J Mater Sci: Mater Med (2008) 19:2663–2667
DOI 10.1007/s10856-007-3365-2

Syntheses, structures and photophysical properties of iron containing hydroxyapatite prepared by a modified pseudo-body solution

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Received: 12 November 2007 / Accepted: 28 December 2007 / Published online: 16 January 2008

Abstract It is known that bones and teeth are mostly composed of hydroxyapatite (HAp) and iron is present in them as a trace element. In order to search for helpful information for understanding the behavior of trace iron element in bones and teeth, very small amounts of iron containing HAp(FeHAp) were synthesized from a modified pseudo-body solution at low temperature. The effects of iron on the structural and photo-absorption properties of FeHAp were characterized by XRD, the Rietveld structural refinement, TEM and UV–vis photo-absorption spectroscopy. The results suggested that Fe(III) ions with high spin could get into the apatite structure and FeHAp with a pure apatitic phase could be obtained. At the same time, iron could modify the photo-absorption property of FeHAp. Compared with the pure HAp material, the prepared iron containing materials showed obviously photo-absorption property in the UV light region.

1 Introduction

Hydroxyapatite (hereafter called HAp) is the main component of hard tissues like bones and teeth. Up to now, HAp has been extensively used for the fabrication of biomaterials due to its good biocompatibility [1] and a composite material with the well known TiO_2 photocatalyst for environmental purification because its good capability in adsorbing bacteria, viruses, NO_x and ammonia [2]. In addition, the photocatalytic activities of HAp [3] and Ti-doped HAp [4] have also been investigated widely under UV light irradiation.

Iron is one of the trace elements contained in bones and teeth and iron has been known to influence the crystallinity and solubility of HAp [5, 6]. As concerns whether iron could be substituted into the crystal structure of HAp, the reliable proofs are still not enough. Recently, Anee et al. reported the influence of Fe(III) ions on the crystallization of calcium phosphate, $CaHPO_4 \cdot 2H_2O$ (hereafter called DCPD) and HAp in agarose gel at a physiological pH of 7.4 [7]. DCPD is known to be one of the precursors of HAp. Morrissey et al. reported the influence of Fe(II) ions on the structural property of HAp prepared by a wet chemical reaction with di-ammonium hydrogen phosphate, calcium nitrate and a ferrous iron nitrate solution [8].

In order to search for more reliable information for understanding the behavior of trace iron element contained in HAp, we tried to prepare HAp containing trace iron element by simulating the formation process of bones and teeth. Small amounts of iron containing HAp (hereafter called FeHAp) were successfully synthesized by adding a $CaCl_2$ solution and an iron containing nitrate solution into a modified pseudo-body solution with an excess of phosphate ion concentration. Here, syntheses and some preliminary

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results on the structural and photo-absorption properties of FeHAp are presented.

2 Materials and methods

2.1 Material preparation

FeHAp containing various amounts of iron (Table 1) were synthesized by modifying the method for preparing apatite-coated TiO_2 photocatalyst in a pseudo-body solution reported by Nonami et al. [2]. First, phosphorus, calcium and iron containing solutions were prepared, respectively. The phosphorus containing solution (hereafter called solution A) with a phosphate ion concentration which is 9.5 times than that of human blood plasma was prepared by dissolving 160 g NaCl (about 2.74 mol), 4 g KCl (about 0.05 mol), 4 g KH_2PO4 (about 0.03 mol) and 23 g Na_2HPO4 (about 0.16 mol) in 2,000 cm^3 distilled water. The calcium containing solution (about 0.7 M, hereafter called solution B) was prepared by dissolving 10 g $CaCl_2 \cdot 2H_2O$ (about 0.7 mol) in 100 cm^3 distilled water. The iron containing solution (about 4.66×10^{-3} M, hereafter called solution C) was prepared by dissolving 53.2 mg iron metal (about 4.66×10^{-4} mol) into a little of 1 M HNO_3 at about 274 K and then diluted to 200 cm^3 with distilled water. Second, FeHAp was synthesized by adding 8 cm^3 solution B, appropriate volume of solution C and 200 cm^3 solution A into 3,800 cm^3 distilled water in a plastic bucket. The mixture solution was magnetically stirred and kept at 313 K for 1 h after its pH was adjusted to about 7.4. The obtained precipitate was separated by a centrifuge, washed with distilled water and dried at 323 K. Calcination treatments were performed at 773, 873, 923, 973 and 1,000 K on all of FeHAp precipitates to ensure whether they were free from the residual impurities or not.

2.2 Analysis and characterization

The crystal phases of all FeHAp synthesized and calcined were examined by a conventional X-ray diffractometer with CuKα radiation ($\lambda = 1.54178$ Å, RIGAKU MiniFlex). The morphology observations were performed by transmission electron microscopy (TEM, JEM-2010, 200 kV). The UV–vis diffuse reflectance spectra were measured by an UV–vis spectrophotometer (HITACHI U3010) with $BaSO_4$ as a reference at room temperature.

