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Synthesis and representation of a new structure for polypyrrole–chitosan nanocomposite and investigation of effect of intermolecular interaction

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ABSTRACT

This study describes the preparation of polypyrrole/chitosan nanocomposite (PPC) in aqueous media by chemical polymerization of pyrrole in presence of ferric chloride ($FeCl_3$) as an oxidant. The products were investigated in terms of morphology and chemical structure with scanning electron microscope (SEM), transmission electron microscope (TEM) and Fourier transform infrared (FTIR) spectroscopy, respectively. The observable experimental IR spectra were compared with the calculated spectra. In theoretical calculations, different models of polypyrrole (PPy), chitosan and PCC were established. All models geometry were optimized without any geometrical constraint by different methods and IR vibrational wavenumbers of these models were calculated using DFT-B3LYP/6-31G and they were compared with experimental FTIR spectrum. By analyzing the results, the actual configurations of PCC were found that have moderate internal hydrogen bonds (IHB).

1. Introduction

Chitosan is a naturally derived polysaccharide-based polymer, moderately inexpensive, nonconducting, electro-active material with excellent biocompatibility. It has received wide attention due to a wide range of biomedical applications [1–3]. Also, Chitosan composite materials have attracted much research interest in bone tissue engineering due to their minimal foreign body reactions, intrinsic antibacterial nature, biocompatibility, biodegradability, and ability to be molded into various geometries and forms [4,5]. Moreover, chitosan has antiacid and antiulcer characteristics, which prevents or weakens drug irritation in the stomach [6]. Its modified analogs have shown many applications biomaterials, cosmetics, agriculture, biochemical separation systems and drug controlled release systems. It has received wide attention due to a wide range of biomedical applications [7–9].

Conducting electroactive polymers such as polypyrrole is complex dynamic structures that captivate the imagination of those involved in intelligent materials research. PPy stands out for its high conductivity and high stability in air [10,11]. The diversity in the synthesis of polypyrrole now enables a range of bioactive surfaces to be created. For example, the incorporation of proteins such as enzymes or antibodies is readily achieved. Combined with the chemical tuning available, this should be applicable to the development of biocompatible surfaces or new surfaces for biotechnology processing applications [10,12,13]. Recently, blends consisting of a conducting and bio-polymers have received attention because possessing appreciable defluoridation capacities, which will be of eco-friendly in nature and to investigate their potential for the removal of fluoride ions from water [14,15]. In addition, by adding PPy component, the resultant PCC will be endowed with new conducting functions. However, up to now, little is known about PCC. It is thus worthy of investigating this new type of conducting composites for possible applications [16]. The design and fabrication of PCC with particular morphology and prediction structure of composite are still a big challenge. Herein, the strategy we develop within this study leads to a new kind of composite hydrogel [17].

To the best of author's knowledge, there are no theoretical study reports on PCC molecular structures or interaction between chitosan and polypyrrole composite in literatures. Therefore, it is

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worthwhile to computationally obtain information about the structure and physicochemical properties of these compounds.

In this article, PCC was prepared in aqueous solution by chemical oxidation and product was investigated in terms of morphology and chemical structure. In the second part, models of PPy, chitosan and a new stable structure of PCC were theoretically investigated. At first all models geometries were optimized at PM3, AM1, HF and DFT levels for finding the most stable geometries, and then IR vibrational wavenumbers were calculated just for DFT-B3LYP/6-31G optimized geometries, finally the calculated IR frequencies were compared with experimental IR spectrum.

2. Experimental details

2.1. Materials and standard solutions

Pyrrole (Py) monomer (%), iron (III) chloride ($FeCl_3$), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were phurchased from Merck, Germany. Chitosan (CTN, $C_{12}H_{24}N_2O_9$) with a degree of deacetylation of 75% was phurchased from Sigma–Aldrich, USA. Pyrrole monomer was purified by simple distillation and stored in refrigerator prior to use. All chemicals were of reagent grade.

2.2. Characterization

In this study, a scanning electron microscope (model XL30) was used to characterize the surface of PCC at very high magnification at an accelerating voltage of 15 kV. Samples were coated with gold and palladium by a sputter coater with conductive materials to improve the quality of micrograph.

The image of transmission electron microscope was obtained with a Zeiss – EM10C. Acceleration voltage for TEM was 80 kV. In the sample preparation of TEM characterizations, small amount of the sample powder was dispersed in an ethanol and was sonicated for 20 minutes. A small drop of this solution was dropped on a Carbon coated copper grid Mesh 300 and was used for TEM characterization.

