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Ceramics International 32 (2006) 951–954

CERAMICS INTERNATIONAL

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Short communication

# Synthesis of single-crystal HAP nanorods

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Received 29 October 2004; received in revised form 13 May 2005; accepted 14 July 2005

## Abstract

Single-crystal hydroxyapatite (HAP) nanorods have been successfully synthesized by the reverse microemulsion method, and characterized by high-resolution transmission electron microscope (HRTEM), infrared spectra (IR), and powder X-ray diffraction (XRD). In this work, the feasibility of using quaternary reverse microemulsion (TX-100 + CTAB/*n*-butanol + *n*-hexanol/cyclohexane/water) to prepare hydroxyapatite nanorods with diameter 8–15 nm and length 25–50 nm, is described. The homogeneity in size and shape of hydroxyapatite nanoparticles observed by TEM is probably attributed to the different stabilization functions of different kinds of surfactant on the interfacial film.

*Keywords:* Hydroxyapatite; Surfactant; Nanoparticles; Reverse microemulsion

## 1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) nanoparticles have been of interest because of their mineral components being similar to bone and teeth of human body[1–4]. Huge efforts have been made in the preparation of nanometer-sized particles. The main issue in the preparation of hydroxyapatite nanoparticles is a careful control of particle size and, even more important, their size distribution [5]. Among the several preparations proposed, a popular method makes use of reverse micelles or water-in-oil microemulsions, undergoing a fast development in the last few years. Microemulsions can be used as nanoreactors to carry out chemical reactions in restricted geometries. These microemulsions consist of nanometer-sized water droplets, which are dispersed in a continuous oil medium in order to prevent phase separation of the particles. The main advantage of this technique is the simplicity of the process. It is a soft technique that provides a good crystallinity without very high temperature requirements and that favors the formation of small crystallites with a sufficient narrow size distribution.

In this paper, the feasibility of using a quaternary water-in-oil microemulsion (TX-100 + CTAB/*n*-butanol + *n*-hexanol/cyclohexane/water) to prepare hydroxyapatite nanorods with desired size and shape is described, and the possible role of alcohols in the quaternary microemulsion is also discussed.

## 2. Experimental

### 2.1. Chemicals

TX-100, CTAB and ammonia solution were purchased from Beijing Chemical Reagents Co. (Beijing, China) and used without further purification. Cyclohexane, *n*-butanol, *n*-hexanol, $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ were obtained from Beijing Beihua Fine Chemicals Co. Ltd. (Beijing, China) and used as received. Deionized water was used to prepare the salt solutions.

### 2.2. Production of hydroxyapatite nanoparticles

Polyoxyethylene (TX-100) and cetyl-trimethyl-amonium bromide (CTAB) were selected as mixed surfactant with *n*-butanol and *n*-hexanol as the mixed cosurfactant, and cyclohexane as the oil phase. An amount of 0.5 M $Ca(NO_3)_2{\cdot}4H_2O$ solution was added to the above mixture, then the same volume of 0.3 M $(NH_4)_2HPO_4$ solution was added, and finally the small amount of ammonia solution was added to adjust the system pH value up to 10. All above procedures are under violent stirring. The composition of microemulsion system used is summarized in Table 1. The weight ratio of cyclohexane to surfactant was 2.28:1 and TX-100 to CTAB was 7.7:1. The volume ratio of *n*-hexanol to *n*-butanol was 5:3. After completely stirring, a transparent solution was obtained, which was aged for 1 day. A small

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0272-8842/$30.00
doi:10.1016/j.ceramint.2005.07.023

Table 1
Composition of the microemulsion system

| | Surfactant phase | Hydrocarbon phase | Aqueous phase |
|---|---|---|---|
| Microemulsion | TX-100 + CTAB + *n*-butanol + *n*-hexanol | Cyclohexane | $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ |
| Weight fraction (%) | 30 | 41 | 29 |

amount of absolute alcohol was added into the transparent solution and centrifuged at 3000 rpm for 5 min to separate the white slurry. The precipitates were washed with absolute alcohol for at least three times. The entire operation was performed at 30 °C, the precipitates dried in an oven at 80 °C for 12 h, followed by sintering at 650 °C for 6 h.

### *2.3. Particles characterization*

The phases of the samples were identified by X-ray diffraction (XRD) with a D/Max 2500 V diffractometer (Cu Kα, λ = 1.5406 Å). TEM morphologies were observed by using a JEM-2010 transmission electron microscope, and FTIR was performed using a Nicolet 210 spectrophotometer.