Table 1 Summary of iron-containing HAp prepared in this study

Sample code	Volume of solution C (cm^3)	Color of precipitate	Amount of precipitate (g)
FeHAp00	0	White	1.35
FeHAp01	1	White	1.22
FeHAp10	10	White	0.95
FeHAp50	50	Light yellow	0.15
FeHAp100	100	Yellow	0.05

3 Results and discussion

3.1 XRD characterization

Figure 1 shows the XRD patterns of FeHAp obtained in this study. FeHAp could be considered to have an apatite structure except FeHAp100 which showed completely different patterns. About iron containing FeHAp01, FeHAp10 and FeHAp50, the degree of crystallinity decreased slowly, amount of the precipitates got fewer and color changed from white to yellow with the increase of iron in quantity. These results suggested that the formation of the apatite phase was suppressed after adding solution C. A trend that the diffraction peaks shifted to the low angle could be observed as shown in Fig. 2. It indicated that some iron ions were doped into the apatite structure and the dimensions of unit cell changed with increasing the solution C. The trend of diffraction peak shifts seemed to be different with that reported by Okazaki et al. [5, 6], but

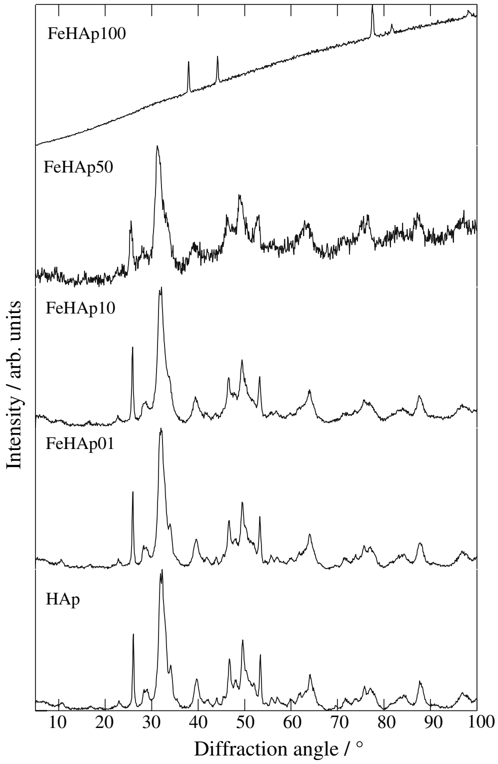

Fig. 1 XRD patterns of FeHAp samples

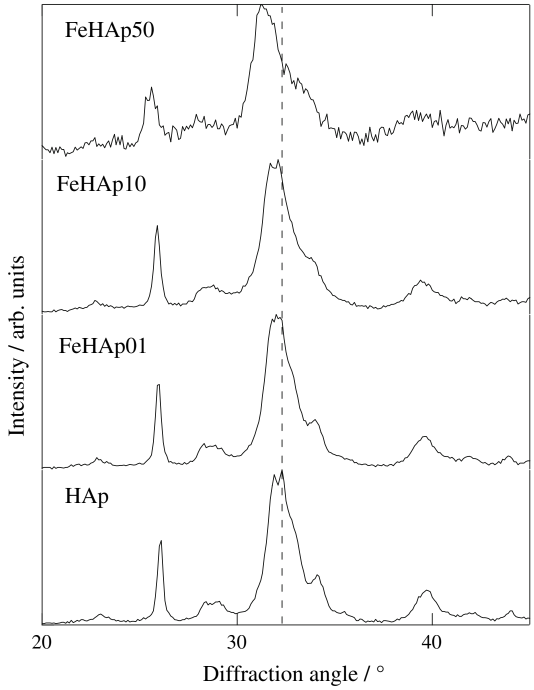

Fig. 2 Diffraction peak shifts of FeHAp samples

to be the same with that reported by Anee et al. [7] and Morrissey et al. [8].

A full-profile structure refinement of the collected XRD data for FeHAp00, FeHAp01, FeHAp10 and FeHAp50 having apatite structure were performed by the Rietveld program RIETAN 97*β* [9]. As a result, their XRD patterns could be refined by using the reported crystal structural data of HAp, $Ca_{10}(PO_4)_6(OH)_2$ (space group: $P6_3/m$) [10]. Among of them, FeHAp50 obtained larger *R* values ($R_{wp} = 15.45\%$, $R_p = 12.18\%$) than that of others($R_{wp} = 12.73\%$, $R_p = 10.11\%$ for FeHAp01). The reason of large *R* values could be considered that impurity contained in FeHAp50 and more large distortion was also possible to exist in its structure. The doped irons were in +3 valence state with high spin according to the results of ^{57}Fe Mössbauer spectroscopy (Wang et al. our unpublished data). Fe(III) (0.64 Å) has a smaller radius and larger charge than that of Ca(II) (0.99 Å) [11]. If Fe(III) substituted at Ca(II) positions, distortion was possible to be formed in the apatite structure.

