Preparation and Characterization of Self-Assembled Graphene Oxide Supramolecular Structures

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***Abstract*—Supramolecular self-assembly of *nanostructures* is widely pursued in different industrial and biological fields for many nano-materials including grapheme oxide (GO). In the present study, we synthesized using chemical method and characterized the self-assembled nanostructures of GO using UV-Vis spectroscopy, Fluorescence spectroscopy, Field emission Scanning electron microscopy and Dynamic light scattering particle size analysis. It was observed that the synthesized self-assembled GO nanostructures product showed the floral patterns. Such patterns were developed due to self-aggregation by nano-sized GO sheets. However, when the individual particle size distribution was observed, it was found to have a size distribution in the range of 50 to 250 nm.**

***Index Terms*—graphene oxide, self-assembly, pyrolysis, FESEM**

I. Introduction

Graphene along with its various functionalized derivatives are important constituents for the self-assembly process [1]. Graphene oxide (GO) is an atomically thin sheet made of graphite that contains covalently bonded oxygen-containing functional groups, on the basal plane and on the edges. The growing popularity of GO is attributed to their remarkable properties, such as reduced toxicity, high photoluminescence, chemical inertness and easy synthesis resulting in formation of sheets smaller than 100 nm [2]. Because of its excellent aqueous processability, amphiphilicity, surface functionalizability, surface enhanced Raman scattering (SERS) and fluorescence quenching ability, GO is considered a promising material for biological applications.

Graphene oxide nanoparticles have an adverse effect on the aquatic organisms like bacteria, algae, plants invertebrates and fish [3]. However, lignin peroxidase can effectively degrade Graphene oxide [4]. Graphene oxide supramolecular structures and its derivatives find many applications in drug delivery [5], [6].They are used as biosensors for the detection of neurotransmitters such as dopamine [7] and chemicals such as glucose [8], sildenafil [9], folic acid [10], ATP and GTP [11], adenosine deaminase [12] and paracetamol [13]. Graphene oxide is also used for fluorescence sensing of DNA [14] and detection of protein [15]. It is also found to trap viruses and brings about their destruction [16]. Graphene oxide shows antibacterial activity against a variety of microorganisms such as *Pseudomonas aeruginosa* [17], *Staphylococcus aureus*, *Escherichia coli* [18], *P. syringae and X. campestris* [19]. It also helps in the detection and removal of methylene blue and lead from waste water [20], [21].Graphene oxide also removes atmospheric air pollutants such as perchloroethylene normally present in air of dry cleaning industries [22].

Self-assembled graphene macromolecular structures are being utilized for various biological and electronic applications. The regulation of self-assembly of graphene oxide is a major challenge. Hence, in our present effort we have synthesized graphene oxide and with alteration of pH we have developed the floral structures of graphene oxide

II. Materials and Methods

A. Materials

All the chemical used are of analytical grade. Citric acid and NaOH were purchased from Himedia India Pvt.Ltd.

B. Pyrolysis of Citric Acid [23]

Citric acid (2g) was taken in a 5 ml test tube and heated at 200^0C. At about 5 min later the sample attains a liquid state. Subsequently the colour changed from pale yellow to black mass in 2 hrs suggesting the formation of graphene oxide. The obtained black mass of graphene oxide (560mg) formed is dissolved in 10mg/ml solution of NaOH to a final volume of 50ml.The sample was sonicated using a probe sonicator (Hielscher Ultrasonics ,UP100H) at 0.8 cycles and an amplitude of 80% for 30 min. The pH of the samples was adjusted to 7 using concentrated Hcl. To observe the controlled growth of floral arrangement of graphene oxide, the sample was diluted 1:7 with MilliQ water. The sample was kept over the slide and allowed to dry at room temperature.

C. Instrumentation

The samples were sonicated for 10min prior to analysis. The pH of the samples was adjusted to 7 using concentrated Hcl. The graphene oxide samples were

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analyzed using UV-Vis spectrophotometer (Perkin Elmer Lamda 35). The graphene oxide samples at a concentration of 0.1mg/ml were used for UV-Vis spectroscopy. The results are shown in Fig. 1.

