Glutamic Acid-mediated Synthesis of Ultralong Hydroxyapatite Nanoribbons under Hydrothermal Conditions

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A facile hydrothermal preparation of hydroxyapatite nanoribbons was successfully established by adding glutamic acid as the modulator. The resultant nanoribbons are elongated along [0001] direction with ≈70 nm in thickness and ≈500 nm in width. The adsorption of glutamate ions on the crystal surfaces led to the formation of uniform ribbon-like morphology.

Organic molecules can alter inorganic microstructures, offering a very powerful tool for the design of novel materials.[1] In biological systems, this tool is often used to create microstructures with surprisingly unusual properties.[1] For example, the superior mechanical properties of vertebrate bones are highly related to the hierarchical structure which is assembled by collagen and plate-like hydroxyapatite (HAp) nanocrystals[2] under the manipulation of some specific proteins with a high content of glutamic and aspartic residues.[1,3] Enamel organ forms ribbon-like HAp nanocrystals at the initial stage of calcification and gradually develops into needle-like crystals owing to the manipulation of other organic molecules.[2,4] In vertebrate bodies the assembly of HAp nanocrystals with these exquisite morphologies and collagen imparts the superior mechanical properties to their teeth and bones.

Thus, many researchers in the fields of materials science and chemistry have been motivated to mimic these morphologies by using the interaction between organic molecules and biominerals as a bioinspired tool with the desire to more completely understand the fundamentals of biomineralization and the potential utility in industrial and biomedical applications.[1,5] Some organic molecules such as amino acids, proteins, monoaccharides etc. have been used to synthesize HAp nanowires and nanorods because of the preferential adsorption of these molecules on the some crystal faces.[6] However, few reports are dealt with the synthesis of HAp nanoribbons with organic molecules. Although previous studies showed that during the preparation of hydroxyapatite, the precursor, octacalcium phosphate (OCP), often has the plate-like morphology,[4] varied results of hydrolysis were reported such as the formation of needle-like[6] or even structureless HAp crystals.[7] There are also reports about the synthesis of the interlayered mixture of OCP and apatite on a cationic selective membrane with the addition of fluoride.[8] However, up to now there is no method for the synthesis of ultralong and uniform hydroxyapatite nanoribbons.

In this communication HAp growth was mediated by glutamic acid, which could be adsorbed onto the surface of HAp crystals because of hydrogen bonding and electrostatic attraction.[9] Previous studies under non-hydrothermal conditions showed that glutamic acid significantly decreased the crystallinity and formed plate-like morphologies.[10] Here, we report for the first time a facile and highly reproducible synthesis of uniform HAp nanoribbons with high crystallinity under hydrothermal conditions.

The synthetic experiments were preformed in a Telfon-lined stainless autoclave. Reagent grade 0.143 g of $Ca(NO_3)_2\cdot 4H_2O$, 0.121 g of $K_2HPO_4\cdot 3H_2O$, and 0.36 g of glutamic acid were added into 30 mL of deionized water. Just after adding about 0.104 g of KOH to raise the pH value to ≈6, the solution turns from transparent to slightly turbid. The solution sealed in the autoclave was heated at 160 °C for 24 hours and then cooled to room temperature. After filtrating and washing with deionized water and absolute alcohol for several times, the powder dispersed with alcohol was transferred on an aluminium sheet and then sputtered with gold for field emission scanning electronic microscope observation (FESEM, JSM-6700F, JEOL, Japan). Phase identification was preformed in an X-ray diffractometer (X'Pert Pro, PANalytical, The Netherlands) at 40 kV voltage and 30 mA current. High resolution transmission electronic microscope (HRTEM) images and selected area electronic diffraction (SAED) patterns were obtained in a JEM-2010F (JEOL, Japan) transmission electron microscope at 200 kV.

As shown in Figure 1, all peaks in the X-ray diffraction (XRD) pattern of the as-synthesized powder can be indexed as the hexagonal hydroxyapatite phase with high crystallinity and no other impure phases were found. However, as compared to the standard card (JCPDS file no. #09-0432), the relative intensities of the planes parallel to (300) gained a substantial increase and that of (002) was weakened, suggesting that there is a preferential orientation in the powder identified.

