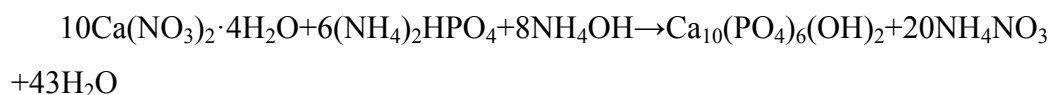


Supplementary Information

Material synthesis

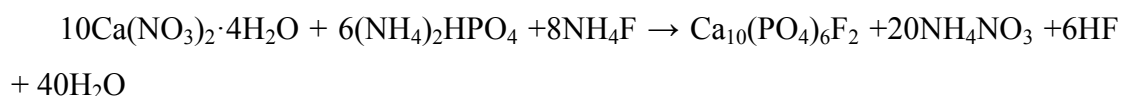
Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 99%, Sinopharm Chemical Reagent Co.Ltd, AR), Diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, 99%, Sinopharm Chemical Reagent Co.Ltd, AR) and ammonia fluoride solution (NH_4F , Shanghai Sanaisi Reagent Co., Ltd. , AR) were selected as Ca-precursor, P-precursor and F-precursor, respectively.

Hydroxyapatite was prepared by a wet precipitation method using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ as starting materials and ammonia solution (NH_4OH) as a reagent for pH adjustment. The following equation illustrates the chemical reaction leading to the precipitation of HA:

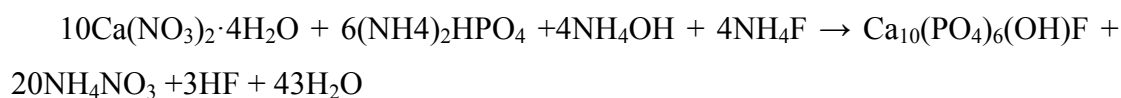


A suspension of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ powder was diluted in deionized water and stirred at 25 °C. A solution of $(\text{NH}_4)_2\text{HPO}_4$ was slowly added drop-wise to the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution. In all experiments, the pH of the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution was kept at 9~10 with ammonia solution. The final solution was stirred at room temperature for 2 hrs. Then the precipitate formed was filtered off, washed with deionized distilled water 3 times to neutral pH, and finally dried under an infrared lamp for 24 h. After drying, the sample was powdered and treated at 120 °C for 24 hrs.

Fluorapatite was obtained using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ according to the following equation:

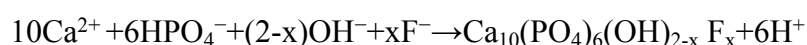


The FHA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})\text{F}$, were prepared by a precipitation method according to the following equation:



The designed degree of substitution of OH^- by F^- was indicated by the x value in the general formula of FHA ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_x(\text{OH})_{2-x}$), where x was selected as 0, 0.2644, 0.5290, 0.7939, 1.0592, 1.5904 and 2. The subsequent samples obtained were named HA, FHA1, FHA2, FHA3, FHA4, FHA5, and FHA6, respectively. Sample designation and nominal compositions of synthesized materials are listed in Table 1.

The reaction of the FHA can be expressed by the reaction :



Identification of the final material and confirmation that the reaction had gone to completion were obtained using powder X-ray diffraction (XRD).

Table S1. Designation and nominal compositions of synthesized FHAs

| Samples | F wt% | X | $\text{Ca}(\text{NO}_3)_2 \cdot$ $4\text{H}_2\text{O}$ (g) | $(\text{NH}_4)_2\text{HPO}_4$ (g) | NH_4F (g) | final sample (g) | F wt% (element analysis) |
|---------|----------|--------|---------------------------------------------------------------|--------------------------------------|------------------------------|---------------------|-----------------------------------|
| HA | 0 | 0 | 47.7071 | 16.0073 | 0 | 20.0800 | 0 |
| FHA1 | 0.50 | 0.2644 | 47.7071 | 16.0073 | 0.2266 | 20.0905 | 0.54 |
| FHA2 | 1 | 0.5290 | 47.7071 | 16.0073 | 0.4533 | 20.1011 | 0.83 |
| FHA3 | 1.50 | 0.7939 | 47.7071 | 16.0073 | 0.6804 | 20.1116 | 1.59 |
| FHA4 | 2 | 1.0592 | 47.7071 | 16.0073 | 0.9076 | 20.1222 | 1.93 |
| FHA5 | 3 | 1.5904 | 47.7071 | 16.0073 | 1.3629 | 20.1433 | 2.2 |
| FHA6 | 3.7 | 2.0000 | 47.7071 | 16.0073 | 1.7138 | 20.1556 | 2.94 |

X-Ray diffraction (XRD) Measurements

XRD spectra were recorded on an x-ray powder diffractometer using $\text{CuK}\alpha$ radiation operating at 40 kV and 30 mA (XRD, Standard attachment XRD 6000, Shimadzu, Tokyo, Japan). The powder samples were placed on an aluminum slide with a thick (2 mm) layer. The samples were scanned at a reflection angle (2θ) using a step rate of 0.5 deg/min.

