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ECONOMICAL SYNTHESIS OF GRAPHENE

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ABSTRACT

Synthesis of reduced graphene oxide nanoparticles carried out by improved hummer's method. Characterization of nanoparticles was done by: XRD and Zetasizer (Particle size analyzer). Where XRD is used for determination of particle size using Debye Scherrer's equation and for the structures of particles using standard XRD indexing chart and for composition. Zetasizer is used to check the homogeneity of particle size and the range in which it lies. To modes of Zetasizer were used (size vs. intensity, size vs. volume), in which size vs. volume gives more accurate size for particles. Also band gap of the particle formed was calculated by UV-Visible spectroscopy.

Keywords: Hummer's Method, Graphene, Graphene oxide, Nanoparticles, Reduced Graphene Oxide, UV-Visible spectroscopy, X-Ray diffraction, Zetasizer

INTRODUCTION

Graphene is 2-dimentional crystalline allotrope of carbon. Its carbon atoms are arranged in a wire mesh structure (hexagonal) and are densely packed. Most common method for preparation of graphene (or RGO) with use of $KMnO_4$, $NaNO_3$, H2SO_4.

Graphene nanoparticles appear as a black powder. Current applications of graphene are that they can be used as catalyst for many reaction (preferred size less than 20nm).Also they are used as reinforcing agents. They also find a wide application in composites.

This paper presents the synthesis of RGO by economical method. Here particles were formed by improved hummer's method (addition of $KMnO_4$ at a single temperature, 0˚C).

Other variations in Hummers can be modified hummers and original hummers method. And then the sample was characterized by XRD, Zetasizer and UV-Visible spectroscopy.

EXPERIMENITAL

1.Material and Methods

To synthesized RGO nanoparticles we used improved hummers method. It is a new method for preparation of nanoparticles with negligible emission of poisonous gases. This method of synthesis involves both exfoliation and oxidation by thermal treatment of solution, it is an economical approach for bulk production of grapheme and to convert graphite to graphene oxide using strong oxidizing agent such as $KMnO_4$. Properties of GO include hydrophilic nature towards water also it is highly non-conductive. In 1859, for the first time graphite oxide was formed by addition of potassium chlorate to slurry of nitric acid (fuming) and graphite, by Brodie. Later by 1958, further work was conducted to obtain bulk production[1]..This was done by hummes which resulted in mass production of Graphene Oxide. This paper talks about Synthesis of RGO by reducing Graphene Oxide with the help of ascorbic acid. For the preparation of RGO nanoparticles by improved hummers method graphite, conc. sulphuric acid, sodium nitrate, potassium permanganate were used as precursors to form Graphene oxide and ascorbic acid to reduce it to RGO .Other chemicals include hydrogen peroxide and hydrogen chloride.

2.General Procedure:

2.1 Preparation of Graphene oxide (GO)

1gm of graphite was mixed with 39ml conc.sulphuric acid and kept for stirring. This was done to increase the gap between the layers of graphite so that the separation is facilitated. [2]Then while stirring 0.5grms sodium nitratewas added at room temperature to further support the separation. An ice bath was prepared to decrease the temperature to 0˚C after which 3gms potassium permanganate was added to the formed solution for oxidation. In the process we added the whole batch at the same temperature as a single step, but the addition was in small quantities.

3% hydrogen peroxide and HCl in same quantities (when needed) along with water for washing. The sample was washed and centrifuged at 10000rpm. This process was repeated till the time the ppt (can be silver or golden) is completely washed off or dissolved. By this process graphene oxide was procured.

2.2Preparation of Reduced Graphene oxide (RGO)

The produced graphene oxide then was reduced by addition of 0.1M ascorbic acid in 1:1 ratio to the produced GO. This mixture was sonicated at 60˚C for 30 mins at amplitude of 40% .The cycle for Sonication was set as 30 sec pulse on and 20 sec pulse off. Sonication was done to disperse ascorbic acid well in the mixture to attain homogenized solution for better particle synthesis

In continuation to Sonication hydrogen peroxide was added in 30%excess to the solution formed. Addition of hydrogen peroxide was done by a burette. Hydrogen peroxide aids reduction process for yielding RGO[3]. After addition again Sonication was performed maintaining the same parameters and the sample thus formed was characterized using different techniques.

