and (b) XRD pattern of Natural Graphite, Pre-Oxidized Graphite, GO Dried and EGD; (c) DSC graph of GO Dried; (d) comparison of GO Dried (left) and EGD (right) from same amount of GO Dried.

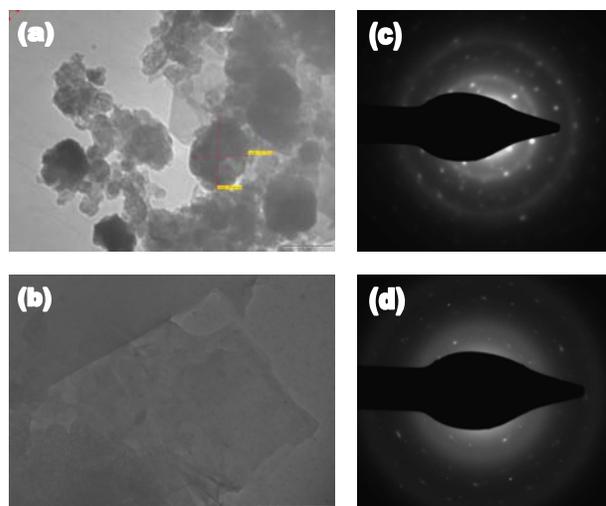


Fig. 2 (a), (b) TEM images of GO slurry and EGD respectively; (c), (d) SAED images of GO slurry and EGD respectively.

Conclusions

Thermal exfoliation has been achieved at lower exfoliation temperature ($\approx 220^\circ\text{C}$), dramatically lower than conventional temperature ($\approx 800\text{-}1000^\circ\text{C}$). This is because of increase in interlayer spacing ($\approx 8.4\text{ \AA}$) in intercalated compound. On another hand increased amount of functionality $\approx 50\text{ wt. \%}$ of GO dried (as compared to $\approx 30\text{ wt \%}$ previously reported) results in more production of gases after decomposition and hence successful exfoliation. Product produced by this method still contains functionalities which can facilitate to be utilized as filler in polymer or other matrix composites where functionality is useful for dispersion of filler into media. Simultaneously functionality plays important role in adhesion between reinforcement and matrix. Low temperature exfoliation technique can immerse as efficient technique to produce exfoliated graphite for many other applications where high degree of exfoliation is required.

References

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