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Physiochemical and optical properties of chitosan based graphene oxide bionanocomposite

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ABSTRACT

In the present investigation an ecofriendly approach and a simple homogeneous solution casting method led to the development of biodegradable chitosan/graphene oxide bionanocomposites. The formation of bionanocomposite was confirmed by UV–vis, FT-IR, Raman spectroscopy, XRD, and further evaluated by thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The circular dichroism (CD) study of chitosan/graphene oxide revealed that the intensity of the negative transition band at wavelength of 200–222 nm decreased with the different pH of chitosan/graphene oxide solutions. It was also found that the pH conditions affect the interaction between chitosan and graphene oxide. Optical properties of chitosan/graphene oxide are evaluated by photoluminescence (PL) spectroscopy which showed blue shift at excitation wavelength of 255 nm compared to graphene oxide. These results strongly suggest that the bionanocomposite materials may open new vistas in biotechnological, biosensor and biomedical applications.

1. Introduction

In recent years, there is a growing interest to develop materials with technological importance in optoelectronic devices, biological labeling and sensing [1–6]. Graphene, an allotrope of carbon arranged in a honeycomb crystal lattice into one atom thick planar sheet has attracted wide interest among the scientific community due to its fascinating high electronic, mechanical and thermal properties [7,8]. Graphene oxide (GO) obtained by exfoliation of graphite with a high yield under simple oxidizing conditions contains hydroxyl and epoxide groups on the basal planes and carboxyl or carbonyl groups mostly at the sheet edges offer unique and desirable characteristics suitable for biomedical applications [9,10]. On the other hand, Chitosan is second most abundant biopolymer in nature after cellulose [11,12] on the other extreme with two types of reactive functional groups amino (NH_2) at C-2 and hydroxyl (OH) at C-3 and C-6 position on its backbone along with interdispersed acetamido groups has been used in biomedical, pharmaceutical and industrial applications due to its biodegradability, biocompatibility and low cytotoxicity [13–18]. Recently, we have demonstrated optical properties of chitosan based dye containing naphthalimide group [19]. Many researchers have modified the biopolymers with inorganic materials to improve several properties such as thermal conductivity and mechanical strength. Graphene oxide can improve the mechanical strength of the alginate/graphene oxide fibers [20]. Another study revealed that the tensile strength of chitosan/graphene oxide composite is 1.7 times higher than that of the pure chitosan at dry state while it is 3 times higher at wet state [21]. The thermal stability and mechanical properties of the cellulose/graphene oxide composite materials are improved significantly over those of pure cellulose [22]. Recently, Li et al. [23] have developed hyaluronic acid–graphene oxide conjugates, with a high loading of photosensitizers as a cancer cell targeted and photoactivity switchable nanoplatform for photodynamic therapy. Some researchers have reported weak broad photoluminescence of graphene oxide, which was believed to originate from the carbon sp^2 domains/clusters embedded within a sp^3 matrix but it was invisible under UV irradiation [24].

Prompted by these results and in continuation of our studies herein, we report the photoluminescence (PL) and circular dichroism (CD) optical activity studies of chitosan/graphene oxide. Efforts have been made to explore the possibility of using the chitosan/graphene oxide bionanocomposite as a platform for development of optical properties for biosensor, detection of molecules and biomedical applications.

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2. Experimental details

2.1. Materials and reagents

Chitosan with a degree of deacetylation (DD) of 79% was supplied by Sigma–Aldrich Chemical Co., (USA). Graphite, 30% H_2O_2, $KMnO_4$, and glacial acetic acid were purchased from Sigma–Aldrich Co., (USA). Hydrochloric acid was obtained from Samchun Pure Chemical Co. Ltd. (South Korea). H_2SO_4 was obtained from Matsunoen Chemicals Ltd. (Osaka, Japan). Deionized water of conductivity 20 μS/cm was generated in the laboratory. All chemicals were used without further purification.

2.2. Measurement and characterization

Fourier transform infrared (FT-IR) spectra of the compounds were recorded on a Jasco FT-IR 300E (Tokyo, Japan) using an attenuated total reflectance method for films. Powder samples were mixed with KBr and pressed into a thin pellet which was used for analysis. The Raman spectra were obtained by a Raman spectroscopy, Horiba Jobin Yvon/LabRam Aramis, laser 514 nm (Ar-ion laser), power = 0.5 mW. X-ray diffraction measurements were performed using a (D/Max2500VB+/Pc, Rigaku, Japan) with a Cu Kα radiation source (wavelength λ = 0.154 nm) at a voltage of 40 kV and a current of 50 mA. The scanning rate was 3°/min and the scanning scope of 2θ was from 2° to 45°. Thermogravimetric analysis (TGA) was performed using a TA instruments Q50 thermal analyser with a nitrogen flow rate of 30 mL/min and heating rate of 10 °C/min. The surface morphology was analysed by field-emission scanning electron microscope (FE-SEM, JSM-6700F, Jeol Ltd., Japan) and high resolution transmission electron microscope (HR-TEM, JEM 3010, Jeol Ltd., Japan). UV–vis absorption spectra were measured on an Agilent 8453 spectrophotometer (USA). Circular dichroism (CD) spectra were recorded on a JASCO J-715 spectrometer in water at room temperature. Cell length was 1.0 cm. Measurements were performed with a scanning speed of 1000 nm/min at a resolution of 1.0 nm. The spectra were corrected by subtracting the background of water and three spectra were accumulated and averaged for each sample. The pH of the solutions was determined with a HM-25R pH Meter, DKK Toa Corporation (Japan). Fluorescence spectra were obtained on a Parkin-Elmer luminescence spectrometer (LS50B).

