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Spectral, Thermal and Morphological Characterization of Biodegradable Graphene Oxide-Chitosan Nanocomposites

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ABSTRACT

Graphene oxide (GO) was chemically synthesized from natural graphite by modified Hummers method. The graphene oxide-chitosan (GO-CHI) nanocomposites were synthesized by simple solution-mixing and evaporation method using ultrasonication. The samples were characterized using FTIR, UV-Vis spectroscopy, TG/DTA, DSC, SEM, TEM and AFM. The FTIR spectrum suggested that interactions existed between CHI and GO as evidenced by the downshift of the C=O stretching vibration of the amide group at 1653 cm^{-1}. UV-Vis spectra shows a bathochromic shift in bands of GO in the nanocomposite. The optical analysis of the GO and GO-CHI nanocomposites gave a direct energy band gap of 1.02 eV and 1.08 eV respectively indicating the highly conducting nature of the synthesized nanocomposite. Thermal stability was studied through TG/DTA which showed an enhancement in degradation temperature of chitosan from 175.4 °C to 302.5 °C in the composite and DSC studies showed an endothermic peak at 94.55 °C which is due to the loss of physisorbed water from the surface of the CHI matrix and an exothermic peak at 302.11 °C due to degradation and deacetylation of chitosan indicating high thermal stability of the composite. SEM micrograph of the nanocomposite showed the presence of the biopolymer chitosan with its porous, rough, granular morphology and the GO with its layered morphology. TEM image of the nanocomposite showed the particle size to be 20 nm and it also showed the presence of exfoliated GO as a fibrous network on the surface of the chitosan matrix. AFM study shows the value of the RMS coefficient for the nanocomposite as 40 nm indicating the formation of composite in the nano dimension. It also revealed the presence of rough surface thus indicating the presence of large number of active sites.

1. Introduction

Graphene is a two-dimensional building block which can be stacked as three dimensional graphite, rolled into one dimensional nanotubes, or folded into zero dimensional fullerenes [1, 2]. The extra quantum confinement of the electrons due to the lack of a third dimension gives graphene various novel properties. For example, electrons interact with carbon atoms in the lattice to create a system that acts like a single mobile charge carrier. The carrier moves over the graphene surface which enables graphene sheets to conduct electricity [3, 4]. Other complex interactions between electrons and the hexagonal lattice make graphene transparent, flexible and strong [5]. These properties and others have attracted many researchers over the last half-decade to study graphene for a variety of uses [6, 7]. Graphite is a three dimensional material made up of millions of layers of graphene. By the oxidation of graphite using strong oxidizing agents, oxygenated functionalities are introduced. This makes the material hydrophilic enabling the graphite oxide to be exfoliated in water using sonication, ultimately producing single or few layer graphene, known as graphene oxide (GO). One of the advantages of GO is its easy dispersability in water and other organic solvents. This is due to the presence of the oxygen functionality groups. The presence of these groups helps in mixing the material with ceramic or polymer matrices when trying to improve their electrical and mechanical properties [8, 9]. Mass production of high quality graphene sheets at low cost is needed for commercial applications. Therefore, it is important to develop environmentally friendly methods for producing graphene nanosheets in large scale.

The chemical approach for producing GO is well suited for mass production because of its low-cost procedure. Furthermore, it can render a large variety of different variants of graphene with chemical modifications [10, 11]. In view of this, the interest of this study is to chemically synthesize GO through a modified Hummers' method, using natural graphite as starting material and then synthesizing the GO-CHI nanocomposites by making use of natural biopolymer chitosan through inexpensive environment friendly simple solution-mixing and evaporation method using ultrasonication.

2. Experimental Methods

2.1 Synthesis of GO

For the synthesis of GO by modified Hummers method, 2 g of graphite and 1 g of sodium nitrate were dissolved in 46 mL of concentrated sulphuric acid in an ice bath. After about 15 min of stirring, 6 g of potassium permanganate was gradually added into the suspension with stirring as slowly as possible in order to control the reaction temperature below 20 °C. The suspension was stirred for 2 h and then maintained at 35 °C for 30 min. Next, 92 mL of deionized water was slowly poured into the suspension, resulting in a quick increase in temperature but which was controlled such that it remained less than 98 °C. After 15 min, the suspension was further diluted to approximately 280 mL with warm deionized water, after which 20 mL of 30% hydrogen peroxide was added to remove the residual potassium permanganate and manganese dioxide to change the color to luminous yellow. The resulting suspension was filtered and washed with deionized water. The sample of GO was dried under vacuum at 50 °C to a constant weight.

