



A facile co-gelation sol gel route to synthesize CaO: P₂O₅: SiO₂ xerogel embedded in chitosan nanocomposite for bio-applications

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Abstract : Calcium phosphosilicate xerogel (CPSX) (35 CaO: 57 SiO₂: 7 P₂O₅) as a bio-glass and (CPSX)/chitosan (CS) nanocomposite were successfully prepared by a simple and effective sol gel method. (CPSX) was firstly synthesized in acidic condition then mixed with CS solution and the resulting nanocomposite was fabricated. The synthesized samples were characterized by X-ray diffraction, Transmission and Scanning Electron Microscopy and Fourier Transform Infrared Spectroscopy. XRD patterns of the synthesized samples exhibit calcium phosphosilicate nano-structure phase embedded in the chitosan matrix. TEM and SEM images indicate the presence of (CPS) nanoparticles of nearly spherical shape with nano-sizes inside the (CS) matrix. Regarding the textural properties, it was observed progressive change in the surface for (CPSX) characteristics after embedded in (CS) matrix. The obtained results were recommending the use of these samples for bio-applications, where the particle size control and morphology control are required.

Keywords: *Sol gel process, Calcium phosphosilicate xerogel, chitosan polymer, Biomaterials.*

1. Introduction

The control on the hydrolysis of metal alkoxides as (TEOS, TEP, TIB,...etc) in the presence of organic groups or inorganic particles additives that is, the sol gel process is producing new materials for different applications^{1,2,3}. The sol-gel process offers a very simple chemical method for the preparation of different types of advanced materials such as films, ceramics, powder and nanoparticles/ polymers^{4,5,6,7}. The calcium phosphosilicate xerogel is formed via the hydrolysis and poly-condensation of silicon and phosphate alkoxides as reported in the previous work^{3,4}. The sol gel chemical reactions occur at room temperature in organic solvents as ethanol or methanol so that organic molecules can be mixed with the starting solutions to give hybrid organic-inorganic composites. Stability, polarity, high surface area, high purity and particle size should be considered in the synthesis of nanoscale structure of biomaterials^{8,9}. Since Hench et al. in 1970s first introduced the idea of bonding bone with prepared materials based on the chemical reactions that take place when a bioactive glass (BG) is implanted into the living body (Bioactivity is a phenomenon whereby a hydroxy-carbonated apatite (HCA) layer, similar to the mineral phase of bone, forms on the bioglass surface), the bioactive glasses have attracted much interest as new biomaterials^{8,9,10}. Glasses in the SiO₂-CaO-P₂O₅ system are classified as bioactive glasses, because their similar to the human bone structure and able to bond well to both hard and soft tissues^{8,9,10}. Sol gel bio-glasses have a higher reactive surface, high surface area allowing a better cross-linking with different types of materials^{4,12}. Meanwhile, surface modification of bio-molecules with nanoscale particles can vastly improve their performance in biomedical applications^{14,15,16}.

Chitosan is one of the most abundant polysaccharides natural polymer present in skeletal for crustaceans cuticles of insects, and cell walls of various fungi, and prepared by N-deacetylation of chitin. Chitosan is biodegradable, biocompatible non toxic and exhibits bioadhesive characteristics^{17,18,19}.

The aim of this research was focused on the sol–gel calcium phosphosilicate xerogel (35 CaO: 57 SiO₂: 7 P₂O₅, in mol %) as a bioactive glasses and embedded in chitoan matrix synthesis, structural characterization of these samples. The organic–inorganic polymer containing was prepared by sol–gel technology via the reaction of (TEOS), (TEP) and calcium nitrate with an acidic catalyst (HNO₃). The dried calcium phosphosilicate xerogel and CPSX/CS were characterized with X-ray diffraction, Transmission and Scanning Electron Microscopy and Fourier Transform Infrared Spectroscopy.

