Synthesis of Hydroxyapatite-Bioglass Nanocomposite Using Modified Sol-Gel Method

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Abstract

The aim of this study is comparing preparation methods of hydroxyapatite-bioglass composite nanopowders which can be prepared in different routes based on sol-gel method for orthopaedic/dental applications. Nanostructure materials present a unique and incomparable character for orthopedic and dental implant. Hydroxyapatite-bioglass composite nanopowders with the same contents of bioglass (20%) as reinforcement have been prepared by using a sol-gel method in four routes: mixing sols before aging time, mixing bioglass sol with hydroxyapatite gel after gelation, mixing calcinated bioglass nanopowder with hydroxyapatite sol, and mixing two calcinated powders by mechanical alloying. Bioactive glass of the type CaO-P_2O_5-SiO_2 was obtained by the source of tetraethylorthosilicate, triethylphosphate and calcium nitrate tetrahydrate. On the other hand, phosphoric pentoxide and also calcium nitrate tetrahydrate were applied as the source of hydroxyapatite. Calcination temperature was 600°C for both compositions. XRD, SEM, and EDS techniques were used to investigate the microstructure and morphology of the nanopowders. Results indicated that because of different mixing time of hydroxyapatite with bioglass in either sol form, gel form or calcinated powder, the morphology, crystallinity, crystallite size and composition of products were varied. bioglass remained amorphous in all routes of synthesis. Because of presence of amorphous bioglass, In situ synthesis of hydroxyapatite-bioglass composite nanopowders resulted in decreasing the crystallinity and the crystallite size of hydroxyapatite. Furthermore, by mixing two nanopowders after calcination, hydroxyapatite crystallinity was maximum and also by using this route proportion of two parts can be easily controlled.

Keywords: Hydroxyapatite, Bioglass, Composite, Nanopowder, Sol-Gel

1. Introduction

Due to its great biocompatibility and similarity to the human bones and teeth chemical composition and structure, hydroxyapatite [HA, $Ca_{10}(PO_4)_6(OH)_2$] has a wide application in biologic system such as dentistry, medicine, orthopaedic and bone implants[1-3]. Although this bio ceramic has so many benefits, because of low mechanical properties, relatively long time for remodeling and slow rate of osseointegration, applications are limited[2]. To improve hydroxyapatite bioactivity and mechanical properties, bioglass has been incorporated [4]. Glasses based on the SiO_2–CaO–P_2O_5 system constitute a significant group of biomaterials which has so many applications in medicine as bone implants[5].It is worth mentioning that introduction of silicate ions into the HA structure enhances its in vivo bioactivity and the formation of a poorly crystalline surface apatite layer of HA after immersing in simulated body fluids[2]. Due to large amount of grain boundaries and large surface area to volume ratio, it has been found that nanostructured materials increase mechanical reliability osteoblast adhesion, proliferation, mineralization and bioactivity, more than coarser crystals[6-8].

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Osteo-conductivity, solubility, sinterability and mechanical properties of hydroxyapatite can be improved by obtaining particle size in nanoscale[9,10].Recently, the sol–gel process as a wet chemical method has been widely applied because of its advantages such as low process temperature, not depending on high PH values and its ability to control crystallite size[11].

The aim of this study was to compare and characterise preparation methods of hydroxyapatite-bioglass composite nanopowders which can be prepared in different routes based on the sol-gel method for orthopaedic/dental applications.