## 3. Results and discussion

### *3.1. Characterization of the microemulsion system*

Since a four component microemulsion (TX-100 + CTAB/*n*-butanol + *n*-hexanol/cyclohexane/water) is adopted during the preparation of the nanoscale hydroxyapatite particles, it is important to understand the role of each component on the microemulsion system, especially the roles of surfactant and cosurfactant. TX-100 is a non-ionic surfactant, the function of which in the reverse microemulsion interfacial film is tridimensional stabilization, while CTAB is an ionic surfactant, whose function is electrostatic stabilization. We adopted the mixed surfactant in the present work, so that we might obtain even smaller hydroxyapatite nanoparticles [6]. The alcohol has two effects on the interfacial properties of the microemulsion from a microstructural standpoint; the alcohol modifies the surfactant packing parameters by absorbing to the interfacial film and thus influencing the radius of curvature of microemulsion droplets. A dynamic role is also played by *n*-butanol and *n*-hexanol, since a droplet formed in these conditions does not show the same interface rigidity observed in ternary microemulsions, where the plain presence of the surfactant makes the interfacial film more compact. The *n*-butanol and *n*-hexanol were chosen as the mixed cosurfactant, which could be attributed to the intensity of interfacial film [7,8].

### *3.2. Characterization of hydroxyapatite nanoparticles*

Fig. 1 shows an XRD pattern of the resulting hydroxyapatite samples. This exhibits multiple intense peaks, perfectly indexed to crystalline hydroxyapatite, not only in peak position but also in their relative intensity indicating that our samples are crystalline hydroxyapatites. The calculated lattice parameters for the unit cell of the hydroxyapatite sample is $a = 9.423$ Å, in good agreement with the known lattice parameters for crystalline hydroxyapatite ($a = 9.424$ Å; JCPDS #74-0566) within the error range.

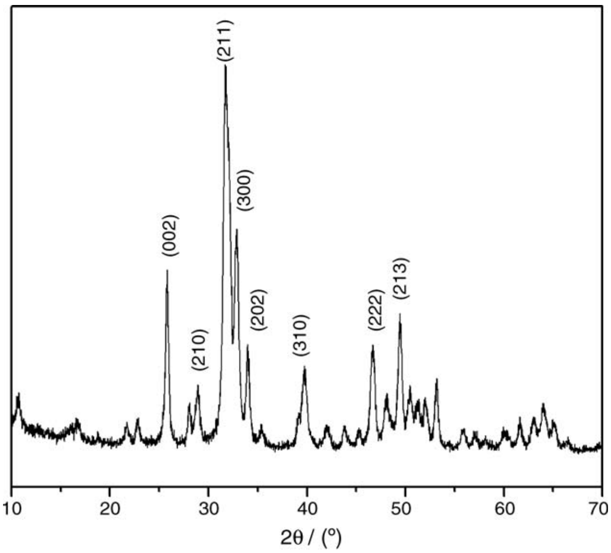

Fig. 1. XRD pattern of the HAP nanopaticles sintered at 650 °C for 6 h.

The size and morphology of the as-synthesized hydorxyapatite products were further examined by TEM and by selected area electron diffraction (ED) pattern (shown in Fig. 2). Fig. 2 shows that the sample possesses a mostly rod-like structure with a shape 8–15 nm in diameter and 25–50 nm in length, and aspect ratio ranging from 1 to 7. Few particles appear to be close to a spherical shape. The ED pattern shown in Fig. 2(inset) indicates that HAP is hexagonal single crystal.

The crystalline structures of the HAP nanocrystals were further confirmed by high-resolution transmission electron microscope (HRTEM) investigations. Fig. 3a and b display two representative HRTEM images of individual HAP nanocrystals.

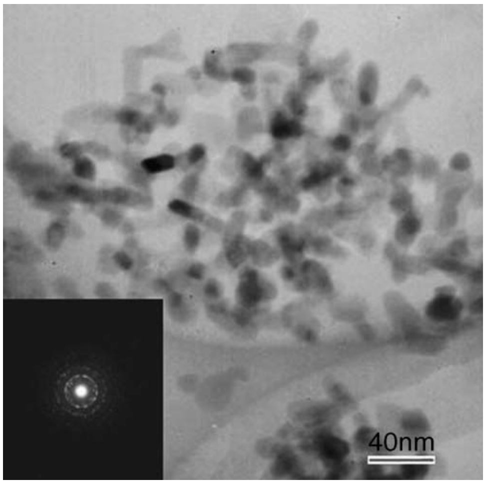

Fig. 2. TEM image showing the typical morphology of HAP nanocrystals and the ED pattern (inset).

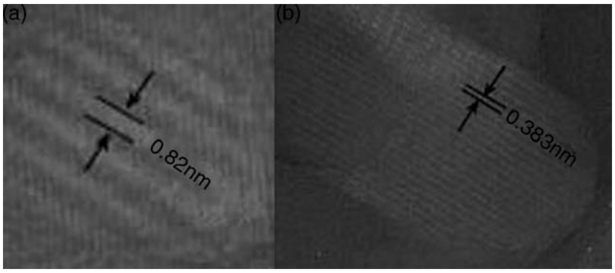

Fig. 3. (a and b) HRTEM image of two HAP nanocrystals.

