Graphene Synthesis via Exfoliation of Graphite by Ultrasonication

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ABSTRACT

Graphene has newly grabbed the attention of many researchers and scholars for it's huge range of properties, mainly high surface area is the most innovative field of research. High surface area property has a great significance for its demand in almost all applications in addition to supercapacitors. Accordingly, an attempt here is accomplished to create the graphene by sonication method using ODCB solvent. Different characterization techniques are mentioned in support of the work accomplished and it is found that the interlayer distance between graphite layers increases with increasing duration of sonication process. In XRD result, it can be found that first peak at 2θ of 26.4 degree disappears and a distinguishable peak at 11.3 degree with inter graphite layer spacing in close value with 0.78 nm in association with some other diffraction peaks appear. SEM images very nicely represent homogeneous graphene film with particle size varying from 42 to 150 nm. UV-VIS absorption spectra suggests that the peak absorption in graphene decreases with high wavelengths. At 210 nm, a peak can be noticed and one more peak around 226 nm with a little bit less intensity of absorption peak can be observed in UV-VIS spectra. The details offered by SEM, XRD and UV-VIS throughputs are also mentioned. It is quoted that upon sonication the distance between graphite layers increases, thereby originating graphene. Thus it can be concluded that the graphene with enormous extraordinary properties (including Super capacitor) can be synthesized following the sonication method using organic solvents. Long hour processing via sonicator leads to formation of homogenous dispersion of graphene in case of ODCB. For thorough exfoliation of graphite, the sonication should be maintained with a very dilute system in order to reduce the importance of the graphene sheets recombination process.

Keywords: *Graphene, ODCB, XRD, UV-VIS and SEM*

I. INTRODUCTION

Graphene, a one-atom-thick layer of carbon atoms set in a honeycomb lattice, has fascinated great interest among physicists and engineers. The mingle of the unique properties of graphene with new device concept and nanotechnology can overcome some of the main limitations of traditional electronic systems in terms of energy density, frequency, power density, maximum linearity and power dissipation. Graphene with unique properties like high surface area, zero band gap, high charge carriers mobility, and carriers confinement to a one atom thick layer only making it extremely flexible and transparent. There are several methods to synthesize graphene like Exfoliation using chemical route and micromechanical, Chemical vapor deposition (CVD) and many more. The incomplexity of chemical method is adopted by most of the researchers. The liquid-phase exfoliation is much appropriable method to produce graphene. The organic solvents such as other polar & nonpolar solvents and N-methyl-2 Pyrroliodone (NMP) have been used to prepare graphene. However the main challenge is selecting a suitable solvent molecules to reduce the Vander Waals attraction between the layers of graphite and the interaction between C-C covalent bonds. The surface energy of graphite is in close proximity with the surface tension of ortho-dichloro benzene(ODCB) solvent and hence the energy required for exfoliation of graphite is minimum [2]. So, exfoliation using ODCB solvent has been chosen. In this paper, an effort has been made to demonstrate the preparation of homogeneous and stable dispersion of graphene in ODCB solvent. Moreover, it is illustrated that sonication for long hours leads to formation of homogenous dispersion of graphene in case of ODCB. Furthermore characterization has been done to provide evidence for the support of work.

II. EXPERIMENTAL PART

A. Materials Used

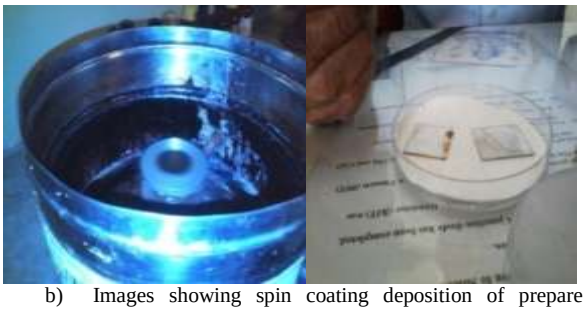
Graphite fine powder (Extra pure), Ortho Di-Chloro Benzene (ODCB) with CAS:95-50-1 were used without any dilution or distillation. The other reagents like Trichloroethylene (TCE), Sulphuric acid (H_2SO_4), Hydrogen Peroxide (H_2O_2), Methanol and De-ionized (DI) water were used.

B. Suspension Synthesis

A simple chemical approach can be used to obtain stable homogenous dispersion of graphene [16]. In a typical process, graphite (0.1 gm) was mixed with ODCB (100ml) in a glass beaker. The mixture was sonicated in an ultrasonic bath (power: 150 W & frequency: 33 KHz) at 50-60°C for 12 hours. Then the sample in dispersion form was kept in vial for overnight and the supernatant was transferred to

another vial. This dispersion was next subjected to 30 minutes centrifugation at 7000 rpm to remove the unexfoliated part of graphite. It was observed that the heavier particles got settled down and were removed from the dispersion. The dispersion was then heated to reduce its volume by 50% so as to make it more viscous and thermodynamically stable. This solution was preserved for further processing. The n-type oxidized silicon wafer and pyrex glass pieces (2.5 x 2.5 cm^2) were cleaned by organic solvents TCE and methanol and then rinsed in DI water for ten minutes. Then the samples were cleaned in a mixture consisting of H_2SO_4 and H_2O_2 in the ratio of 3:1 for 10 minutes (Piranha cleaning) and then rinsed in DI water for 15 minutes. The samples were dried in oven at 100 °C for 30 minutes and the above dispersion solution was deposited on cleaned samples by spin coating at a rate of 2000 rpm for 30 seconds. The coated film was dried at 90 °C for 15 minutes in the oven. This process was repeated seven times to obtain the desired thickness of the film. Finally the prepared samples were sent for XRD, UV-VIS spectroscopy and SEM characterization.

