Surfactant-assisted preparation of fluoride-substituted hydroxyapatite nanorods

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Abstract

Fluoride-substituted hydroxyapatite (FHAp) nanorods have been successfully prepared by adding Tween80. As compared to the spheroidal morphology without any surfactant, the FHAp nanorods prepared with Tween80 were elongated along the c-axis. The reason was attributable to the enlarged difference between the growth rates of crystal surfaces due to the adsorption of Tween80. The effects of the pH value on the apatite formation were investigated by calculating the solubility isotherms of the Ca$^{2+}$–$\text{PO}_4^{3-}$–$\text{F}^-$–$\text{H}_2\text{O}$ system in conjunction with experimental results, and it was found that acidic solutions were unfavorable to FHAp preparation and the proper pH should be controlled at about 9 when preparing the FHAp nanorods with the addition of Tween80.

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1. Introduction

Hydroxyapatite (HAp) is generally accepted as a prototype for theapatite minerals in calcified tissues. Among these minerals, the lattice ions of HAp are substituted, to different extents, by other ions, including F$^-$, Cl$^-$, CO$_3^{2-}$, Na$^+$, K$^+$, Mg$^{2+}$, Sr$^{2+}$, etc. Such substitutions have much influence on the physical and chemical as well as physiochemical properties of apatites [1]. It was reported that the substitution of fluorine for OH sites and formation of fluoride-substituted hydroxyapatite (FHAp) enhanced the acid resistance [2] and the mechanical properties [3] of hydroxyapatite bioceramics, and induced better biological response [4].

In fact, fluorine exists in bone and teeth of vertebrate bodies. It is well known that the FHAp nanocrystals are platelet-like in bone and needlelike in enamel [5]. The nucleation and morphological development of these FHAp nanocrystals are under the control of some specific interaction between apatite crystals and functional organic molecules [6]. Previous studies on FHAp synthesis mainly focused on hydrolysis [7], sol–gel synthesis [8,9], direct precipitation from Ca$^{2+}$, $\text{PO}_4^{3-}$ and F$^-$ containing stock solutions [10–14], solid-state reaction [15], mechanochemical route [16], microwave-mediated metathesis reaction [17], etc. Due to the lack of the direction of functional organic molecules, these methods cannot synthesize FHAp crystals with desired morphologies as effectively as biological systems do. Some surfactants, which can adsorb on the crystal surface and influence the crystal growth, have been widely used to prepare nanocrystals with various morphologies [18]. However, to our knowledge, no investigations were reported about surfactant-assisted FHAp synthesis. So the aim of this paper is to prepare FHAp nanorods by adding a non-ionic surfactant.

2. Experimental

Analytical grade calcium acetate (Ca(CH$_3$COO)$_2$·H$_2$O), di-ammonium hydrogen phosphate ((NH$_4$)$_2$HPO$_4$) and sodium fluoride (NaF) were purchased from the Beijing
Chemicals Corp., China and used as the starting materials. Varied amounts of Tween80 [poly(oxyethylene)sorbitan monooleate] and calcium acetate were added into 80°C deionized water, which was vigorously stirred. After calcium acetate was completely dissolved, the aqueous solution containing di-ammonium hydrogen phosphate and sodium fluoride were dropped into the solution. The total concentrations of calcium ions and phosphate ions were respectively controlled at 0.1 and 0.06 M and the added amount of sodium fluoride determined according to the desired fluoridation. The pH value was adjusted by adding ammonia hydroxide or dilute nitric acid. After aging for 24 h at ~80 °C, the precipitate was filtered with a Buchner funnel, and then dried in an air oven at 60 °C overnight.

The morphology of the precipitate was observed by a field emission scanning electron microscope (FESEM, JSM-6700F, JEOL, Japan) and a transmission electron microscope (TEM, H-700, Hitachi, Japan). The phase identification was performed by an X-ray diffractometer (X’Pert Pro, PANalytical, The Netherlands) with CuKα radiation at a scanning rate of 20°/min. Fourier transform infrared (FTIR) spectra were recorded using a KBr pellet technique in a FTIR spectrometer (Equinox 55, Bruker, Germany) over 400~4000 cm⁻¹ at a resolution 4 cm⁻¹. The fluoride content was analyzed using fluoride ion electrode method (PF-1, Shanghai Leici, China).

3. Results and discussion

Fig. 1 is the X-ray diffraction (XRD) pattern of the as-prepared powder with Tween80 as the growth modifier, which shows a typical apatite pattern without any other phases (as compared to the

![XRD pattern of the as-prepared powder by adding 1.65 g Tween 80 at pH=9.](image)

Fig. 1. XRD pattern of the as-prepared powder by adding 1.65 g Tween 80 at pH=9.

![FTIR spectrum of the as-prepared powder by adding 1.65 g Tween 80 at pH=9.](image)

Fig. 2. FTIR spectrum of the as-prepared powder by adding 1.65 g Tween 80 at pH=9.

![FESEM images of FHAp prepared (a) at 80 °C by directly mixing and aging for 24 h (b) at 80 °C with 3.2 g/l Tween 80 and aging for 24 h, (c) at 80 °C with 6.5 g/l Tween 80 and aging for 24 h.](image)

Fig. 3. FESEM images of FHAp prepared (a) at 80 °C by directly mixing and aging for 24 h (b) at 80 °C with 3.2 g/l Tween 80 and aging for 24 h, (c) at 80 °C with 6.5 g/l Tween 80 and aging for 24 h.
standard card of fluorapatite JCPDS #15-876). The relatively large half width of peaks indicates the small size of particles.

