

Characterization of the fluoridating process of hydroxyapatite

Xiao-liang Guo^a, Qun-li Rao^{a,*}, Ling-ling Li^a, Yajuan Zou^a and Chengchei Wu^b

^aInstrumental Analysis Center

^bDepartment of Healthcare Administration, Asia University & China Asia Associated University, 500 Lioufeng Rd., Wufeng, Taichung 41354, Taiwan

F-substituted hydroxyapatites were synthesized by chemical precipitation method using $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and KH_2PO_4 as reactants and $\text{KF} \cdot 2\text{H}_2\text{O}$ as fluorination agent. Fourier transform infrared spectrometer (FTIR), X-ray diffraction (XRD) and X-ray fluorescence spectrometer (XRF) were used to characterize samples. The results showed that the more fluorine was added the more OH ions replaced by F. Moreover, OH-F bond was formed between crystalline, and the bond was stronger than that of original OH-OH, so the grains of hydroxyapatite grew larger and the crystallinity increased as F content increased.

Key words: Hydroxyapatite, Fluoride-substituted, OH-F bond, Crystallinity.

Introduction

HA (hydroxyapatite) as main substitute of the human bone is extensively used because of its excellent biocompatibility and bioactivity [1-2]. It can be integrated with the human tissues quickly after implanted into the human body with non-toxic effects. In addition, due to its good mechanical properties like enduring stress to some extent [3-4], HA has become the fundamental inorganic component in human substituted hard tissue. However, in the acid environment, the applications of HA is limited because of the thermal decomposition and the poor corrosion [5-7]. Thus, the enhancement of stability by adding F ion has been studied based on special synthesis methods [2, 5-8]. In further experiments of cultivating biologic cells [9-10], fluoridated HA was also proven exhibiting a good biocompatibility, thermal stability and corrosion resistance that it benefited for the cell growth.

Recently, we prepared highly interconnected multipolar scaffolds using FHA powders synthesized by chemical method, and the FHA powders exhibited good ability to form high quality scaffold [11]. The scaffolds behaved in good bioactivity when examined in simulated body fluid (SBF) [12]. In this paper, we further investigate the synthesis process of FHA by a variety of characterizations.

Materials and Methods

Preparation of fluoride-containing hydroxyapatites

FHAs were prepared using $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, KH_2PO_4 and $\text{KF} \cdot 2\text{H}_2\text{O}$ as reagents, and $\text{NH}_3 \cdot \text{H}_2\text{O}$ to

adjust the pH value. FHAs ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{F}_{2x}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$; symbolized as 00FHA, 02FHA, 04FHA, 06FHA, 08FHA, 10FHA, respectively.) were synthesized as follow processes: 0.04 mol $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and 0.024 mol KH_2PO_4 were dissolved with 200 ml and 120 ml ultra-pure water, respectively; then different quality of $\text{KF} \cdot 2\text{H}_2\text{O}$ was added to KH_2PO_4 solution; finally two solutions were mixed dropwise and the pH value was held at 7 by $\text{NH}_3 \cdot \text{H}_2\text{O}$ adjusting. The reaction was conducted with electromagnetic stirring for 4 hrs and then the solution was aged for 24 hrs. Precipitates were washed and dried at 90 °C.

Samples characterization

The phase constitutes of samples were detected by X-ray powder diffraction (XRD, D8 Advance, Bruker, Germany) using $\text{Cu K}\alpha$ radiation. Data were acquired at 40 kV and 40 mA, operating in the range 20 ~ 60° (2 θ) and at a step size of 4 °/min. The molar ratio of F to Ca was acquired by X-ray fluorescence spectrometer (XRF-1800, Shimadzu) and measured at 40 kV and 95 mA. FTIR spectra were detected using an FTIR spectrometer (Thermo Fisher, Nicolet 6700) and scanned between 400 and 4000 cm^{-1} at 4 cm^{-1} resolution.

