Effects of solvents on properties of nanocrystalline hydroxyapatite produced from hydrothermal process

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Abstract

Hydroxyapatite (HA) particles have been synthesised in isopropanol–water solvent via hydrothermal process. The influences of isopropanol on crystallisation, such as phase evolution, crystallite size, crystallinity degree, chemical composition, and agglomeration of the HA nanoparticles have been investigated by using XRD, FTIR, TEM, BET, TG-DSC and laser diffraction method. All HA nanoparticles prepared in the water–isopropanol mixed solvent have been found to be carbonated HA, and the amount of carbonate increased with increase of alcohol in the solvent. However, the crystallite size and crystallinity degree of the HA nanoparticles decreased with the addition of isopropanol. In addition, there was little change in morphology of HA particles produced in different solvents, though the aspect ratio of the HA increased slightly with increasing concentration of alcohol. The agglomeration was found to be mainly controlled by the zeta-potential and not by the change of solvent.
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1. Introduction

Synthesis of hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2$, HA) is of great importance for various industrial purposes, such as medicine, biology and fertilizer production.[1] So far, several techniques have been used for preparation of HA powder, which can be divided into two major routes: wet methods and solid-state reaction. The wet methods include co-precipitation,[2–4] hydrothermal process,[5–7] sol–gel synthesis,[8] mechanochemical method,[9,10] post-reaction refinement by emulsion.[11–13] Depending on the technique, materials with various morphologies, composition, and crystallinity degree have been obtained, which will essentially affect the bioactivity, mechanical properties and dissolution behavior in biological environment.[14,15] Therefore, it is becoming important to develop HA synthesis methods with precise control of particle size, morphology, crystallinity degree and chemical composition.

Hydrothermal process has been used to produce crystalline materials from solutions or sols into the desired crystalline phases at elevated temperature and pressure, typically at <350 °C and <150 atm. Particle size and morphology of products from hydrothermal process can be controlled by experimental conditions that regulate nucleation, growth and aging processes.[16] Nanocrystalline HA was reported to be prepared by hydrothermal methods with high crystallinity, homogeneity and close Ca/P ratio to 1.67 as in HA.[5,7,14] Our previous work showed that nanocrystalline HA was synthesized from hydrothermal processing in water.[17] However, the control of particle composition and crystallinity degree in aqueous solvent is poor.

Solvent effects on crystallite size, morphology, agglomeration and phase formation in solvo-thermal processing have been reported previously.[18,19] Physico-chemical properties of solvent, such as dielectric constant, interionic attraction, and the solute–solvent interaction strongly influence the solubility and diffusion behavior of the chemical precursors in the solvent. The addition of alcohol, e.g. isopropanol, could have a significant effect on the crystal growth, phase formation and particle agglomeration of synthesized materials. The effect of methanol on the morphology of HA crystals have been studied by Nagata et al. under hydrothermal conditions. The results indicated that only rod-like crystals about 20–100 nm in size formed without methanol and the addition of methanol increased the ratio of plate-like crystals, when add 50% methanol by weight, only

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plate-like crystals 20–200 nm in size were observed.[7] Riman et al. reported that HA crystals synthesized in isopropanol (50%)–water solution had low aspect ratios ranging between 2 and 3.[14] Furthermore, our recent work indicated that the agglomeration of yttria-stabilized zirconia (YSZ) nanopowder synthesized in ethanol–isopropanol mixture solvent was hindered and a well-dispersed YSZ nano suspension was obtained. This result can not be explained by the DLVO theory but by solvation effect in alcohol solution.[19] In this article, the effects of isopropanol on crystallization of nanocrystalline HA were studied, in an attempt to control the crystallite properties and agglomeration.

2. Experiment procedures

2.1. Powder synthesis

Analytical pure $Ca(OH)_2$ and 85% H_3PO_4 were used as starting materials. 3.71 g (0.05 mol) $Ca(OH)_2$ was dispersed in 100 ml deionized water, and stirring for 5 h to form a uniform suspension. At the same time, 2 ml 85% H_3PO_4 (0.03 mol) was diluted by 8 ml deionized water. The ratio of Ca/P was kept at 1.67 as HA. Then the diluted H_3PO_4 solution was added to the $Ca(OH)_2$ suspension drop by drop while stirring gently (the dropping rate is about 1 ml/min). Finally a white calcium phosphate precursor (termed as HA precursor) was formed at the end of titration. For hydrothermal processing of the precursor, a fixed amount of precursor was centrifugally separated and redispersed in 0, 20, 50, 70 vol.% isopropanol in water, respectively. The HA precursor suspension in solvent was transferred to a 300 ml autoclave (pressure vessel), then placed in a mantle heater and treated hydrothermally at 220 °C for 10 h. A temperature program was used to control the heater around the external surface of the pressure vessel, while the actual reaction temperature was monitored using an internal thermocouple. The final product was washed in water and ethanol twice, respectively, and then vacuum filtered, dried in air for characterization.