Flow chart showing the synthesis of graphene and reduced graphene oxide

Graphite (1gm)+conc. Sulphuric acid(39ml)+magnetic stirrer
At Room temperature + sodium nitrate(0.5gms)

⇩ Cool to 0˚c

Potassium permanganate (3gms)(slow addition)
Stirring (2hrs)

⇩ Formation of green slurry and room temp was attained

Batch was transferred to 100 ml beaker, Drop wise 3%hydrogen peroxide was added and overnight stirring was carried

⇩

Filtration was accomplished by several washing of H_2O_2/HCl(1:1) and centrifugation till no silver precipitation was visible

⇩ Formation of graphene -oxide

1M ascorbic acid +GO(1:1) was sonicated at 60^0c for 30 min And 30% excess H_2O_2 was added drop wise ,sonicated again and centrifuged at 1000rpm to give RGO

3. Detection Method

For the determination of RGO nanoparticles different properties like- Crystal structure, size of the particles, band gap etc. we used different characterization techniques. To characterized the RGO nanoparticles properties we used X-ray Diffractometer, UV-VIS spectroscopy, Zetasizer.

4. Advantages over other methods

In this method there is no variation of temperatures hence less complications also the yield compared to other methods is very high. One major advantage is that the production of harmful gases is controlled to large extend.[4]

5. Potential Applications

- Graphene can be used as an additive for lubricants.
- Graphene is used as re-enforcement material
- With high conductivity it can also be used to enhance electrical properties.
- It can also be used for biosensors
- It finds a wide application in biomedical

RESULTS AND DISCUSSION

1.XRD

After X-Ray diffraction pattern of synthesized Reduced Graphene oxide nanoparticles is shown in fig.1.From the obtained graph particle size was measured by using Debye scherrer's equation. Calculated particle size is 2.599 nm. The graph obtained is compared with the standard graph[5] of RGO sample reported in literature. the peak obtained was at angle 27. Also there are no other peaks present indicated the formation of high purity RGO.

Debye scherrer's equation:- $D = \frac{K\lambda}{\beta(in\ rad.)\times cos\theta}$

K: having constant value of 0.89.

λ:- wavelength of X-ray used, having value 1.5406 A^0.

β_{rad}: full width at half maximum (FWHM) factor in radians, having different values for different peaks.

Cosθ: θ= 2theta /2 values for different peaks.

D: Average crystal size.

By this formula we can measure the average crystal size of prepared sample. In place of θ value at which peak is obtained is substituted which is in radian.

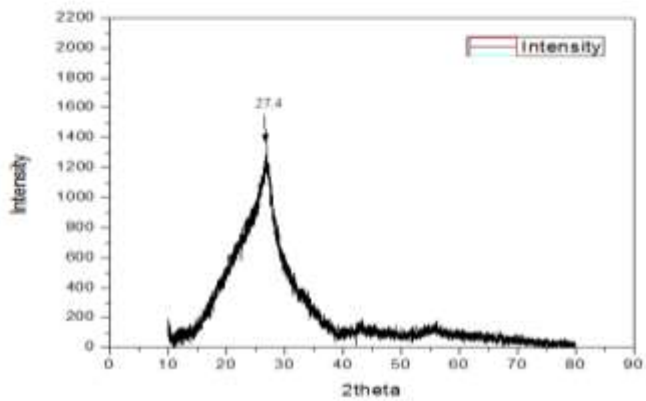

Fig.1. XRD pattern of RGO sample prepared.

3.2 UV-VIS

After determining the phases and particle size with the help of X-ray Diffractometer, we determined the band gap value with the help of UV-VIS spectroscopy. Absorbance of RGO nanoparticles was measured by UV-VIS spectrometry for RGO was dissolved in water and sonicated for better dispersion. So the absorbance of light due to the RGO nanoparticles was measured and results are shown inFig.2. Here a single spectral line is obtained at 271 nm which shows that energy absorbed only at a particular wavelength and electron excited from one state to another. Usually in this type of absorption in the case of organic materials we get only one single line due to energy absorption for excitation of electron from valance band to conduction band. Therefore here we can calculate Energy band gap of prepared sample RGO .

Energy correspond to this wavelength can be calculated by the use of Planck's equation:-

$$\boldsymbol{E = hv}$$

Where E = energy

h = plank's constant

v = *Frequency* = c/ λ , where Lamda is wavelength of transition and c is velocity of light.