Results and Discussion

Crystal structure

As shown in Fig. 1, the main peaks in diffraction patterns of six samples lie consistently in that all include the diffraction planes of (002), (021), (200), (310), (040), (213) and (141). This revealed the crystal structure was still HCP after adding fluoride while impurities (such as CaF_2) were not generated in final products. Fluoridated hydroxyapatites were synthesized as the following reaction;

*Corresponding author:
Tel : +86-21-3420-6175
Fax: +86-21-3420-6997
E-mail: qlrao@sjtu.edu.cn

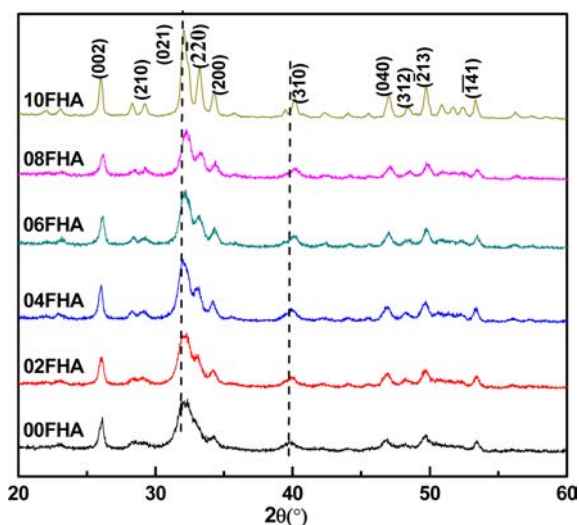
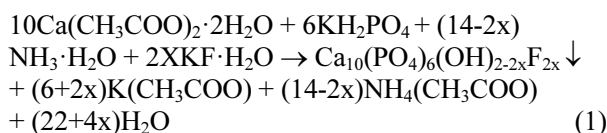


Fig. 1. XRD patterns of FHAs. F addition increases from bottom to top.



Compared with the patterns in Fig.1, it is showed that the diffraction peaks of some planes shift to high-angle direction as fluoride content increasing, especially the one of (310) plane, which indicates the decrease of cell lattice. In addition, the peak shape alters manifestly. The peak of (021) plane becomes sharper with the intensity increasing and the full width at half maximum of peak profile narrowing. At the same time, the reflection peaks of (200), (040) and (002) turn to sharper, which indicates the increase of crystallinity. With fluoride content increasing, HA crystallites grow more regularly along a, b and c axis with lower distortion and strain.

With different F additions

The molar ratio of F to Ca in FHAs is illustrated in Fig. 2 ("X" value in horizontal axis is derived from $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{F}_{2x}$). The theoretical ratio is represented by black line and actual ratio by red line, which is obtained using XRF. By comparing with two lines, it is apparent that fluoride was fully incorporated into the apatite structure when $X \leq 0.2$. While when $X > 0.2$ the experimental values deviate the theoretical ones and the gap of them enlarges with fluoride content growing. The curve of the theoretical ratio increased linearly, but the line slope of experimental ratio is lower than that of theoretical line. Results above indicate that the ability of fluoride combining with apatite changes at the point $X = 0.2$, and the combination of fluoride into hydroxyapatite lattice cell becomes more difficult above that point. The efficiency of fluoride utilized in preparing solution was estimated by the ratio of theoretical value to experimental. When $X = 0.2$ the ratio was 100%, then the ratio decreased to 54.5% at

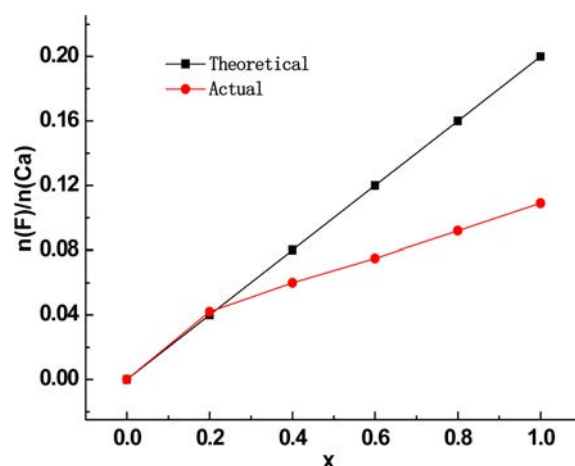


Fig. 2. The molar ratio of F /Ca in FHAs offsets the designated value when X over 0.2 fluorine content. The black and red lines indicate the theoretical and actual F/Ca ratio, respectively.