a) Images of prepared Graphene Dispersion in ODCB solvent



b) Images showing spin coating deposition of prepare ODCB suspension deposited glass substrates

Fig 1(a-b): Showing preparation of Graphene dispersions and sample preparation.

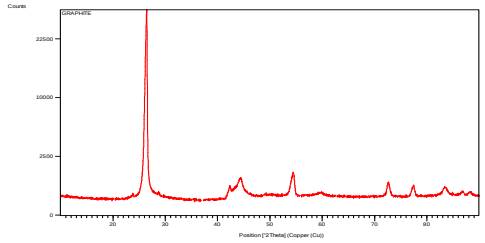
III. CHARACTERIZATION TECHNIQUES

A. XRD

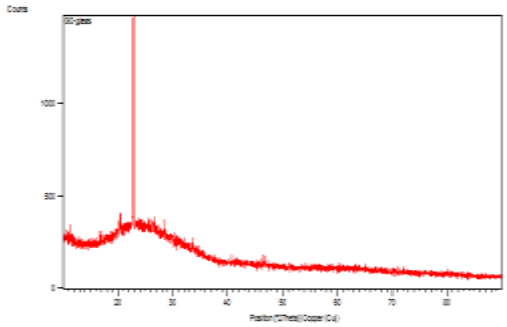
This is the basic analysis to know the crystal configuration and orientation of the nano crystalline material. A diffraction pattern results, when the X-rays comes in contact with a crystalline phase and show the different orientations and the inter layer spacing of atomic layers. The grain size can be calculated by Scherrer's Formula ,

$D = 0.9\lambda / \beta \cos(\theta)$

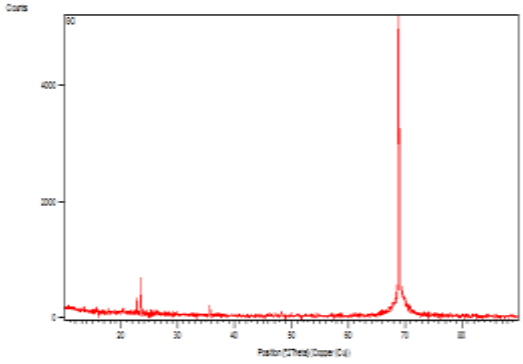
D is the mean grain size, λ is the wave length of X-ray radiation used, β is the line broadening of full width at half maxima (FWHM) in radians and θ is the Bragg's diffraction angle in degrees.



(a) XRD results of natural graphite powder



(b) XRD obtained on glass substrate



(c) XRD results on oxidized silicon substrate

Fig 2 (a-c): XRD results of natural graphite and graphene dispersion deposited on glass and oxidized silicon substrate.

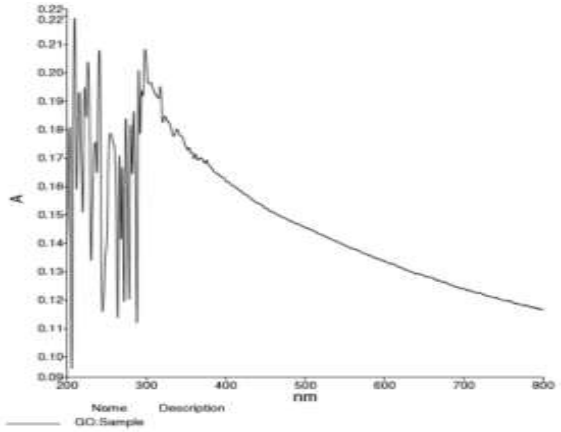


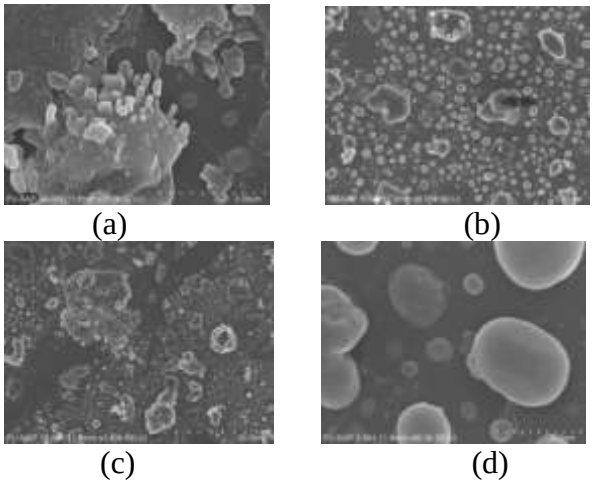
Fig 3: UV- Vis Spectrum on glass.