2.2 Synthesis of GO-CHI Nanocomposite

GO (0.05 g) was dissolved in 100 mL distilled water and placed in ultrasonic bath for an hour until a brown colour was formed. To this, 2 g CHI was added with stirring at 27 °C for an hour at 350 rpm. The mixture was filtered and dried at 70 °C for 8 h. The dried composite were soaked in 2% sodium hydroxide for an hour and dried at 70 °C for 6 h and used for characterization.

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2.3 Characterization

The conformation and constitution of the nanocomposites were characterized by UV-Vis and FTIR spectroscopy. For recording UV-Vis absorption spectra, a computer controlled JASCO V-530 dual beam spectrophotometer with DRS support was used. The FTIR spectra were recorded using SHIMADZU spectrometer by pelletizing the samples using KBr in the frequency range of 400 – 4000 cm^{-1}. The morphology of the synthesized material was studied using microscopic techniques like scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM micrographs were recorded using SEM instrument model: JEOL JSM 6360 operating at 25 kV. AFM of the samples were recorded using Nanosurf Easy Scan 2 Controller by dissolving the nanocomposites in DMSO after sonication for fifteen minutes and then coating the sample on a glass plate.

3. Results and Discussion

3.1 UV-Vis Spectral Studies

The UV-Vis spectrum of the GO-CHI composite is shown in Fig. 1. Pure GO (Fig. 1a) shows two absorption peaks one at 234 nm and another at 304 nm [12, 13]. As per literature, the CHI peaks are expected at 240 nm and 280 nm [14]. After attachment with CHI, the peaks of GO have shown a bathochromic shift. This shift in absorption maxima might be attributed to the formation of particles in the nano scale. This also indicate the strong covalent interaction between GO and CHI where the active ester group of GO might have reacted with the amine groups on CHI, forming an amide bond between GO and CHI. Optical analysis shows the band gap energy of GO to be 1.02 eV and that of the nanocomposite to be 1.08 eV. Since these values are within the range of semiconductor indicating that the conductivity of the constituents are retained in the composites thus enabling their application in the field of optoelectronics.

