

Short communication

Synthesis of single-crystal HAP nanorods

Yuxiu Sun, Guangsheng Guo*, Zihua Wang, Hongyou Guo

*Key Lab. For Science and Technology of Controllable Chemical Reactions, Education Ministry,
Beijing University of Chemical Technology, Beijing 100029, China*

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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.

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1. Introduction

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, 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, $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ 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-ammonium 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 $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution was added to the above mixture, then the same volume of 0.3 M $(\text{NH}_4)_2\text{HPO}_4$ 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

* Corresponding author. Tel.: +86 10 644 23089; fax: +86 10 64423089.

E-mail address: guogs@mail.buct.edu.cn (G. Guo).

Table 1
Composition of the microemulsion system

	Surfactant phase	Hydrocarbon phase	Aqueous phase
Microemulsion	TX-100 + CTAB + <i>n</i> -butanol + <i>n</i> -hexanol	Cyclohexane	Ca(NO ₃) ₂ and (NH ₄) ₂ HPO 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 K α , $\lambda = 1.5406 \text{ \AA}$). 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

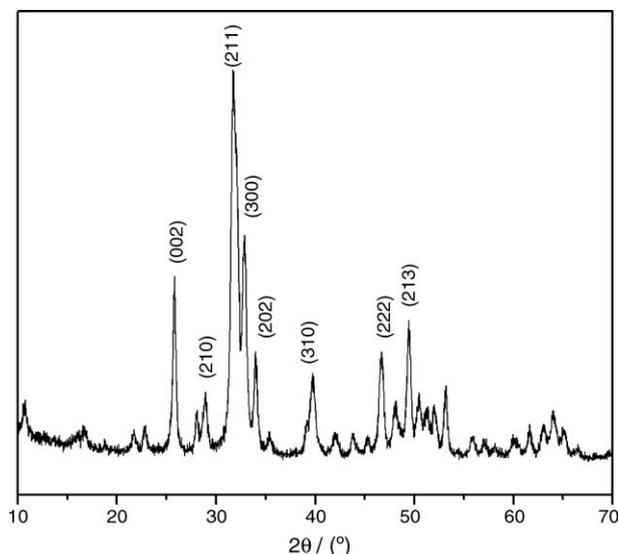


Fig. 1. XRD pattern of the HAP nanoparticles sintered at 650 °C for 6 h.

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 $a = 9.423 \text{ \AA}$, in good agreement with the known lattice parameters for crystalline hydroxyapatite ($a = 9.424 \text{ \AA}$; JCPDS #74-0566) within the error range.

The size and morphology of the as-synthesized hydroxyapatite 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.

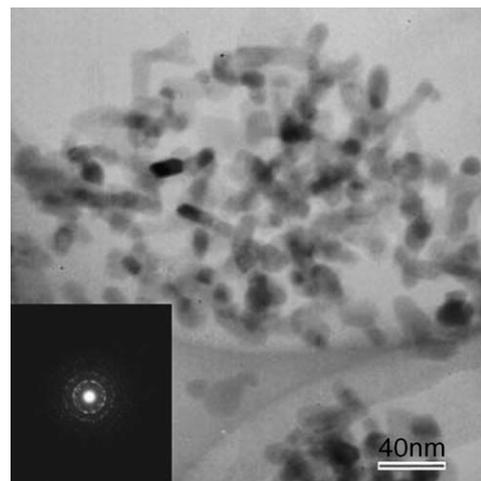


Fig. 2. TEM image showing the typical morphology of HAP nanocrystals and the ED pattern (inset).

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