2. Experimental procedure

2.1. 1. Bioactive glass preparation

The studied calcium phosphosilicate sample with the formula (35 CaO: 57 SiO₂: 7 P₂O₅, in mol %) was prepared by simple sol–gel process from solutions of Si(OC₂H₅)₄ (TEOS), (C₂H₅O)₃PO (TEP), HNO₃ and Ca(NO₃)₂·4H₂O in acidic conditions starting materials of analytical purity grade. Each precursor was mixed with the appropriate solvent (distilled water and/or ethanol) then the mixture was stirred for about 3h and the pH of the obtained solution was ≈ 3. The obtained solution was stirred another 1h at 40°C.

2.1.2. Preparation of chitoan/CPSX nanocomposite

Chitosan (1.5 g) (80% was purchased from Sigma-Aldrich) was dissolved in a 1% acetic acid solution with continuous magnetic stirring at room temperature for 10 h to form a viscous and pale yellow solution. Then, the calcium phosphosilicate xerogel was mixed (10 ml) diethylamine then embedded through the chitosan system under vigorous stirring for 3h. The produced solution was dried at 60°C for one week to allow the formation of homogeneous nanocomposite. The XRD (Bruker D8 Advance) patterns were obtained using CuKα radiation (λ=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°. A photographic plate of the transmission electron microscopy (TEM type JEOL JEM-1230 operating at 120 kV attached to a CCD camera) employed in the present work to investigate the nano-structure of the prepared samples. The morphological feature was measured using scanning electron microscopy (SEM) (Quanta, FEG 250). The chemistry of the xerogel and nanocomposite were analyzed using a FT-IR spectrometer (Nicolet Magma 550 series II, Midac, USA) at wavelengths ranging from 2000 to 400 cm⁻¹.

3. Results and discussion

3.1. X-ray diffraction

According to X-ray patterns presented in Fig. 1 (a, b) for sol gel calcium phosphosilicate xerogel(CPSX) and (CPSX) embedded in chitosan matrix ((CPSX)/CS), the obtained (CPSX) sample exhibit an amorphous behavior with the characteristic hump for silica gel between 2θ 17° to 28° as shown in Fig.1(a). After embedded the (CPSX) in chitosan matrix, the nanocomposite sample present some peaks at 2θ= 11.2°, 16.7°, 20.3°, 28.2° and 37.4° for orthorhombic chitosan (C₆H₁₁NO₄)_x according to JCPDS card no. (39-1894), that in cross-linkage with (CPSX) at the same planes according to JCPDS card no. (21-0157) orthorhombic calcium phosphosilicate (Ca₃P₂SiO₁₂), as shown in Fig. 1(b)^{3,20}. The embedded (CPSX) was interfered with the chitosan chains through the polymerization, thus enhancing the crystalline domain of (CPSX)/chitosan nanocomposite.

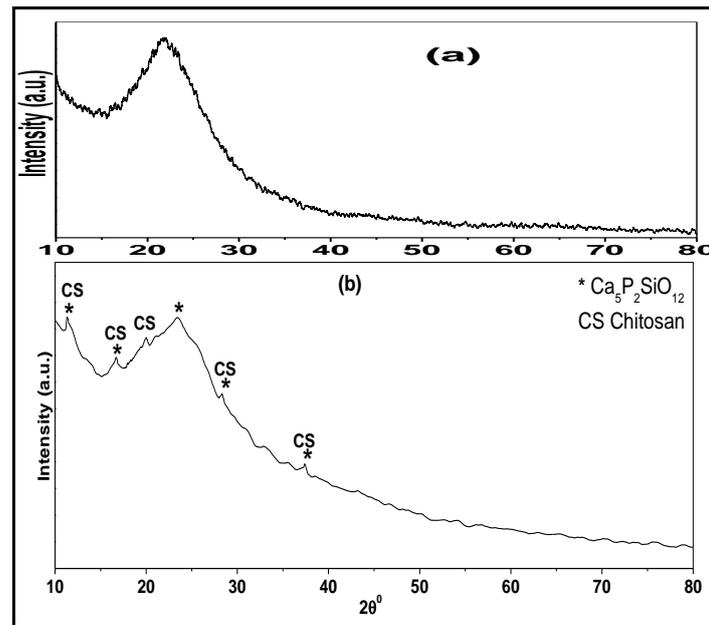


Fig. 1. (a) XRD spectrum of (CPS) xerogel (b) XRD spectrum of (CPSX)/CS nanocomposite.