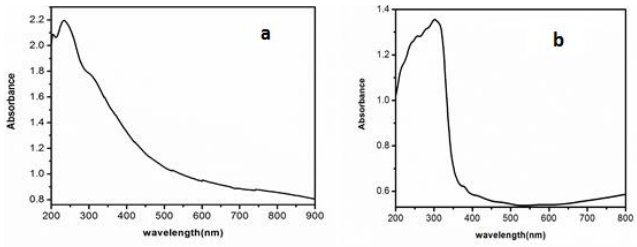

Fig. 1 UV-Vis spectra of a) graphene oxide and b) GO-CHI nanocomposite

3.2 FTIR Spectra

The FTIR spectrum of GO as shown in Fig. 2a shows a broad peak at 3386.75 cm^{-1} in the high frequency area together with a sharp peak at 1650.01 cm^{-1} corresponding to the stretching and bending vibration of OH groups of water molecules adsorbed on graphene oxide [15, 16]. This implies that the sample has strong hydrophilicity. The absorption peak at 1620 cm^{-1} can be ascribed to the presence of benzene rings [17]. The absorption peaks at 2922.07 cm^{-1} represent the symmetric and anti-symmetric stretching vibrations of CH_2, while the presence of two absorption peaks observed in the medium frequency area, at 1650.01 cm^{-1} and 668.61 cm^{-1} can be attributed to the stretching vibration of C=C and C=O of carboxylic acid and carbonyl groups present at the edges of graphene oxide [18]. Finally the absorption peaks at 1384.56 cm^{-1} and 1093.98 cm^{-1} correspond to the stretching vibration of C-O of carboxylic acid and C-OH of alcohol, respectively. The presence of these oxygen containing groups reveals that the graphite has been oxidized. The polar groups, especially the surface hydroxyl groups, result in the formation of hydrogen bonds between graphite and water molecules; this further explains the hydrophilic nature of graphene oxide. Fig. 2b shows the peaks at 1069, 1321, and 1626 cm^{-1} correspond to C–O–C stretching vibrations, C–OH stretching, and the C–C stretching mode of the sp^2 carbon skeletal network, respectively, while peaks located at 1653 and 3386 cm^{-1} correspond to C–O stretching vibrations of the–COOH groups and O–H stretching vibration, respectively. These functional groups make GO highly hydrophilic and render it dispersible. In the spectrum of CHI, it is reported in literature that there are two characteristic absorbance bands centered at 1650 and 1591 cm^{-1}, which corresponded to the C=O stretching vibration of amide I and the N–H bending of $–NH_2$, respectively [19]. The FTIR spectrum of the GO-CHI composite showed a combination of characteristic peaks of the pristine CHI and GO. In the spectrum of CHI, peaks corresponding to NH_2 absorbance vibration are at 1591 cm^{-1}. In the spectrum of GO, peaks corresponding to C=O stretch of carboxylic group is at 1734 cm^{-1}. In the spectrum of GO-CHI, both of the above peaks disappeared, which suggested that interactions existed between CHI and GO. Moreover, the C=O characteristic stretching band of the amide at 1653 cm^{-1} was downshifted due to the synergistic effect of hydrogen bonding between CHI and the oxygenated groups in GO and the electrostatic interaction between polycationic CHI and the negative charge on the surface of GO. These interactions may have a strong impact on the mechanical properties, swelling, and degradation of the composite [20].

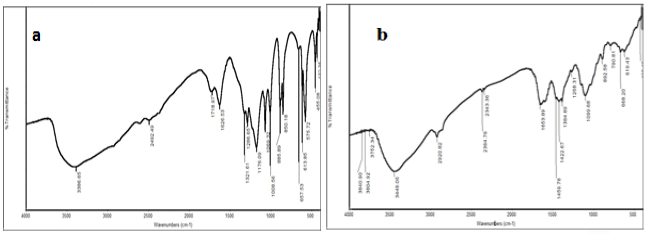

Fig. 2 FTIR spectra of (a) graphene oxide (b) GO-CHI composite

3.3 Thermal Analysis

The DSC thermogram of GO-CHI composites (Fig. 3a) shows an endothermic peak at 94.55 °C which is due to the loss of physisorbed water from the surface of the CHI matrix with the glass transition at 245 °C and an exothermic peak at 302.11 °C due to degradation and deacetylation of chitosan [21, 22]. The Tg of CHI as per literature is 175.4 °C [23]. Due to the presence of exfoliated GO in the CHI matrix Tg of the composite has increased to 260 °C. This increase may be due to the effective attachment of GO to CHI that prevents the segmental motion of CHI chains by hydrogen bonding and electrostatic interaction [24, 25]. Similar result was obtained in TG/DTA studies.

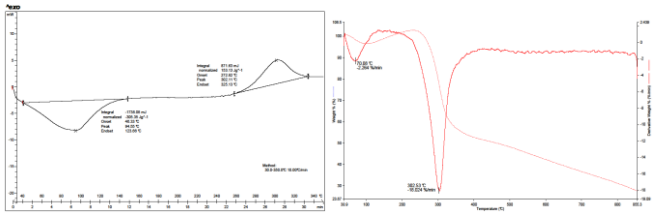

Fig. 3 a) DSC thermogram and b) TG/DTA of GO-CHI nanocomposite

3.4 SEM Analysis

In the case of SEM image of GO-CHI composite (Fig. 4) the presence of the biopolymer Chitosan with its porous, rough and granular morphology, and the GO with its layered morphology could be seen. The presence of exfoliated GO is also clearly seen as a fibrous network on the surface of the Chitosan matrix. This is an indication of good adhesion and interaction between chitosan and graphene oxide in the composites.