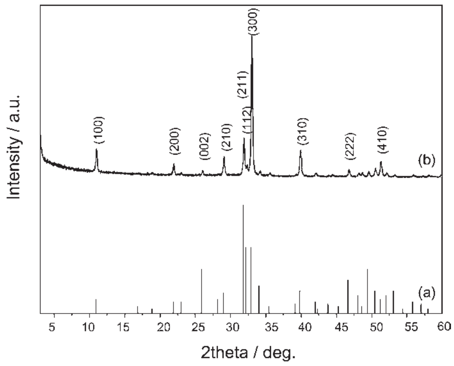

Figure 1. XRD patterns of (a) JCPDS #09-0432 and (b) the as-synthesized powders.

The morphology of the as-synthesized HAp crystals was characterized by a field emission scanning electron microscope. The images in Figure 2 from different angles clearly showed that the morphology of the HAp synthesized by this simple hydrothermal process was ribbon-like with the uniform thickness of

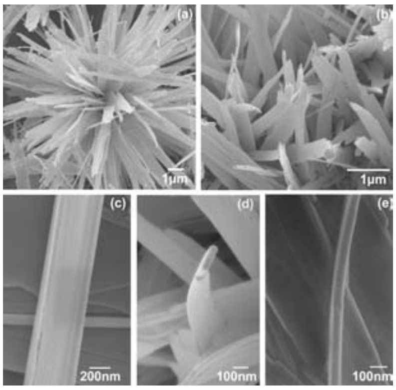

Figure 2. FESEM images of the as-synthesized HAp nanoribbons (a)–(e) with the different magnification and orientation.

≈70 nm. The width of the nanoribbons is about 500 nm, while the length is over 8 µm.

Transmission electron microscopy (TEM) analyses provide further insight into the morphological and microstructural details of the HAp nanoribbons. Figure 3(a) shows a typical TEM image of the plate-like top face of a nanoribbon. The electron diffraction pattern in the insert reveals that the elongated direction is along [0001] and the normal direction of the wide surface of the nanoribbon $[10\bar{1}0]$. The HRTEM image in Figure 3(b) received around the long fringe of a HAp nanoribbon shows that the spacing of atomic planes parallel to the side surface is 0.816 nm, which corresponds to the $\{01\bar{1}0\}$ planes of hydroxyapatite. The diffraction pattern obtained by a fast Fourier transformation (FFT) technique further confirms that the nanoribbon is elongated along [0001] and the incident electron beam is along $[2\bar{1}\bar{1}0]$. All of the above results clearly show that hydroxyapatite nanoribbons elongated along the crystallographic *c* axis were synthesized by adding glutamic acid under hydrothermal conditions.

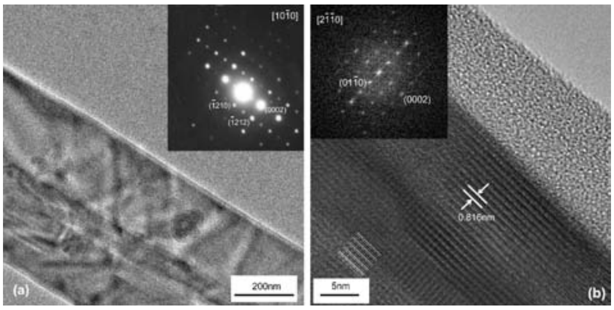

Figure 3. HRTEM image and SAED patterns of HAp nanoribbons.