3.2. Transmission electron microscopy

The size and shape of the prepared (CPSX) and (CPSX)/CS nanocomposite were analyzed by TEM analysis. Fig. 2 shows the TEM analysis for sol gel (CPSX) and embedded in chitosan matrix to form the (CPSX)/CS nanocomposite. The prepared (CPSX) was nearly spherical in shape with particle size 11 nm as shown in Fig. 2(a). For the synthesized (CPSX)/CS nanocomposite the particle size is 15 nm and the (CPSX) nanoparticles were well distributed in the synthesized nanocomposite as in Fig. 2(b).

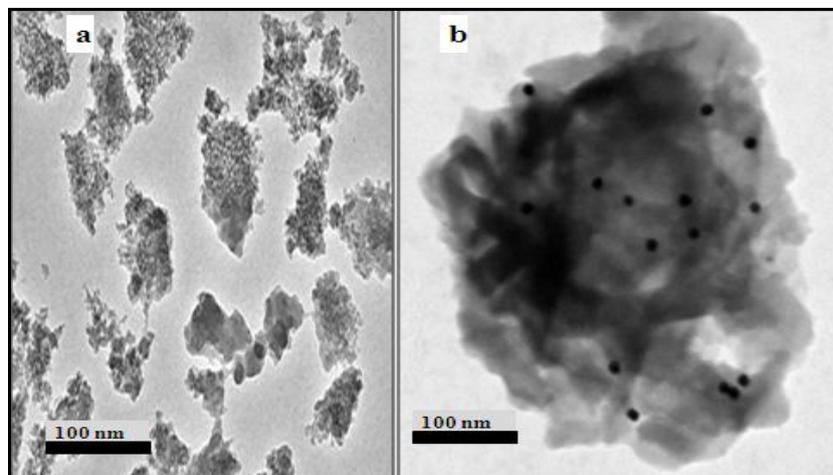


Fig. 2. (a) TEM image of sol gel (CPS) xerogel (b) TEM image of (CPSX)/CS nanocomposite.

3.3 Scanning electron microscopy

Fig.3 shows the SEM images for (CPSX) and (CPSX)/CS nanocomposite prepared using sol gel process. SEM examination Fig. 1 (a) confirmed the prepared calcium phosphosilicate xerogel to be composed of highly porous regular network. After embedded the (CPSX) in chitosan matrix, the nanocomposite appeared open, forming an irregular branched network morphology consisting of dense grains surrounded by less dense material. Individual grains could be easily seen by SEM instrument, suggesting the synthesized samples were typically in nano-size as shown in Fig. 3(b).

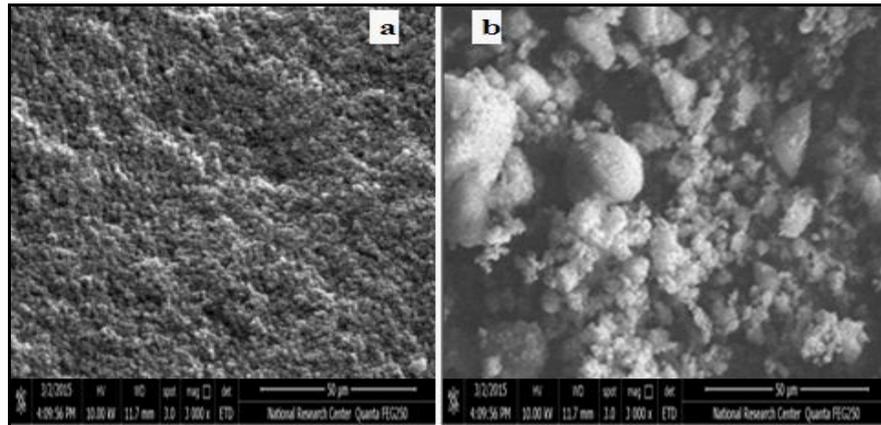


Fig. 3. (a) SEM image of (CPS) xerogel (b) SEM image of (CPSX)/CS nanocomposite.