2. Materials and Methods

HA sols were prepared by mixing dissolved phosphoric pentoxide (P_2O_5), and calcium nitrate tetrahydrate [$Ca(NO_3)_2.4H_2O$] in alcoholic media (C_2H_5OH). The composition of studied bioactive glass belongs to the system CaO–SiO_2–P_2O_5 with 57.44% CaO, 35.42% SiO_2 and 7.15%P_2O_5 in molar percentages. Tetraethylortho-silicate (TEOS, $C_8H_{20}O_4Si$), triethylphosphate (TEP) and calcium nitrate tetrahydrate were selected as bioglass precursors for the sols, and prepared in alcoholic media using distilled water, and hydrochloric acid as the catalyst. The sol–gel processes for four different

preparation routes of composite nanopowders are shown in Fig. 1.:
a) Mixing sols before aging time, b) Mixing bioglass sol with hydroxyapatite gel after gelation, c) Mixing calcinated bioglass nanopowder with hydroxyapatite sol, and d) Mixing two calcinated powders by mechanical alloying. The samples were numbered as it's shown in Table. 1.

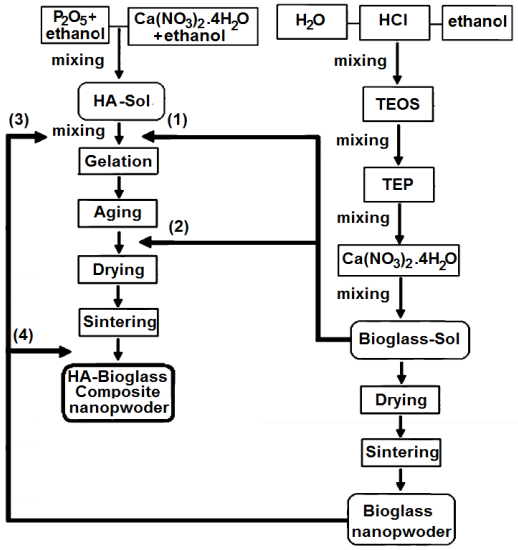

Fig. 1. Sol–gel processes for preparation of composite nanopowders in four routes.

The phase composition and crystallinity of nanopowders were analyzed by X-ray diffraction (XRD, Philips X'Pert; Philips, Amsterdam, The Netherlands) using Cu Ka radiations (λ=0.15406 nm, radiation at 40 kV and 30 mA) over the 2h range of 20–70u.The obtained patterns were compared with the standard patterns of Joint Committee on Powder Diffraction and Standards [12]. The fractions of crystalline phase Xc of HA in each sample were evaluated using the following equation [13].

$$XC = 1 - \frac{V112/300}{I300} \quad (1)$$

Where I300 is the intensity of (3 0 0) diffraction peak and V112/300 is the intensity of the hollow between (1 1 2) and (3 0 0) diffraction peaks of HA phase. Hydroxyapatite crystallite size in composite nanopowders was determined using the Scherrer's equation [13].

$$\beta = \frac{k\lambda}{t\cos\theta} \quad (2)$$

Where b is the width of peak at the half of its height (rad) calculated by SigmaPlot software, λ is the wavelength of monochromatic X-ray beam (λ=0.15406 nm), θ is the Bragg angle (˚), k is a constant (K=0.9) and t is the apparent crystallite size (nm). The diffraction peak at 2θ=26.04˚ was chosen for calculation of the crystallite size because it was sharper and isolated from others. This peak assigns to (002) Miller's plane family and shows the crystal growth along the c-axis of the HA crystalline structure [14].
Scanning electron microscopy (SEM, Phillips XL30-30KV) technique was used to study the microstructure and morphology of the composite nanopowders. Furthermore, using energy dispersive X-ray analysis (EDS) system, the presence of chemical species in each nanopowder sample was determined.

3. Results and Discussion

Fig. 2. shows the XRD patterns for S1, S2, S3 and S4 nanopowder samples mentioned in the Table. 1.

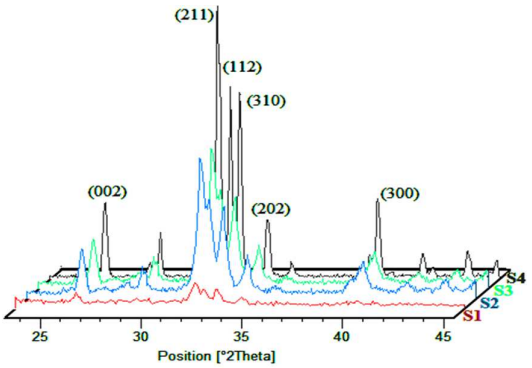

Fig. 2. XRD patterns of hydroxyapatite nanopowder and composite nanopowders.

