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Synthesis of hybrid chitosan/calcium aluminosilicate using a sol-gel method for optical applications

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ABSTRACT

Hybrid chitosan (CS)/calcium aluminosilicate nanocomposites thin films and membranes were prepared using a sol–gel method with three different concentrations of Al_2O_3 (5, 7 and 10 mol. %). The prepared nanocomposites were characterized by transmission electron microscopy, X-ray diffraction and Fourier Transform Infrared spectroscopy. The optical properties of the prepared samples were analyzed by UV/Vis spectrophotometry and photoluminescence (PL) spectroscopy. The optical parameters revealed an increase in both the refractive index and band gap of the nanocomposites with increasing Al concentration. In addition, the PL spectra revealed a blue shift that was consistent with an increase in the optical band gap. These results suggest that CS/calcium aluminosilicate in two different forms can be a good candidate for optical sensors applications.

1. Introduction

One of the major challenges in designing organic-inorganic nanocomposites is the ability to control the size and morphology of the nanoparticles as well as achieving a homogeneous distribution throughout the polymer matrix. The sol-gel process is considered one of the most practical methods for preparing chemically homogeneous coatings, membranes, ceramics, and powders with a variety of useful applications, such as coating materials, adsorbents, catalysts, and sensors [1–3].

The sol–gel method has several advantages over traditional synthesis methods, including the wide range of compositions achievable, lower processing temperature, easier composition control, and better chemical homogeneity of the product [4,5]. Therefore, nanocomposites obtained via sol-gel processes and synthesized from organic polymers and inorganic nanoparticles are a new class of nano-materials that exhibit novel performance compared to their nano- or micro-particle counterparts [6,7].

The incorporation of silica-based nanoparticles in a chitosan matrix through a sol-gel process has been carried out either through the polymerization of chitosan in the presence of silicic acid or with a solution of the polymeric matrix or polymerizable monomer solution [8–10]. Chitosan is a natural polymer derivative of chitin, which is found in the shells of crustaceans, such as shrimps, lobsters, prawns, and crabs. Chitosan has many distinctive physic-chemical, biomedical, biosensor, pharmaceutical, textile, wastewater-treatable, and biological properties, such as excellent biocompatibility, non-toxicity, good water permeability, high mechanical strength, biodegradability, and susceptibility to chemical modification due to the presence of reactive hydroxyl and amino functional groups [11].

In this study, a combination of chitosan with calcium aluminosilicate nanoparticles was prepared using a sol–gel method in membrane and thin film form with three different Al_2O_3 concentrations (5, 7 and 10 mol. %) to enhance the morphology and optical properties for optical applications. The samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectrophotometry (FT-IR), and transmission electron microscopy (TEM). The optical properties were measured using both UV/Vis spectrophotometry and photoluminescence (PL). Moreover, the optical

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parameters, such as the refractive index and band gap, were calculated.

2. Experimental work

2.1. Preparation of hybrid CS/calcium aluminosilicate membranes and thin films

Chitosan with 80% deacetylation was purchased from Sigma–Aldrich. Tetraethylorthosilicate ($Si(C_2H_5O)_4$, TEOS, 99.999%), acetic acid (A.A), hydrochloric acid, ethanol absolute, calcium nitrate ($Ca(NO_3)_2{\cdot}4H_2O$), and aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$) were used as the starting materials (Sigma–Aldrich). Distilled water was used in all preparation procedures. All chemicals and reagents are of analytical grade and used as received.

Inorganic calcium silicate, Ca_2SiO_4 sol doped with three different concentrations of Al_2O_3 (5, 7 and 10 mol. %) by mixing SiO_2, CaO, Al_2O_3, and HCl with continuous magnetic stirring at 60 °C for 3 h, as a modifier as described elsewhere [19]. Chitosan (1.5 g) was dissolved in a 2% acetic acid solution with continuous magnetic stirring at room temperature for 8 h to form a viscous and pale yellow solution. After 12 h, the calcium silicate sol was mixed with the chitosan system. The three mixtures initially composed of two phases were made uniform by stirring vigorously until the inorganic domains were distributed evenly in the aqueous solution while the hydrolysis reaction took place. After stirring for 5 h at 40 °C, the above mixed solutions were aging for one night before casing in petri dishes to allow the formation of homogeneous membranes by keeping them at room temperature in a clean room until all films had dried. Finally, the dried CS/calcium aluminosilicate membranes were baked at 80 °C for 2 h in air. The CS/calcium aluminosilicate thin films were obtained by dipping glass substrates (2 cm × 4 cm) in CS/calcium aluminosilicate solutions. The same solutions were used to prepare the membranes. After dip-coating, the coated substrates were dried in air at 40 °C for 30 min and then heat-treated at 60 °C and 80 °C for 12 h in air, as shown schematically in Fig. 1.