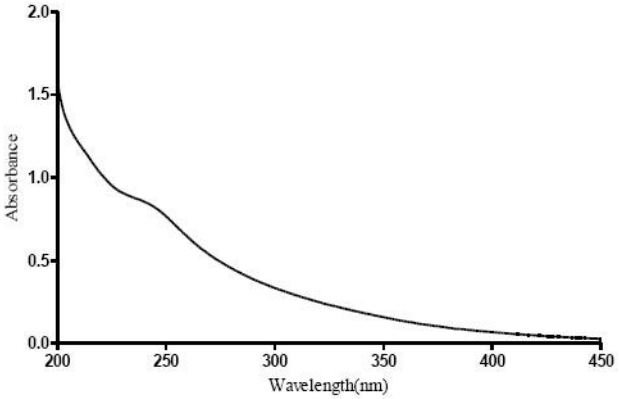


Figure 1. UV-Visible spectroscopy of Graphene oxide

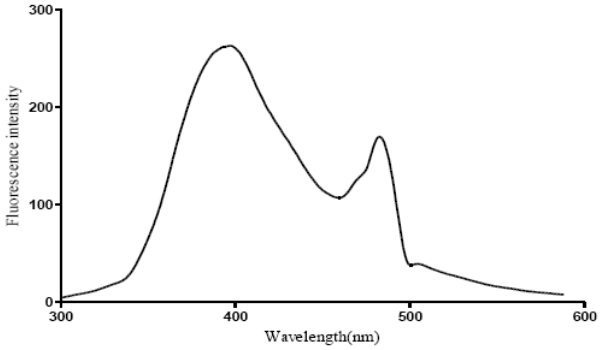


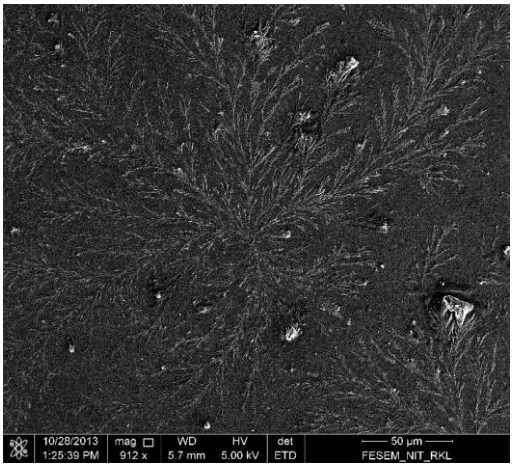
Figure 2. Fluorescence spectroscopy of Graphene oxide

Fluorescence spectroscopy was carried out using LS 55 Spectrofluorometer. The graphene oxide samples at a concentration of 0.1 mg/ml were used for Fluorescence spectroscopy. The results are shown in Fig. 2. Field emission scanning electron microscopy was carried out using FEI-NanoSEM. The suspension of graphene oxide was spread over glass slides and allowed to dry at room temperature. The samples were coated with gold for 30 seconds before analysis. The results are shown in Fig. 3. Dynamic light scattering for particle size analysis was carried out using Malvern ZSNano. The results are shown in Fig. 4.

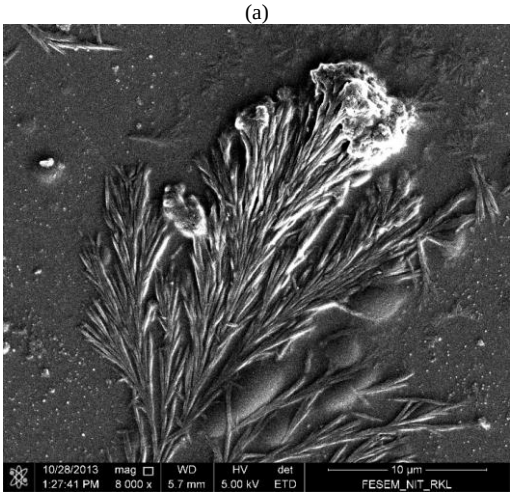
III. Results and Discussion

When we characterized the GO solution using a UV-Vis spectroscopy, GO shows a broad absorption peak around 235 nm and a still fainter shoulder peak at 344 nm as shown in Fig. 1. However in the present case the shoulder peak at 344 nm is not clearly identified. We also have performed fluorescence spectroscopy of Graphene oxide which shows an emission peak at 400 nm (Fig. 2) when excited at 235 nm with an excitation slit width of 5nm and emission slit width of 10 nm. The contribution of fluorescence exhibited by GO has many applications.