Because bioglass is amorphous, no bioglass peak was observed in the XRD patterns. However presence of bioglass has influenced on peak sharpness in S1, S2 and S3 samples. It shows that In situ synthesis of HA-bioglass composite nanopowders has resulted in decreasing the crystallite size of hydroxyapatite. By determining the crystallinity of powders using equation (1) it was obviously realized that in these three samples, crystallinity has been decreased, but there is no significant difference between pure HA [15] and the S4 sample. The crystallinity and crystallite size of HA in composite nanopowders are given in the Table. 1. Bioglass composition including silica phase can easily release SiO_2 in the hydroxyapatite sols. The HA sols including bioglass (in situ synthesis: S1, S2, S3) resulted in lower crystallite size than pure HA. In fact, the silica phase acts as a barrier to crystallization for HA phase by limiting atomic arrangement [16]. It's been indicated that the presence of silica in the composite sols reduces the HA crystallite growth [17].
Fig. 3. shows the SEM micrograph and EDS analysis of composite nanopowders. As it can be seen, the

micrograph of S1 is different from others. In other routes of synthesis the HA gel or nanopowder had been formed before mixing, but mixing sols for S1 has been led to coarse agglomerates. Moreover because of presence of calcium in bioglass sol, the ratio of Ca/P in HA gel increased. Size of agglomerates in S4 sample is bigger than other samples. It appears that this sample consists of spherical and very fine particles formed in mechanical alloying process, which tend to agglomerate.

Table. 1. The crystallinity and crystallite size of HA.

Sample	Crystallite size (nm)	Crystallinity
S1: Mixed sols before aging	27.8	0.65
S2: Bioglass sol + HA gel	55.3	0.66
S3: Bioglass powder + HA sol	53.7	0.66
S4: Mixed powders	58.2	0.70

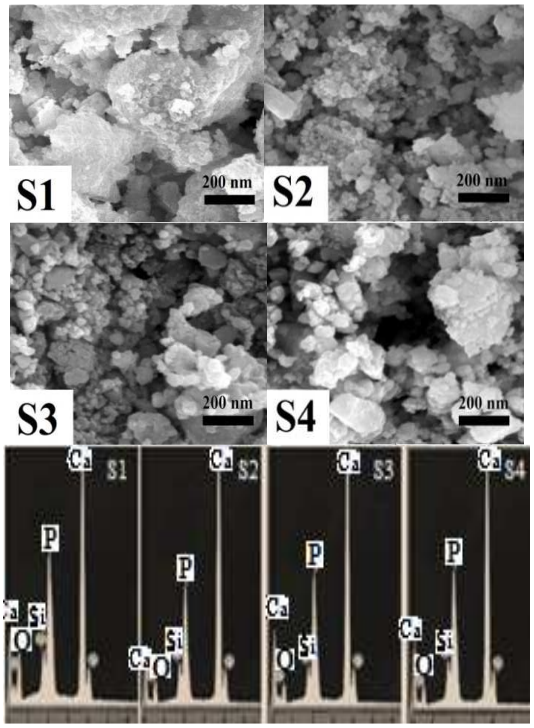

Fig. 3. SEM micrograph and EDS analysis of S1, S2, S3 and S4. EDS analysis for all samples were approximately the same.

4. Conclusions

1-In situ synthesis routes including S1, S2, S3 samples led to lower crystallinity and crystallite size of HA.

2. With mixing calcinated powders by mechanical alloying (S4) appeared to form spherical and fine particles with high tendency to agglomerate, the crystallinity of this composite was maximum.

3. The S3 sample route was chosen as the best route for composite nanopowder synthesis.

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