Template-free Preparation of Hollow Hexagonal Fluorapatite Nanoprisms

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Hollow hexagonal fluorapatite (FHAp) nanoprisms have been successfully prepared via a template-free method with the assistance of Na_2EDTA/citric acid (CA) mixed chelating reagent. These novel hollow FHAp nanoprisms have an outer length of about 1 µm, an average outer diameter of 150 nm, and a shell thickness of about 50 nm. The effects of reaction temperature and chelating reagent on the formation of final products were studied. A possible formation mechanism for the hollow FHAp nanoprisms is proposed.

Hollow nanostructures have attracted increasing attention owing to the unique properties and potential applications in chemistry, biotechnology, and materials science.[1–3] In general, the common hollow nanostructures with high aspect ratios are nanotubes, which always have two open ends.[4,5] Recently, the fabrication of inorganic nanostructure with an interior space and closed ends has aroused significant attention.[6] For example, Yu et al. prepared hexagonal ZnO microprisms with regular interior space and found that such hollow microprisms exhibit unique emitting characteristics.[7] As far as we know, the fabrication of hollow nanostructure with an interior space and two closed ends has rarely been reported to date. Many approaches have been explored to fabricate hollow nanostructures, which can be broadly categorized into template methods: self-assembly and physical formation.[8–10] Hollow structures prepared by the template method usually suffer from disadvantages related to high cost and tedious procedures, which may prevent large-scale applications. Therefore, further development of a facile, low-cost, and template-free preparation method is quite necessary.

Fluorapatite (FHAp) is considered as an alternative biomaterial because of its low solubility and good biocompatibility in comparison to hydroxyapatite (HAp).[11] The application of FHAp depends on the crystal shape, size, crystallinity, thermal stability, and solubility.[12] Recently, it has been found that porous spherical HAp granules could be used as carriers in controlled drug release systems for targeted and time-controlled drug delivery.[13] To date, there are few reports on the fabrication of hollow HAp or FHAp nanostructures, and as a consequence, the application of hollow HAp or FHAp in drug delivery systems is limited. Here, we report the first example of the preparation of hollow hexagonal FHAp nanoprisms by a template-free hydrothermal method assisted by Na_2EDTA/citric acid (CA) mixed chelating reagent. Significantly, this kind of hollow nanostructure can find applications in controlled drug release systems. In addition, this work may provide new insights into preparing other inorganic hollow nanostructures.

In a typical experiment for the preparation of hollow FHAp, 0.0025 mol of Na_2EDTA and 0.0025 mol of CA were dissolved in 80 mL of distilled water in a 250-mL three-neck flask. Under continuous stirring, 0.0025 mol of $Ca(NO_3)_2$, 0.0015 mol of $(NH_4)_2HPO_4$, and 0.0004 mol NaF were placed in the flask, sequentially. Then the pH value was adjusted to 10.0 using NaOH. After being stirred for 20 min, the mixture was transferred into a Teflon-lined stainless autoclave and kept at 130 °C for 8 h. After the autoclave was cooled to room temperature on standing, the precipitates were separated by centrifugation, washed with distilled water and ethanol in sequence, and then dried in a vacuum oven at 50 °C for 8 h. The products were characterized using X-ray diffraction (XRD, D8 Advance X-ray diffraction), field emission scanning electron microscopy (FESEM, Hitachi S-4800 II), and transmission electron microscopy (TEM, JEOL-JEM-2010).

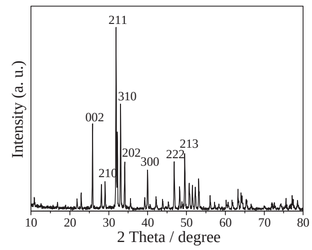

Figure 1. XRD pattern of the as-prepared FAHp.

The composition and phase purity of the products were investigated using XRD. Figure 1 shows an XRD pattern of typical sample prepared by using Na_2EDTA and CA with hydrothermal treatment at 120 °C for 8 h under pH 4.9. The XRD pattern of the material proves its crystalline nature, and the peaks match well with standard FHAp reflections (JCPDS card No. 15-0876). No evidence of impurities can be found in the XRD pattern.

Figure 2a presents a typical FESEM image of FHAp products in the presence of the mixed chelating reagents, indicating that the as-prepared products consist of a large quantity of uniform nanorods with lengths and diameters of about 1 µm and 150 nm, respectively. From the magnified FESEM image in Figure 2b, surprisingly, it can be found that these hexagonal prism-like nanorods with closed ends have hollow structures. Hollow interior space can be observed clearly from some fractured hollow nanorods (indicated with white arrows), as a result of ultrasonication and washing in the process of the experiment. In order to reveal the interior structure of these nanoprisms, the solid sample obtained after 8 h of reaction time was ground and then characterized by FESEM. Figure 2c and inset are the FESEM images of the nanoprisms broken by grinding, from which we can observe that most of the broken nanoprisms are hollow (about 70%). The broken hollow nanorods have a mean thickness of about 50 nm (Figure 2d). The morphology of the as-prepared sample was further characterized by TEM. From the TEM image (Figure 2e), it can be clearly found that the hollow nanoprisms show a pale center and dark edge, suggesting the hollow nature of the nanoprisms. Figure 2f shows a typical high-resolution transmission electron microscope (HRTEM) image of the hollow nanoprisms, revealing that the fringe spacing is about 0.348 nm, which corresponds to the (002) lattice