Fig. 2 illustrates the FTIR spectrum of the as-prepared FHAp, which indicates typical P–O vibration mode, including the antisymmetric P–O stretching mode at the bands of 1092 and 1048 cm\(^{-1}\), the symmetric P–O stretching mode at 962 cm\(^{-1}\), the O–P–O bending mode at the bands of 602, 565, and 471 cm\(^{-1}\) [19]. The absorption at 875 and 1456 cm\(^{-1}\) indicates that a small amount of carbonate ions substituted PO\(_4\)\(^{3-}\) tetrahedron and formed B-type substituted FHAp [20]. The analysis of fluoride ion electrode shows that the as-prepared powder contains 1.8 wt.% fluorine, which, in conjunction with the analyses of XRD and FTIR identification, indicates that the powder obtained is fluoride-substituted hydroxyapatite.

Tween80 had significant effects on the growth and morphological development of FHAp crystals as shown in Fig. 3. Without the addition of any surfactant, the resultant FHAp showed a spheroidal shape with a relatively broad size distribution of 80–300 nm. When a little amount of Tween80 was added, rod-like FHAp formed as shown in Fig. 3b and however, some nearly-spherical particles remained and mingled in the cluster of the FHAp nanorods. In contrast, FHAp particles synthesized in the solution with 6.5 g/l Tween80 (Fig. 3c) developed a relatively uniform rod-like shape distribution with the average diameter of about 50 nm. To increase the concentration of Tween80 further did not have more significant influence on the morphology of synthesized FHAp and however led to a lot of bubbles, which caused difficulty during filtration, thus, the amount of Tween80 should be appropriately controlled.

The TEM image of the as-prepared FHAp is given in Fig. 4, which clearly shows the rod-like shape and the electron diffraction indicated that the crystal is elongated along the [001] direction. The elongated growth along the c-axis resulted from the addition of any surfactant.
the interaction between FHAp surfaces and Tween80, whose structure, as shown in Fig. 5, has a hydrophilic head and a hydrophobic tail. Previous studies suggested that the interaction between the HAp crystal and organic molecules was attributable to electrostatic attraction, formation of calcium complex, and hydrogen bonds [21]. Since Tween80 is a non-ionic surfactant, the possibility of electrostatic action may be eliminated. Although one carboxylic-ester group exists in the middle of Tween80 molecule, the steric effect hinders the adsorption on the nanoparticle surface via the carboxylic-ester group [22]. Therefore, three end hydroxyl groups and abundant ether oxygen may contribute to the adsorption. The hydrophobic alkyl tail was exposed outside of the surfaces and hindered the diffusion of the growth units onto the crystal surfaces. Such adsorption and steric hindrance led to the enlarged difference between the growth rates of crystal faces, so that the FHAp crystal showed anisotropic growth.

The elongated growth along the c-axis was because the adsorption had more influence upon the growth rates of crystal faces parallel to the c-axis than upon those crystal faces perpendicular to the c-axis. The process of shape evolution could be depicted in Fig. 5. At the beginning of mixing, plenty of nuclei formed due to high supersaturation. When Tween80 adsorbed on the surfaces of the newly formed nuclei, the growth of crystal faces parallel to the c-axis was relatively retarded in comparison with that of crystal faces perpendicular to the c-axis. Consequently, the rod-like crystals were elongated along the c-axis.

The pH value is an important factor that influences the precipitation of apatite phase from aqueous solutions. Previous studies [23] showed that to control the pH variation from acid to basic range was favorable to the development of whisker-like pure HAp because the acid condition led to the formation of the whisker-like precursor octacalcium phosphate (OCP). When pH values were raised, OCP was transformed into HAp and the whisker-like morphology kept. Thus, the influence of pH value upon the FHAp precipitation was systematically investigated with the expectation for long FHAp whiskers. The phase composition during the pH variation was shown in Fig. 6. At a pH value of 4, the resultant phase was CaF2. When the pH values were raised, CaF2 formed in the acid range was transformed into FHAp, but did not develop the whisker-like morphology.

The reason for the difference at the varied pH values could be sought from solubility isotherms. According to the literature data [24–26], the solubility isotherms were calculated and shown in Fig. 7. It is clear that CaF2 is the most stable phase at pH<4.2, which explained the occurrence of CaF2 in Fig. 6a. In the pH range of 4.2~10, apatite is the stable phase and have a minimum solubility around pH=9. Although, when pH values were recycled around pH=9. Although, when pH values were recycled, CO2 raises the solubility of apatites. So the proper pH value should be controlled at about 9.

4. Conclusion

FHAp nanorods were successfully prepared by adding Tween80. The analyses of XRD, FTIR and fluoride ion selective electrode showed that the as-prepared powder was fluoride-substituted hydroxyapatite without any impure phase. The clear morphological variation, after adding Tween80, was attributable to the enlarged difference between the growth rates of crystal face due to the adsorption of Tween80. Experimental results and the analyses of solubility isotherms of Ca2+–PO43−–F−–H2O system showed that the pH value should be controlled at about 9 when preparing the FHAp nanorods with the addition of Tween80.

References