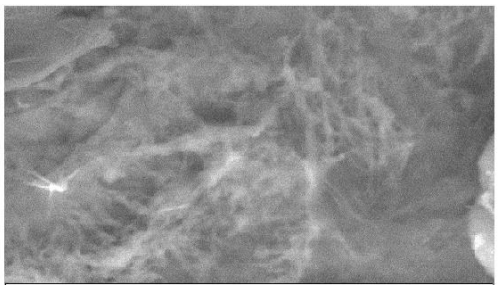

Fig. 4 SEM micrograph of GO-CHI nanocomposite

3.5 AFM Studies

AFM spectra was recorded for the nanocomposite by depositing it on a glass plate using DMSO as solvent. Fig. 5 shows the topography (3.13 ×3.13 μm) of the surface of GO-CHI nanocomposites. The topography changes within a range of 0 to 106 nm. Analyzing the cross-sections across the surface we see the changes in height amount to several nanometers along the cross-section of 88.9 nm. The value of the RMS coefficient for the nanocomposite amounts to RMS 40 nm which proves the better development of the surface of the nanocomposite. As a result the nanocomposites may possess a larger specific surface area because the decrease in size always results in an increase in specific surface area. As the surface roughness increases, the effective surface area of the material increases. This increases the number of active sites and number of defects [26].

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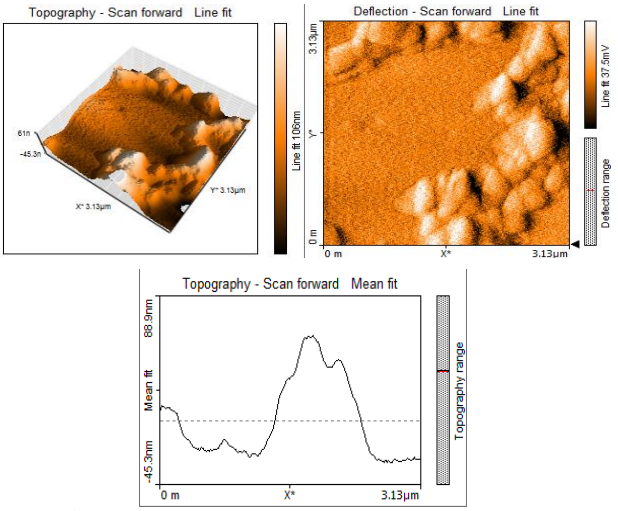

Fig. 4 AFM of GO-CHI nanocomposites

3.6 TEM Studies

TEM image (Fig. 5) of the nanocomposite shows the presence of exfoliated GO as dark strands in the matrix of the biopolymer chitosan seen as a light coloured cloud with the particle size of 21 nm. The SAED pattern of the nanocomposite shows its crystalline nature.

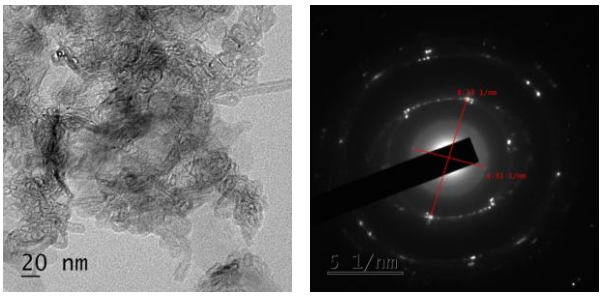

Fig. 5 TEM and SAED pattern of the nanocomposite

4. Conclusion

Graphene oxide was successfully synthesized by environment friendly modified Hummers method from natural graphite. Nanocomposite of GO was successfully synthesised using natural biopolymer chitosan by simple solution mixing and evaporation method using ultrasonication. Presence of both the components of the nanocomposite was confirmed by UV-Vis and FTIR spectral studies. These studies also indicate the strong interaction between GO and CHI in the nanocomposites. Band gap energy calculations show the highly conducting nature of the nanocomposite. The synthesized composite was found to have greater thermal stability. The presence of exfoliated GO is seen as a fibrous network on the surface of the chitosan matrix from the SEM images. TEM analysis showed similar result with the formation of crystalline nanocomposite with the particle size of 21 nm. AFM images show formation of composite in nanoscale as well as the presence of number of active sites.

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