2.2. Instruments

The nanostructure of the silica monolith was examined by TEM (JEM-1230) measurements. The XRD (Bruker D8 Advance) patterns were obtained using CuK_α radiation ($\lambda = 1.540$ Å) operating at 40 kV and 40 mA. The scans were performed with a detector step size of 0.02° over an angular range of 2θ starting from 10 to 80°. The chemistry of the hybrids was analyzed using a FT-IR spectrometer (Nicolet Magma 550 series II, Midac, USA) at wavelengths ranging from 4000 to 400 cm^{-1}. The optical absorption/transmission spectra were measured on a Jasco V-570 spectrophotometer over the wavelength range, 0.2–2.5 μm. The PL emission spectra were obtained at room temperature using the 280 nm line from a 150 W Xeon arc lamp as the excitation source. The light emitted by the sample was analyzed using a Jasco FP-6500 spectrofluorometer over the wavelength range, 300–550 nm. Both the excitation and emission monochromatic slit widths were 5 μm.

3. Results and discussion

3.1. Transmission electron microscopy

Fig. 2 shows TEM images of calcium silicate nanoparticles doped with three different concentrations of Al_2O_3 (5, 7 and 10 mol. %), embedded in a chitosan matrix and dried at 60 °C for 12 h. The images confirmed the synthesis of a nano-organization of the organic–inorganic network due to the confinement brought about by the cross linking reaction between the inorganic species and the organic system. As shown, the particles were relatively aggregated and distributed widely, particularly at higher concentrations of Al_2O_3 embedded in the chitosan nanocomposites for the thin films and membranes. Fig. 2(a, d) shows the dispersion of calcium silicate doped with 5 mol. % Al_2O_3 dispersed in the chitosan polymeric matrix. The nanoparticles were not well dispersed because some agglomerates can be observed clearly, confirming the dense microstructure of a representative particle of the starting multi-phase calcium aluminosilicate nanocomposites. With increasing Al_2O_3 content (7 and 10 mol. %) in the nanocomposites, spherical nanoparticles were dispersed homogeneously in all samples with slight aggregation, as shown in Fig. 2(b), (c), (e) and (f). The spherical nanoparticle size was in the range, 5–55 nm in diameter. TEM confirmed that the CS/calcium aluminosilicate nanocomposites in its different forms (membranes and thin films) were synthesized successfully and cross-linked within the chitosan matrix.

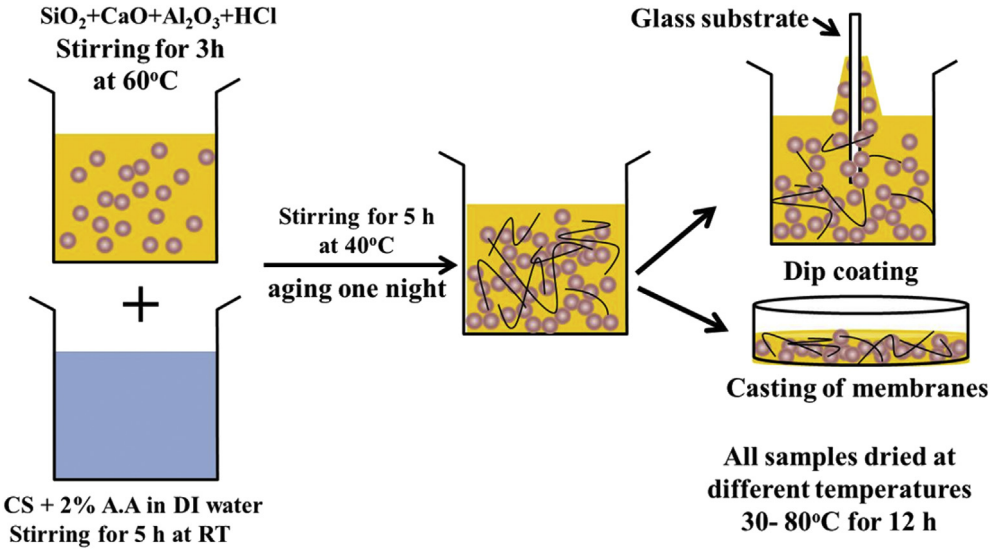

Fig. 1. Schematic diagram of the synthesis process of the hybrid CS/calcium aluminosilicate nanoparticles in thin films and membranes forms.