2.3. Synthesis

2.3.1. Synthesis of graphene oxide

Graphene oxide (GO) was prepared by the oxidation of graphite using a modified Hummers method [25,26]. In a 250 mL of round bottomed flask 3 g natural graphite was added to 69 mL of cold concentrated H_2SO_4 under stirring in an ice-bath. After that, 9 g $KMnO_4$ was added slowly into the flask under stirring in an ice-bath. The mixture was then stirred at 35 °C for 2 h, then 138 mL distilled water was added slowly into the mixture and it was stirred for another 15 min below 100 °C temperature. Then 420 mL of aqueous 30% H_2O_2 solution was added to the mixture. Finally, the product was filtered with 800 mL of 10% HCl aqueous solution to remove metal ions and then obtained powder was washed with distilled water. The obtained brown yellow powder of GO was dried under reduced pressure for 24 h.

2.3.2. Preparation of chitosan/graphene oxide bionanocomposite

Two hundred milligram of chitosan was dissolved into 10 mL of 1.5% aqueous acetic acid to prepare chitosan solution. The mixture was stirred continuously at room temperature for 20 h. The graphene oxide powder (0.030 g) was dispersed into 2 mL of distilled water and was treated by mild ultrasound for 30 min to forms a homogeneous solution. The graphene oxide was added in chitosan solution under stirring at 35 °C for 2 h followed by sonication for 2 h to ensure a homogeneous dispersion of chitosan/graphene oxide in solution. The mixed solution was cast on glass plate to a desired thickness and dried under atmospheric conditions at room temperature for about 36 h. We have adopted different ratio of GO in chitosan/graphene oxide films (CS/GO-0.060 and CS/GO-0.120) to obtain chitosan/graphene oxide bionanocomposite films and were carefully detached from the glass plates.

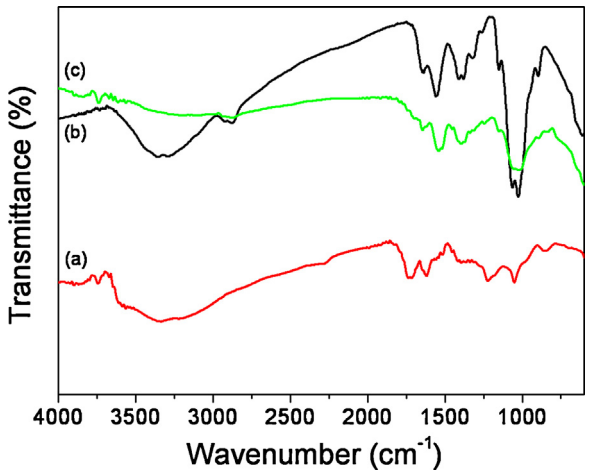

Fig. 1. FT-IR of pristine graphene oxide (a), pure chitosan (b) and chitosan/graphene oxide bionanocomposite (c).

3. Results and discussion

3.1. FT-IR spectroscopy

The FT-IR spectra of the pristine graphene oxide, pure chitosan, and chitosan/graphene oxide bionanocomposite are shown in Fig. 1a, b and c respectively. In the FT-IR spectra of pristine graphene oxide the absorption band (Fig. 1a) at 1724 cm^{-1} is characteristic of C=O stretching. The absorption peak at 1620 cm^{-1} is either assigned to the deformation of the OH band of the water absorbed by graphene oxide, or stretching of the aromatic C=C bond [27] and 846 cm^{-1} to the characteristic absorption peak of epoxy groups. The FT-IR characteristic peak of the chitosan film (Fig. 1b) is assigned to the stretching of intra and intermolecular O–H vibrations at 3411–3248 cm^{-1} overlapped with N–H stretch. 2950–2865 cm^{-1} corresponds to symmetric and asymmetric C–H vibrations. Amide I vibration band at 1640 cm^{-1} due to C–O stretch of acetyl group and amide II band at 1552 cm^{-1} due to N–H stretch have been observed. The absorption peak at 1062 cm^{-1} assigned to skeletal vibration of the bridge C–O stretch of glucosamine residue [28,29]. The characteristic absorption peak of the chitosan/graphene oxide films at 2878 cm^{-1} which can be assigned to the C–H asymmetric vibration due to chitosan incorporation. The new vibration band appeared at 1694 cm^{-1} due to the C=O stretching whereas the carboxylic group bands at 1724 and 1221 cm^{-1} of pristine graphene oxide disappeared (Fig. 1c) [30]. When graphene oxide was added with chitosan the absorption peak at 3411–3248 cm^{-1} was broadened. The FT-IR analysis of chitosan/graphene oxide clearly indicates that the graphene oxide interacts with chitosan through intermolecular hydrogen bonds, so there should be good miscibility between graphene oxide and chitosan.