Using this equation we get the energy = 4.5ev, which is its energy band gap, as this is the energy needed to transition of electron from valance band to conduction band, which is near to theoretical energy band gap of RGO.[6]

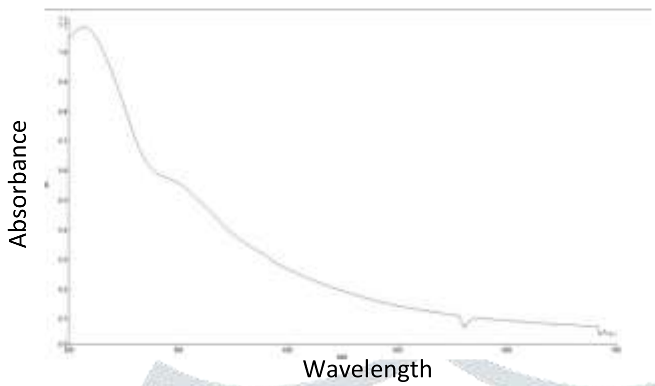

FIG.2. Absorption vs. Wavelength graph.

3.3 Zetasizer

Characterization technique uses Brownian motion of the particles for characterization. Brownian motion is the randomness in the particles. Small amount of particles were added to a beaker containing water and sonicated for 4 min, with a pulse cycle of 30 sec pulse on and 10 sec pulse off, maintain amplitude of 40%.This diffused solution was used as a sample for Zetasizer. Average particles is around12.26nm with an standard deviation of 0.8499nm

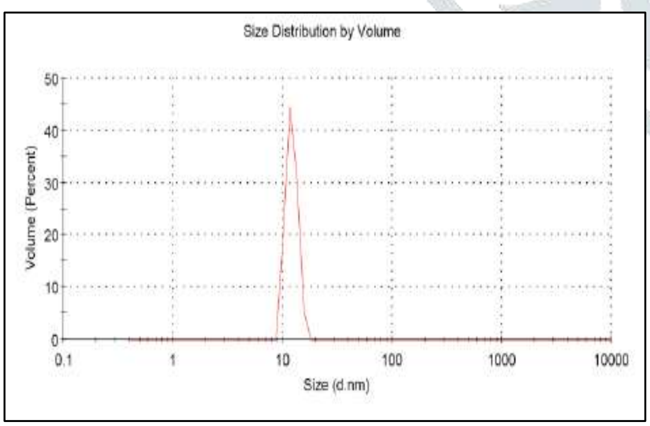

FIG 3.1 size vs. volume distribution

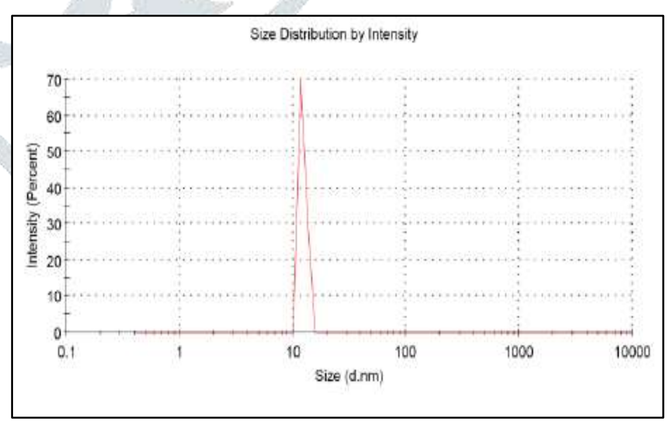

FIG 3.2 size vs. intensity distribution

Slight variation in graph is observed when the parameters are changed from intensity to volume this is because in size vs. volume particle volume is taken in consideration which is not uniform for every particle(due to slight variations in size). In some cases even small peaks are absent in case of volume which is a result of negligible volume of those particles in that range.

CONCLUSION

The RGO nanoparticles were successfully prepared via improved hummers method. The crystallite size of RGO was found to be 12.26 nmwith an standard deviation of 0.8499nm. Optical properties of RGO nanoparticles were analyzed/ clarified through UV absorption. The direct band gap of RGO nanoparticles was found to be 4.5ev.Zetasizer results indicates that there no/very little agglomeration.

The variation in size observed in zetasizer and XRD is due to agglomeration which occurs in nanoparticles when smaller than certain size

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