3.4. FT-IR characterization

The Ca phosphosilicate xerogel system formed in the first step of a sol-gel preparation method contain silica network connected by Si–O–Si bonds linked with phosphate network in Si–O–P bonds and dissociated Ca^{2+} and nitrate ions. The room temperature FTIR transmittance spectra of calcium phosphosilicate xerogel (CPSX) and (CPSX)/CS nanocomposite were recorded in the range, 2000–400 cm^{-1} . The FTIR spectrum of (CPSX) free sample is dominated by a strong, large band positioned at 1090 cm^{-1} which contains contribution from Si–O– linkages with silicate and phosphate tetrahedral units, P–O and P–O–Ca stretching vibrational mode of calcium phosphosilicate phase and P–O asymmetric stretching vibration of the orthophosphate units^{21,22,23}. The absorption band at 1637 cm^{-1} is assigned to the bending vibration of adsorbed water molecules and shifted to higher wavenumber after embedded the (CPSX) in chitosan matrix^{24,25}. The band at 960 cm^{-1} that shift to lower wavenumber after embedded the (CPSX) in chitosan matrix is assigned to stretching vibration of P–O linkages from PO_4^{4-} units, Si–O– stretching in silica tetrahedral units with three non-bridging oxygen (NBO) atoms and Si–OH vibrations signal^{26,27,28}. The absorption band at 797 cm^{-1} is attributed to bending vibrations of Si–O–Si, Si–O–P and Si–O–Ca bridges^{24,24}. The appearance of double peaks at 625 cm^{-1} and 656 cm^{-1} are due to the P–O bending vibration in PO_4^{4-} tetrahedra and is characteristic for crystalline phosphate system^{23,24,25,26,27,28,29}. The band at 462 cm^{-1} is assigned to rocking vibration of Si–O–Si bridges^{3,4,29}. Main changes for the synthesized samples are reflected in the FTIR spectra in the range from 797 to 1245 cm^{-1} .

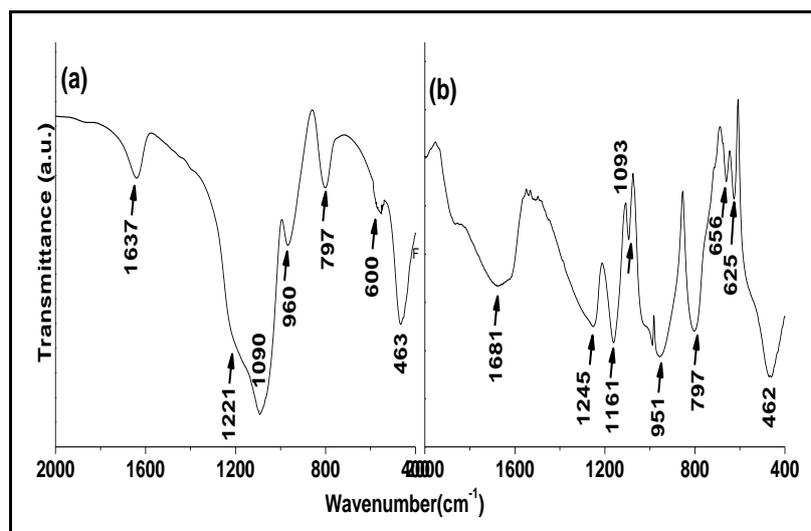


Fig. 4. (a) FTIR spectrum of (CPS) xerogel (b) FTIR spectrum of (CPSX)/CS nanocomposite

4. Conclusions

SiO₂- based containing (35 CaO: 57 SiO₂: 7 P₂O₅) xerogel sample was synthesized by sol-gel method. The sol-gel process is successfully synthesized (CPSX) as bio-glass and (CPSX)/CS nanocomposite. In fact, the presence of the Si-O-Si, Si-O-P, P-O-P and Si-O-Ca bonds was evidenced by FTIR. The results obtained after embedded (CPSX) in chitosan matrix revealed the positive role of bioactive glass and its nanocomposite. We succeeded to produce the attractive calcium phosphosilicate as a bio-glass and embedded chitosan matrix, which can be further used in various medical fields such as drug delivery and biosensors.

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