$X = 1.0$.

Chemical structure

FTIR spectra of FHAs within wavenumber of $400 \sim 900 \text{ cm}^{-1}$ were displayed in Fig. 3. Hydroxyl bending vibration stretch was observed at 633 cm^{-1} [13] in samples 00FHA and 02FHA, and it disappeared as fluoride content increasing, therefore the peak was considered as the structure of $\cdots\text{OHOHOH}\cdots$. A new band corresponding to the structure of OH-F appeared at 716 cm^{-1} [14] in sample 02FHA, and then this band shifted continuously from 716 cm^{-1} to 751 cm^{-1} in the range 02FHA $\sim$ 10FHA. Due to stronger electronegativity of fluoride, the bond energy increased as hydroxyl was replaced by fluoride. The number of $\text{OH}\cdots\text{F}$ increased and this value directly related with the degree of OH replaced by fluoride. OH and F was possibly arranged along c axis according the follow three styles; (1) $\cdots\text{OHOHOH}\cdots$, (2) $\text{F}(\text{HO})_n\text{F}$ and (3) $\cdots\text{FFF}\cdots$. The style (1) was the situation in Sample 00FHA, while the style (2) was mainly corresponding to the cases in Sample 02FHA $\sim$ 10FHA. The n value decreased with the growing number of OH replaced by F which resulted in the shift from 716 cm^{-1} to 751 cm^{-1} . With n value decreasing, the effect of hydrogen band was enhanced owing to the bond energy of $\text{OH}\cdots\text{F}$ stronger than that of $\text{OH}\cdots\text{OH}$. Therefore, the crystallites growth under such higher hydrogen band control was improved with order lattice alignment, and the crystallinity of FHAs was also promoted as fluoride content increasing. The style (3) was not detected in the experiment. Due to the added fluoride, the content of hydroxyl was gradually decreased, and then the initial combined fluoride in lattice cell formed the repulsion to the latter added fluoride. It became more difficult for fluoride to combine with HA with higher F addition, so hydroxyl of 10FHA was not completely replaced by fluoride. This result was consistent with that of XRF.

Hydroxyl asymmetric stretching vibration peak was

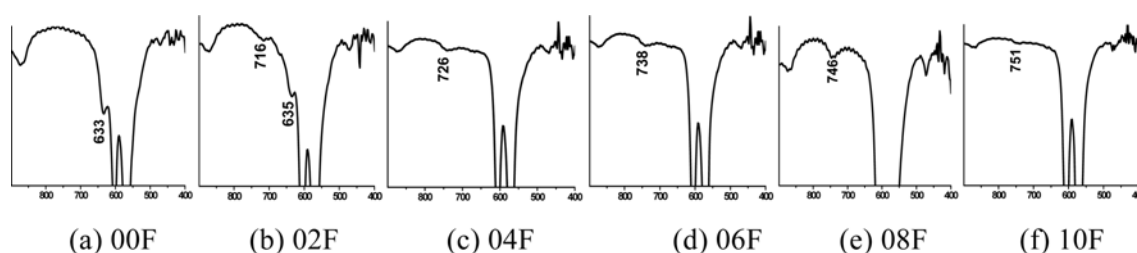


Fig. 3. Narrow FTIR spectra of FHAs within wavenumber of $400 \sim 900 \text{ cm}^{-1}$. Hydroxyl bending vibration stretch is dying out as F% increasing and the OH-F band is found when X over 0.2.