Although it is difficult to directly investigate the exact synthetic mechanism of reactions in autoclaves, the formation of uniform HAp nanoribbons should be related to the presence of glutamic acid. Previous studies had showed that the adsorption of glutamic acid through hydrogen bonding and electrostatic attraction significantly inhibits the growth of HAp crystals and influences the morphological development.[10] The elongated direction of HAp nanoribbons along [0001] is usually due to the fast growth along *c* axis which has been observed in the syntheses of HAp nanowires or nanorods.[11] However, the difference between *a* and *b* axis appears to be inconsistent with the hexagonal symmetry. The reason could be sought from the forming process of HAp nanoribbons. In the supersaturated solution containing Ca^{2+} and PO$_4{}^{3-}$ there exist various hydrated complex ions and cluster,[11] which are the building blocks of calcium phosphate precipitates. When the building blocks stack onto the nucleus, they are ready to form a structure including a water layer, which is similar to the OCP interlayer structure.[4,6] However, this structure is metastable and finally hydrolyze to form the thermodynamically stable HAp under the hydrothermal conditions. When glutamate ions adsorb on the crystal surfaces, the above processes are slowed down. The direction perpendicular to the water layer of OCP-like growing fronts is much influenced, because glutamate ions prefer to adsorb on the faces parallel to the water layer because of their similarity to the OCP (100) faces,[3,6] and this direction requires a large number of ions to assemble and thus depends too much upon the migration of building blocks.[4] Thus, these differences lead to the formation of ribbon-like HAp nanocrystals. It is the adsorption of glutamate ions that modulates the growth of the different crystal surfaces under the hydrothermal conditions, allows the ordered assembly of building blocks and mediates the formation of the uniform shapes which we emphasize in this communication.

In summary, HAp nanoribbons with uniform morphology were successfully synthesized via a hydrothermal route. The resultant nanoribbons are elongated along [0001] direction with ≈70 nm in thickness and ≈500 nm in width. The hydrothermal condition and the modulation of glutamic acid produce uniform shape of HAp nanoribbons. The method of organic manipulator and hydrothermal conditions expand the synthesis of HAp nanomaterials. The HAp nanoribbons obtained have the potential utility for both biomedical and industrial applications.

References

1 S. I. Stupp and P. V. Braun, *Science*, **277**, 1242 (1997); S. Mann, D. D. Archibald, J. M. Didymus, T. Douglas, B. R. Heywood, F. C. Meidrum, and N. J. Reeves, *Science*, **261**, 1286 (1993).
2 S. V. Dorozhkin and M. Epple, *Angew. Chem., Int. Ed.*, **41**, 3130 (2002).
3 A. Bigi, E. Boanini, M. Gazzano, M. A. Kojdecki, and K. Rubini, *J. Mater. Chem.*, **14**, 274 (2004); A. Tsortos and G. H. Nancollas, *J. Colloid Interface Sci.*, **250**, 159 (2002); K. Flade, C. Lau, M. Mertig, and W. Pompe, *Chem. Mater.*, **13**, 3596 (2001).
4 W. E. Brown, M. Mathew, and L. C. Chow, in "Adsorption on and Surface Chemistry of Hydroxyapatite," ed. by D. N. Misra, Plenum Press, New York (1984), p 13; M. Iijima and J. Moradian-Oldak, *J. Mater. Chem.*, **14**, 2189 (2004).
5 W. L. Murphy and D. J. Mooney, *J. Am. Chem. Soc.*, **124**, 1910 (2002); A. Bigi, E. Boanini, D. Walsh, and S. Mann, *Angew. Chem., Int. Ed.*, **41**, 2163 (2002); K. Sato, T. Kogure, Y. Kumagai, and J. Tanaka, *J. Colloid Interface Sci.*, **240**, 133 (2001).
6 A. Bigi, E. Boanini, B. Bracci, G. Falini, and K. Rubini, *J. Inorg. Biochem.*, **95**, 291 (2003); R. Gonzalez-McQuire, J. Y. Chane-Ching, E. Vignaud, A. Lebugle, and S. Mann, *J. Mater. Chem.*, **14**, 2277 (2004).
7 S. Graham and P. W. Brown, *J. Cryst. Growth*, **165**, 106 (1996).
8 M. Iijima, H. Tohda, and Y. Moriwaki, *J. Cryst. Growth*, **116**, 319 (1992).
9 N. Spanos, P. G. Klepetsanis, and P. G. Koutsoukos, *J. Colloid Interface Sci.*, **236**, 260 (2001).
10 T. Matsumoto, M. Okazaki, M. Inoue, Y. Hamada, M. Taira, and J. Takahashi, *Biomaterials*, **23**, 2241 (2002); S. Koutsoukos and E. Dalas, *J. Cryst. Growth*, **217**, 410 (2000).
11 M. Cao, Y. Wang, C. Guo, Y. Qi, and C. Hu, *Langmuir*, **20**, 4784 (2004); K. Onuma and A. Ito, *Chem. Mater.*, **10**, 3346 (1998).