X-ray Photoelectron Spectroscopy (XPS) Measurements

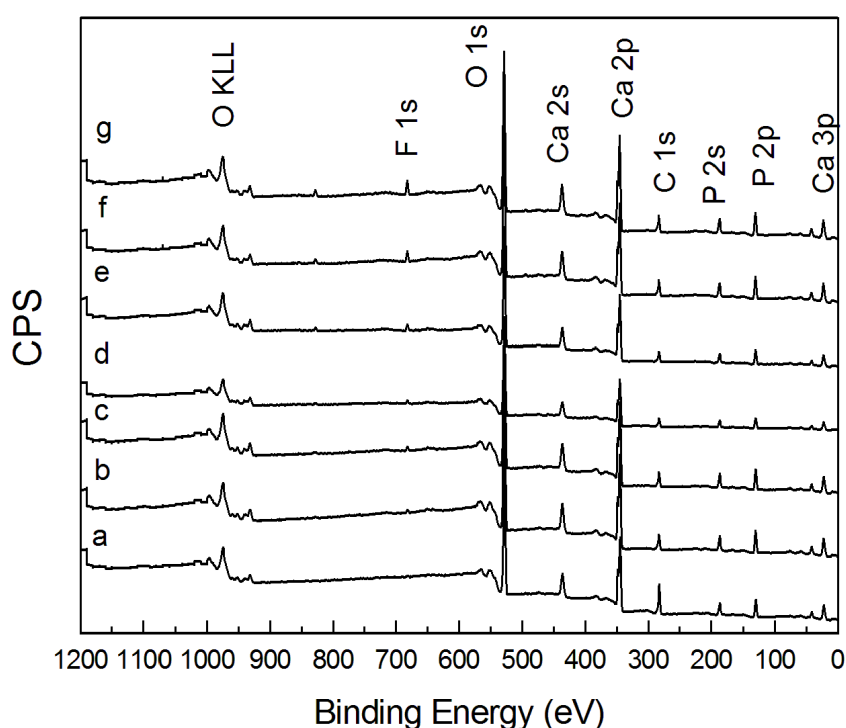


Fig.S1 XPS spectra of fluorohydroxyapatites containing different fluoride levels (a: 0wt%, b: 0.54wt%, c:0.83wt%, d:1.59wt%, e: 1.93wt%, f: 2.2wt%, g: 2.94wt%).

The X-ray Photoelectron Spectroscopy (XPS) spectra were recorded on Kratos Axis Ultra X-ray Photoelectron Spectrometer (Shimadzu Research Laboratory, Japan), using a monochromated Al $\text{K}\alpha$ X-ray source. The XPS spectrum of fluorohydroxyapatites containing different fluoride levels were shown in Fig. S2. One peak corresponding to F 1s was revealed at 684.3 eV. It is the fingerprint of F^- in the FHA structure, indicating that F^- ions have been successfully incorporated into the HA lattice structure.

Solid State NMR Spectroscopy

Solid-state ^1H and ^{31}P NMR experiments were performed on a Varian VNMRJ 400 MHz NMR spectrometer using a single pulse excitation. A single channel 6 mm MAS probe tuned to 81.01 MHz and a 6 mm zirconia rotor were used under 8 kHz magic angle spinning condition at room temperature (25 °C). ^{31}P chemical shift spectra are referenced with H_3PO_4 at 0 ppm. Solid-state ^{43}Ca NMR experiments were run on a Bruker 830 MHz NMR spectrometer at the National High Magnetic Field Laboratory (NHMFL, Tallahassee, FL), using a single-resonance 4 mm MAS probe with a spinning frequency of 10 kHz at room temperature (25 °C). ^{43}Ca chemical shift spectra are referenced with respect to $\text{CaCl}_2/\text{H}_2\text{O}$ saturated solution at 0 ppm. Other experimental details are given in the figure caption.

Raman Measurements

The Raman system consisted of a Renishaw RM 2000 spectrometer (Renishaw LC, UK) and a Leica microscope using a $\times 50$ objective. A 785 nm laser with 100 mW power at the sample was used. The laser spot size was calculated to be 10 μm wide. The spectrometer was set up with a spectrometer slit of 50 μm and 8 CCD (charge-coupled device) pixels. The powdered samples were placed on a quartz slide and 60s spectra were taken between Raman wave number shifts of 600 and 3800 cm^{-1} . Quartz was used as a calibration material with the main Raman resonance peak at around 521 cm^{-1} .

Reference:

S1. K. Cheng, W. Weng, H. Wang, S. Zhang, In vitro behavior of osteoblast-like cells on fluoridated hydroxyapatite coatings, *Biomaterials*, 26 (2005) 6288-6295.

S2. B.H. Yoon, H.W. Kim, S.H. Lee, C.J. Bae, Y.H. Koh, Y.M. Kong, H.E. Kim, Stability and cellular responses to fluorapatite–collagen composites, *Biomaterials*, 26 (2005) 2957-2963.

S3. Y. Wang, S. Zhang, X. Zeng, L.L. Ma, W. Weng, W. Yan, M. Qian, Osteoblastic cell response on fluoridated hydroxyapatite coatings, *Acta biomaterialia*, 3 (2007) 191-197.

S4. M. Fathi, E.M. Zahrani, Fabrication and characterization of fluoridated hydroxyapatite nanopowders via mechanical alloying, *Journal of Alloys and Compounds*, 475 (2009) 408-414.

S5. L. Rodriguez-Lorenzo, J. Hart, K. Gross, Influence of fluorine in the synthesis of apatites. Synthesis of solid solutions of hydroxy-fluorapatite, *Biomaterials*, 24 (2003) 3777-3785.