Studies on the interaction between the polymer and the chitosan particles have been investigated by Fourier Transform Infrared spectrometer (Shimadzu model 4100, Japan). Spectra were collected with a spectrometer using KBr pellets. The ratio of the sample to KBr was 1:100. In each case, 1.0 mg of dried sample and 100 mg of KBr are homogenized using mortar and pestle thereafter pressed into a transparent tablet at 200 kg_f/cm^2 for 5 min. The pellets are analyzed with a FTIR Spectrometer in the transmittance (%) mode with a scan resolution of 4 cm^{-1} and 64 scans by spectrum, over the 4000–400 cm^{-1} region.

2.3. Preparation of PPy/CS nanocomposite

PCC was prepared by the chemical polymerization of pyrrole in the presence of a chitosan in HCl aqueous solution. In a typical experiment, 0.5 g chitosan was added to 100 mL of HCl (1 M) and then uniform solution was resulted by using magnetic mixer. The prepared chitosan solution was mixed with 5 g of $FeCl_3$ and 1 mL fresh distilled pyrrole. The reaction was carried out for 5 h at room temperature. Consequently, the product was filtered and to separate the impurities, product was washed several times with deionized water and dried at temperature about 60 °C in oven for 24 h.

3. Computational details

All calculations were carried out using GAMESS-US version May 1, 2013 (R1) software code [18]. For modeling polypyrrole, Chitosan and interactions of both polymers in water, PM3, AM1, Hartree–Fock and Density functional theory (DFT) methods using the Becke's three parameters hybrid exchange functional, in combination with the correlation functional of Lee, Yang and Parr (B3LYP) were used. At first all model's structures were optimized without any geometrical constraint then the vibrational (IR) spectra were just calculated for the DFT optimized structures at the same level of theory.

The calculations were performed by using the standard 6-31G basis sets for all atoms. The solvent effect was simulated using the solvation model density (SMD) [19,20].

For building structures and visualizing all models, Gabedit v2.4.0, Jmol v13.0.16 and wxMacMolPlt v7.4.4 were used [21–23].

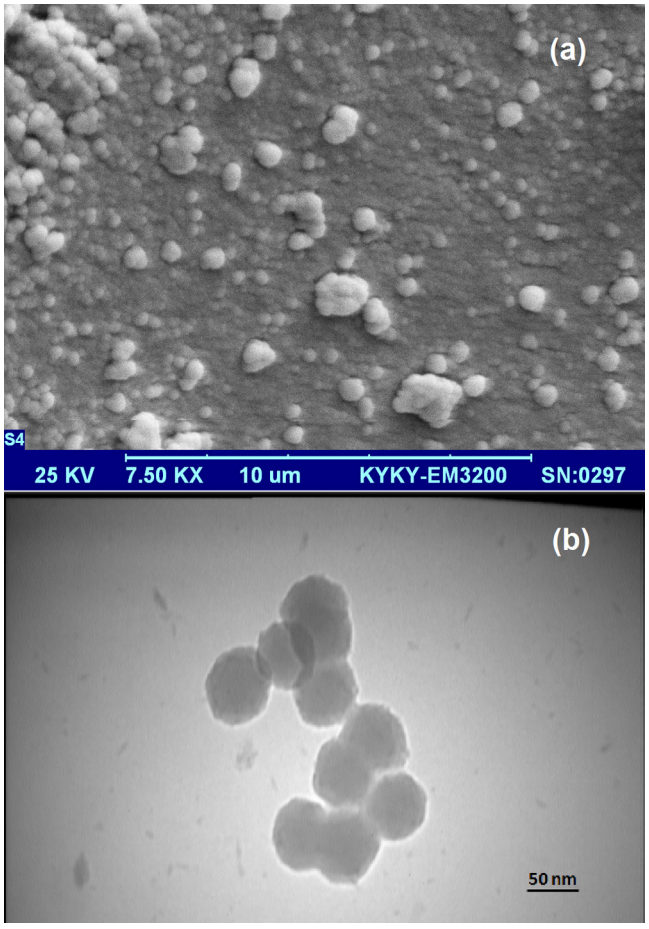

Fig. 1. (a) SEM and (b) TEM image of polypyrrole/chitosan nanocomposite.

4. Results and discussion

4.1. Morphology

Fig. 1(a–b) shows typical SEM and TEM images of PCC core–shell nanospheres. The SEM image in Fig. 1(a) reveals that the resulting product is composed of a large number of spherical PPy nanoparticles that were successfully covered with a thin layer of chitosan. TEM image in Fig. 1(b) shows well defined particles which contained the light contrast chitosan shell and the dark contrast PPy core. Through TEM observation it can be confirmed that the 50 ± 5 nm PPy nanosphere was covered with very thin chitosan shell while the mean thickness of the chitosan shell is 10 ± 1 nm.