It can be seen that each HAP nanocrystal shows the expected lattice fringes, with interplanar spacings of 0.82 and 0.383 nm correspond to the [1 0 0] and [1 1 1] planes of hexagonal HAP, respectively. The visible lattice fringes further confirm that as-obtained HAP nanocrystals are single crystals.

Fig. 4 shows the infrared (IR) absorption spectrum of the HAP sample as received at 650 °C. The two sharp and weak peaks at 2852 and 2921 $cm^{-1}$ are attributed to a small amount of residual CTAB, while a broad and weak bimodal peak at 1414 and 1456 $cm^{-1}$ is attributed to carbonate traces. The broad bands at 3441 and 1633 $cm^{-1}$ correspond to adsorbed water, while a weak sharp peak at 3572 $cm^{-1}$ corresponds to the stretching vibration of the lattice $OH^-$ ions [9], and a medium sharp peak at 633 $cm^{-1}$ is assigned to the O–H bending deformation mode. The characteristic bands for $PO_4^{3-}$ $cm^{-1}$ appear at 472, 570, 603, 963, 1042 and 1094 $cm^{-1}$[10]. The observation of the $\upsilon_1$ symmetric P–O stretching vibration of the $PO_4^3$ band at 963 $cm^{-1}$ as a distinguishable peak, together with the bands at 603, 570 $cm^{-1}$ corresponding to the triply degenerate $\upsilon_4$ bending vibrations, and the band at 472 $cm^{-1}$ as attributed to $\upsilon_2$ bending vibration, lead to conclude that the sample is pure HAP [11].

Samples with different size have been prepared according to different preparation conditions by modulating $P_0$ (shown in Fig. 5). $P_0$ stands for the molar ratio between alcohol and surfactant. We found that the mean particle size increases in length sharply when $P_0$ ranges from 1.8 to 6.3; and particle size increases gradually in length as $P_0$ ranges from 6.3 to 18.0, which may be attributed to the fact that the flexibility of the interfacial film strengthens when $P_0$ increases. However a weaker dependence on $W_0$ ($W_0$ represents the molar ratio between water and surfactant) is observed. This experimental evidence is apparently in contrast with the typical strong dependence of the onset and peak position on the $W_0$, indicating that the particle growth is mainly governed by the dimensions of the droplet water core.

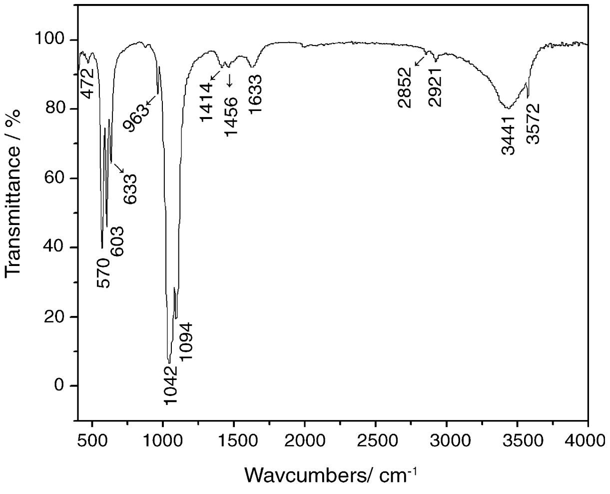

Fig. 4. The infrared spectrum of the HAP sample.

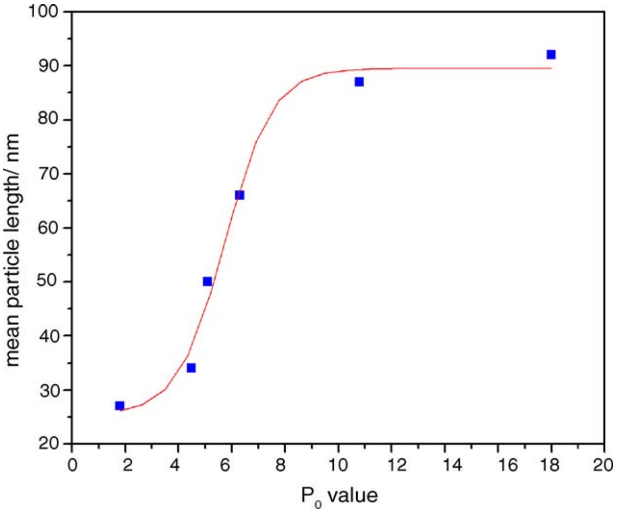

Fig. 5. The relationship between $P_0$-value and the mean HAP particle length.

## 4. Conclusions

The quaternary (TX-100 + CTAB/*n*-butanol + *n*-hexanol/cyclohexane/water) reverse microemulsion represents an effective route to prepare HAP single-crystal nanorods, by modulating microemulsion parameters. The presence of the alcohol in the microemulsion and the double stabilization function of the mixed surfactant on the interfacial film are important factors in regulating the particle size, acting on the particles growth by influencing the flexibility of the interfacial film.

## Acknowledgement

The authors are grateful to the National Natural Science Found of China (No. 20271006) for the financial support.

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