B. UV-VIS

This is used to measure absorption or transmission in transparent or opaque solids and liquids. In this technique, a beam of light is passed through sample and the remaining light is monitored in a detector. The range of wavelength is 200-800 nm in the case of UV-VIS spectrometer. As the light falls on the sample the light which is being passed through sample gets absorbed by some of the molecules present on the sample depending upon there structure and chemical bonding giving peaks at various wavelengths in this range. The first figure 3 shows the absorbance peaks at various wavelengths in the case of ODCB suspension.

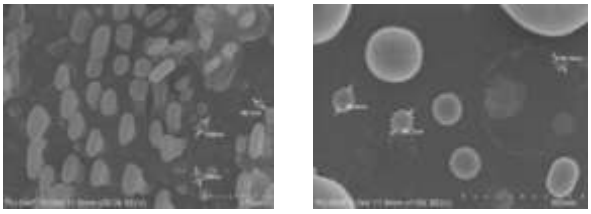
C. SEM

For morphological and structural analysis scanning electron microscope images using SU8000 series in Lens mode are provided here at different magnifi - cations. Scanning electron microscopy (SEM) is a visualization tool for imaging on the order of 30 nm to 1 µm. The surface details of the exfoliated graphite samples were analyzed from the SEM images.



(a) (b)

(c) (d)



(e) (f)

Fig- 4(a-f): SEM results for Graphene at different magnifications.

IV. RESULTS AND DISCUSSIONS

The formation of homogenous dispersion of graphene in ODCB can be elaborated through interaction between solvent and graphite. Sonication throughput is the separation of graphite layers and once the graphite sheets are separate out, solvent molecules (ODCB) penetrate inside the interatomic layers of graphite and adhere to graphite layers. This results into the formation of sonopolymer. Moreover ODCB is agreed to deteriorate during sonication to set free chlorine which can easily penetrate inside graphite layers. By escalating this sonication time the growth of polymer associated graphite sheets raise with increase in distance between the graphite layers and graphite exfoliation takes place. Fig. 2 (a) presents the XRD results of natural graphite powder in which diffraction peaks corresponds to crystallographic orientations (002), (100) and (101) etc. at different angles. Fig. 2 (b) presents XRD pattern of the film deposited on glass. This figure clearly presents that the the main intense peak (002), is at $2\theta = 26.4°$ approaching d-spacing equal to 0.335 nm of the original graphite goes in vain after exfoliation, while an additional peak at lower angle at $2\theta = 11.3°$ appeared close to the (001) diffraction peak of graphene oxide (GO) and the d-spacing also becomes superior to 0.784 nm. Another significant peak at 22.8° states the formation of graphene [1, 17]. These results are in near concord with results reported earlier in literature. The particle size of nano particles of graphene at different diffraction peaks varies from 32 to 84 nm as calculated from Scherrer's Formula. Fig. 2 (c) presents the XRD pattern on oxidized silicon substrate. These results also presents the crystalline nature of the exfoliated graphite. The strong and pointed peak at 66.8° may perhaps be due to the crystalline nature of silicon substrate itself. The grain size differs from 43 to 127 nm. The throughput of XRD using ODCB dispersion thus prove the successful synthesis of GO and graphene nano particles/sheets.

The GO and graphene formation with sonication method can also be described using UV-VIS spectroscopy studies for the optical absorption range from 200 nm to 800 nm as shown in figure 3. The figure 3 shows the results obtained from ODCB suspension [1, 18]. A piercing peak at 210 nm can be noticed and one more peak around 226 nm with a little

bit less intensity of absorption peak is also observed due to Π-Π* bondings of the C-C aromatic rings [19].

The figure 4(a-f) show the morphological changes in exfoliated graphite at various magnifications. The structural advancements can be notified and therefore graphene formation can be noticed. The images displayed from SEM at a variety of magnifications ranging 1.8 K to 110 K show various scaled particle size. It can be notified that the particles as small as 42 nm and as big as 150 nm are observed. The throughputs considered using Scherrer's formula as already explained in XRD result discussion, are quite in close relation with SEM results. Thus the exfoliation and the porosity of the material is confirmed from SEM.

V. CONCLUSION

The XRD results obtained confirm the exfoliation in graphite. Synthesis of graphene is due to increase in the distance between the layers of graphene due to intercalation. The absorption peaks too states the exfoliation due to the action of ODCB. Further SEM analysis states various particle sizes claiming exfoliation of graphite by sonication process. Thus it can be stated that the graphene with enormous extraordinary properties (including Super capacitor) can be synthesized following the sonication method using organic solvents. To further exfoliate the expanded graphite, a very dilute system must be choosen to use sonication in order to reduce the importance of the recombination process of graphene sheets. The gigantic difficulty of employing this process is that the quantity of graphene obtained is generally very small and hence further efforts are required to improve the process.

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