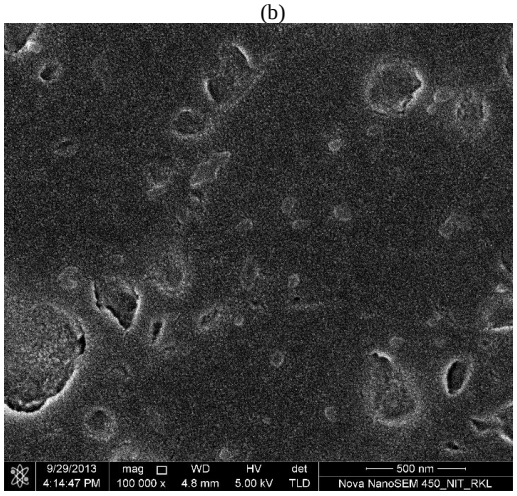
The GO solution was further examined in FESEM. The samples of GO upon drying show a distinct branched pattern like structure (see Fig. 3a). It clearly looked to be branched floral kind of arrangement which originated from a same point. Upon higher magnification as shown in Fig. 3(b) clear floral structures are seen .These self-assembly of supra molecular structures are in an organized manner.



(a)



(b)



(c)

Figure 3. (a). Branched pattern of Graphene oxide; 3(b). Floral pattern of Graphene oxide at higher magnification; 3(c). Irregular structures of Graphene oxide in the size range of 50 nm-250nm

When we diminished the floral arrangement using lightly heating followed by sonication at a medium frequency, we found the size distribution of individual

particles in FESEM. At higher magnification the disordered structures of graphene oxide are clearly seen. The GO particle size varied from 50 nm to 250 nm as seen in Fig. 3(c).

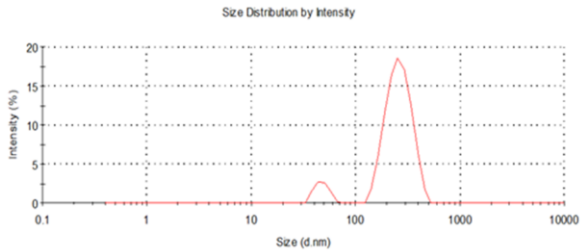


Figure 4. DLS particle size analysis of Graphene oxide

Particle size analysis as shown by Dynamic light scattering clearly shows two peaks corresponding to particle sizes of 50 nm and 250 nm which is in agreement with the FESEM images taken for Graphene oxide.

IV. Conclusion

Graphene oxide, a 2D soft molecule with amphiphilic nature, is characterized by plentiful self-concentrating phenomena at interfaces, and these interfacial properties together with the developed self-assembly techniques provide simple and effective strategies for producing a variety of novel carbon nanostructures and materials with designed functions. This contribution reviews the self-concentrating phenomena at various interfaces, currently developed self-assembly techniques, and self-assembled nanostructures at the interfaces and the applications of the resulting functionalized materials. Graphene oxide has been used to finding many applications including biological, medical, and electronics field. The unique and fascinating properties of graphene derivatives such as functionalizable surfaces, strong UV absorption, and fluorescence and fluorescence quenching ability make them one of the most promising materials for biosensors, therapeutics, and tissue engineering as well as electronics. Despite rapid advances in finding self-concentrating phenomena at interfaces and developing interface-directed self-assembly for GO-based or graphene-based nanostructures and bulk materials, several important challenges still need to be overcome before interfacial self-assembly becomes a major strategy for preparing functionalized carbons with designed structure and controlled properties. The chemically inert property of Graphene oxide along with its ability to form self-assembled macromolecular structures may find many applications in designing biocompatible scaffolds for tissue engineering applications.

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