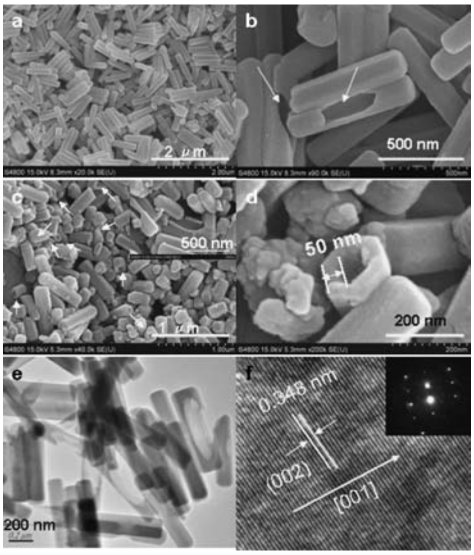

Figure 2. (a–d) The typical SEM images of the as-prepared hollow FHAp nanoprisms, (e) TEM image of the hollow FHAp nanoprisms, and (f) HRTEM image of the hollow nanoprisms. The inset in Figure 2f is the SEAD pattern of hollow nanoprisms.

plane of hexagonal FHAp. The corresponding selected area electron diffraction (SAED) pattern (inset of Figure 2f) clearly shows a single-crystalline structure of the nanoprisms. The SAED and HRTEM analyses reveal that the growth direction along the long axis of FHAp particles is [001] (*c* axis).

Recently, Yang and Zeng proposed the Ostwald ripening process model for the formation of hollow TiO_2 nanospheres,[14] which was further verified in the formation of hollow Cu_2O and ZnS nanospheres. Here, we presume that the formation of hollow FHAp nanoprisms might be controlled by a chelating reagent-assisted Ostwald ripening process. To get direct information on the formation mechanism of the hollow FHAp nanoprisms, some control experiments have been carried out. Firstly, it was found that temperature was an important factor for the growth of hollow FHAp nanoprisms. When the hydrothermal temperature was increased up to 150 °C and the other reaction conditions were fixed, the hollow nanoprisms were still produced, as shown in Figure 3a. With comparison to a sample obtained at 130 °C, the size of the nanoprisms enlarged, while the inner hollow space in the middle section of the nanoprisms became smaller. As the hydrothermal temperature was decreased to 100 °C, no hollow nanoprisms were obtained (Figure 3b). The TEM image clearly displays that these as-prepared nanorods are solid (inset in Figure 3b). Secondly, we found that the mixed chelating reagent was crucial to the hollow FHAp structures. When Na_2EDTA was used, the FHAp sample consisted of nanorods with lengths of 2–5 µm and diameter of about 500 nm (Figure 3c). Obviously, these nanorods are not hollow. Also, in the presence of CA, the product is mainly composed of dumbbell-like crystals,

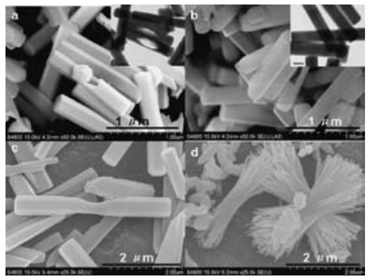

Figure 3. (a) and (b) FESEM (TEM images, inset) images of FHAp sample obtained in the presence of mixed chelating reagent at 150 and 100 °C, respectively; (c) and (d) FESEM images of FHAp obtained at 150 °C in the presence of Na_2EDTA and CA, respectively. The inset bar is 200 nm.

shown in Figure 3d. Based on the above experimental results, we speculate that the formation of the hollow FHAp nanoprisms depend on the coeffect of two different kinds of chelating reagent. However, at present the detailed mechanism involved is not entirely clear and requires further investigation.

In summary, we have developed a facile and novel method for the fabrication of hollow FAHp nanoprisms via a hydrothermal process. The hydrothermal preparation temperature plays a key role in the formation process of hollow nanoprisms, which might provide a suitable chemical environment to favor the formation of hollow FHAp nanostructures. It was found that the fabrication of hollow nanostructures also depended on the nature of the chelating reagent. The formation of the hollow FHAp nanoprisms might be due to a mixed chelating reagent-induced Ostwald ripening process.

References

1 F. Caruso, R. A. Caruso, H. Möhwald, *Science* **1998**, *282*, 1111.
2 F. Caruso, *Chem.—Eur. J.* **2000**, *6*, 413.
3 P. F. Noble, O. J. Cayre, R. G. Alargova, O. D. Velev, V. N. Paunov, *J. Am. Chem. Soc.* **2004**, *126*, 8092.
4 H. Watanabe, T. Kunitake, *Chem. Mater.* **2008**, *20*, 4998.
5 D. Liu, M. Z. Yates, *Langmuir* **2007**, *23*, 10333.
6 X. Wang, J. Zhuang, Q. Peng, Y. Li, *Nature* **2005**, *437*, 121.
7 S.-Y. Yu, H.-J. Zhang, Z.-P. Peng, L.-N. Sun, W.-D. Shi, *Inorg. Chem.* **2007**, *46*, 8019.
8 J. H. Bang, K. S. Suslick, *J. Am. Chem. Soc.* **2007**, *129*, 2242.
9 J. J. Zhu, S. Xu, H. Wang, J. M. Zhu, H.-Y. Chen, *Adv. Mater.* **2003**, *15*, 156.
10 X. Zhang, Z. Chen, F. Würthner, *J. Am. Chem. Soc.* **2007**, *129*, 4886.
11 H. Qu, M. Wei, *Acta Biomater.* **2006**, *2*, 113.
12 J. Vandiver, D. Dean, N. Patel, W. Bonfield, C. Ortiz, *Biomaterials* **2005**, *26*, 271.
13 V. S. Komlev, S. M. Barinov, E. V. Koplik, *Biomaterials* **2002**, *23*, 3449.
14 H. G. Yang, H. C. Zeng, *J. Phys. Chem. B* **2004**, *108*, 3492.

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