2.2. Powder characterization

X-ray diffraction (XRD) analysis of powders was conducted using a Philips diffractometer (PW3710) with Cu Kα radiation over the 2θ range of 5–85° at room temperature with a step size of 0.02°. Infrared spectra (FTIR) of HA powders were obtained using Perkin-Elmer system 2000 spectrometer. Pellets for FTIR analysis were prepared from 1:150 HA–KBr mixtures (by weight), which were ground in a mortar and pestle for 15 min and pressed into pellets using a cold press. Thermal analysis was carried out on the powder by TG-DSC from 20 to 1200 °C in air atmosphere with a heating rate of 5 °C/min. Specific surface area measurements were made using the BET method utilizing adsorption of N_2 gas at −196 °C (Coulter SA3100 surface analyzer) after outgas at 250 °C for 15 min. Particle size distributions and mean particle sizes of samples were measured by Mastersizer microplus (Malvern Ltd., UK).

Zeta potentials of those HA powders at various pH values have been examined by using the Coulter DELSA 440SX. For zeta-potential measurements, samples were prepared by diluting a 3 wt% stock suspension into 0.01 M KCl at pH 12 to obtain a working concentration of 0.03 wt%. Each suspension was titrated to various pH values and dispersed ultrasonically before analysis. The morphology of HA powders were determined by a transmission electron microscope (TEM, Philips, CM200) at 200 kV.

The crystallite size of the synthesized HA was calculated from the broadening in the XRD pattern. According to the Scherrer equation:[20]

$$t_{(hkl)} = \frac{0.9\lambda}{\beta \cos \theta_{(hkl)}}$$

where $t_{(hkl)}$ is the crystallite size, λ the wavelength of the monochromatic X-ray beam ($\lambda_{Cu} = 0.154056$ nm), β the full width at half maximum (FWHM), $\theta_{(hkl)}$ the peak diffraction angle and satisfies the Bragg's law for the $(h\,k\,l)$ Miller's plane. To determine the full width at half maximum (FWHM) we used the basal reflection Miller's plane $(0\,0\,2)$ peak since it is sharp and isolated from others. This peak also shows the crystal growth along the c-axis of the HA crystalline structure. In addition, the crystallite size based on the $(3\,0\,0)$ Miller's plane, which indicates the crystal growth along the a-axis of HA, was also calculated in order to compare with that along $(0\,0\,2)$. Meanwhile, crystallite size was also measured from the TEM images. The width and length of 50 crystals were measured from five randomly selected areas of each sample, average width and length was calculated from the measurements.

The measurement of crystallinity degree was performed with X-ray diffraction and infrared spectroscopy.[21] For XRD measurements, the crystallinity index (CI) for HA is based on the degree of resolution of the four X-ray reflection between 30° and 35° by using the semi-quantitative method of Person et al.: $CI = (h(2\,0\,2) + h(3\,0\,0) + h(1\,1\,2))/h(2\,1\,1)$ $(h(2\,0\,2)$ means the height of $(2\,0\,2)$ reflection), which is more practical and more accurate than the classic measurement of the $(0\,0\,2)$ reflection breadth at half-height.[22,23] The heights of the $(2\,0\,2)$, $(3\,0\,0)$ and $(1\,1\,2)$ diffraction peaks were measured between the average value of distance between the top of the peak and the 'valley' separating it from the next peak (illustrated in Fig. 1A). $h(2\,1\,1)$ is the height of the highest peak $(2\,1\,1)$, subtracting the value of the baseline taken between 24° and 38° of 2θ. The CI was given as the average value of three measurements with an error of ±0.01.

For FTIR measurements, the splitting factor (SF) as an indication of crystallinity was calculated using the method given by Weiner and Bar-Yosef.[24] After a baseline correction between 495 and 750 cm^{-1}, the intensity of the two $\gamma_4(PO_4)^{3-}$ vibration bands at 605 cm^{-1} (a) and 565 cm^{-1} (b) in the absorbance mode was measured and their sum was then divided by the intensity (c) of the valley between these absorption bands above the baseline; i.e. $SF = (a + b)/c$ (illustrated in Fig. 1B). Higher is the value of CI or SF, higher is the crystallinity degree.