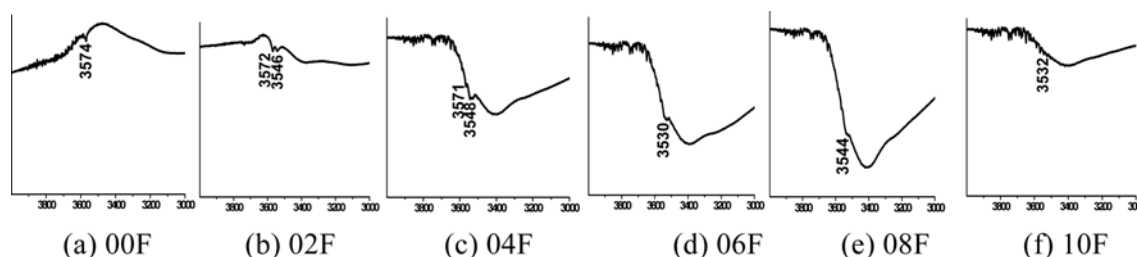


Fig. 4. Wide FTIR spectra of FHAs within wavenumber of $3000 \sim 4000 \text{ cm}^{-1}$. The wide FTIR spectra also indicate the weakening OH band and the strengthening OH-F band, which is consistent with narrow FTIR spectra.

observed at 3574 cm^{-1} [15] in Fig. 4, and the stretch was detected in samples 00FHA ~ 04FHA, with strength gradually weakening. The stretch disappeared in samples 06FHA ~ 10FHA. A new stretch, defined to OH...F stretching vibration [14], was found at 3540 cm^{-1} in Sample 02FHA. As fluoride content increasing, the peak wavenumber fluctuated between 3530 cm^{-1} and 3548 cm^{-1} [16-17] owing to strong electronegativity of fluoride and hydroxyl. According to FTIR results, it was concluded that after fluoride combining with HA, hydroxyl was partly replaced by fluoride and the remained hydroxyl formed OH-F with fluoride.

Conclusions

FHAs with different fluoride contents were prepared by chemical precipitation method at room temperature, using $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, KH_2PO_4 and $\text{KF} \cdot 2\text{H}_2\text{O}$ as raw materials. By FTIR analysis, it was concluded that OH-F hydrogen bond formed with fluoride content increasing in FHAs. The lattice cell was aligned orderly and the crystal grains grew largely, owing to stronger OH-F hydrogen bond. Meanwhile, the crystallinity of FHAs was improved significantly.

References

1. F.P. Chen, Q.L. Hu, J. Wu, J.C. Shen, Chinese J. Mater. Res. 20[3] (2006) 250-254.
2. K.A. Gross, L.M. Rodriguez-Lorenzo, Biomaterials 25 (2004) 1375-1384.
3. T.P. Hoepfner, E.D. Case, Ceramics International 29[6] (2003) 699-706.
4. B. Viswanath, V.V. Shastri, U. Ramamurty, N. Ravishankar, Acta Materialia 58[14] (2010) 4841-4848.
5. K.A. Gross, L.M. Rodriguez-Lorenzo, Biomaterials 25 (2004) 1385-1394.
6. K.A. Gross, L.M. Rodriguez-Lorenzo, Biomaterials 25 (2004) 1395-1405.
7. Y. Chen, X. Miao, Biomaterials 26 (2005) 1205-1210.
8. M. Okazaki, H. Tohda, T. Yanagisawa, M. Taira, J. Takahashi, Biomaterials 19 (1998) 611-616.
9. H. Qu, M. Wei, Acta Biomaterialia 2 (2006) 113-119.
10. R.Z. LeGeros, Clinical Orthopaedics and Related Research 395 (2002) 81-98.
11. M.A. Gong, Q.L. Rao, H.L. Wang, Journal of Inorganic Materials 29[3] (2014) 289-293.
12. Q.L. Rao, X.L. Guo, X.L. Fan, B.N. Dai, J.S. Wu, M.A. Gong, C.C. Wu, Ceramics International 42[2B] (2016) 3442-3451.
13. J.M. Hughes, M. Cameron, K.D. Crowley, American Mineralogist 76[11-12] (1991) 1857-1862.
14. F. Freund, R.M. Knobel, Journal of the Chemical Society, Dalton Transactions 11 (1977) 1136-1140.
15. M. Wei, J.H. Evans, T. Bostrom, and et al., Journal of Materials Science: Materials in Medicine 14[4] (2003) 311-320.
16. Y.Q. Zhai, K.Z. Li, C. Wang, H. Liu, Mater. Chem. Phys. 106[1] (2007) 22-26.
17. P. Kanchana, C. Sekar, Journal of Crystal Growth 312[6] (2010) 808-816.