Figures 3–4 show the XRD patterns of FeHAp01 and FeHAp10 calcined at 323, 773, 873, 923 and 973 K, respectively. Behavior of the XRD patterns for FeHAp00 calcined at various temperatures was similar to that of FeHAp01. No clear change could be observed from the XRD patterns after they were calcined at 773 K for FeHAp01 and 873 K for FeHAp10. The crystallinity was improved in degree after FeHAp01 was calcined at 873 K. A phase transition happened at about 923 K to FeHAp00,

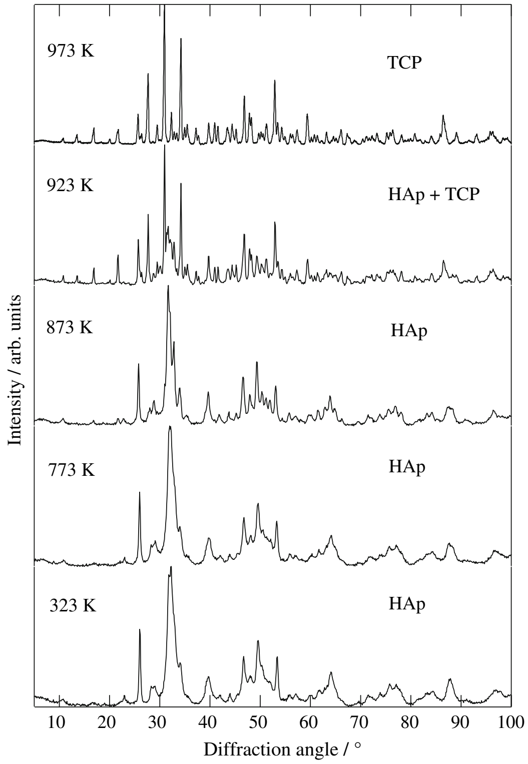

Fig. 3 XRD patterns of FeHAp01sample and it was calcined at 323, 773, 873, 923 and 973 K, respectively

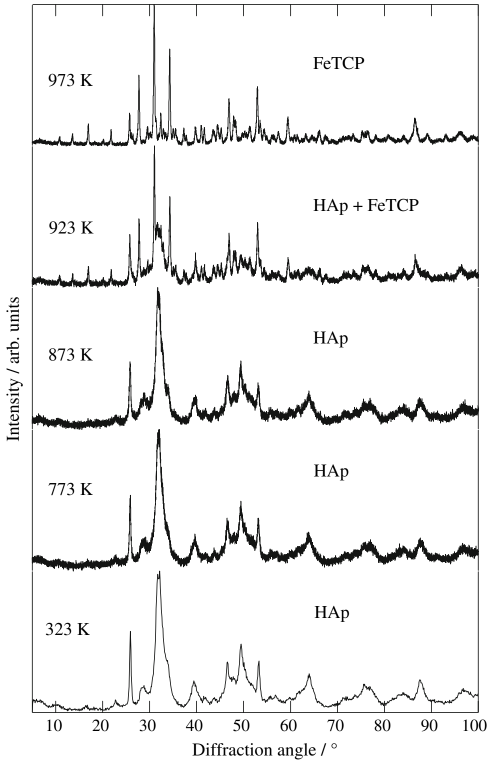

Fig. 4 XRD patterns of FeHAp10 sample and it was calcined at 323, 773, 873, 923 and 973 K, respectively

FeHAp01 and FeHAp10. The apatite phase clearly decreased and new phase appeared after they were calcined at 923 K. The apatite phase completely disappeared after they were calcined at 973 and 1,273 K. The XRD patterns of the new phase were in good agreement with tricalcium phosphate, TCP, β-$Ca_3(PO_4)_2$ (JCPDS No. 70-2065) for FeHAp00 and FeHAp01 and calcium iron phosphate, FeTCP, $Ca_{19}Fe_2(PO_4)_{14}$(JCPDF No. 49-1223) for FeHAp10 and no other phase could be found. These results suggested again that all of iron was substituted into the apatite structures for FeHAp01 and FeHAp10, and no other phase, such as iron oxide, iron hydroxide, ferrihydrite, or iron phosphate was contained in them. The XRD patterns for FeHAp50 at various temperatures showed a different behavior. Two phase (apatite and other one) were confirmed from the XRD patterns for FeHAp50 at 773, 873, 923, 973 and 1,273 K, respectively. The other phase was confirmed to be the same as that of FeHAp100. This indicated that FeHAp50 contained impurity except the apatite phase, maybe an amorphous iron phase, such as iron oxide or hydroxide.

3.2 TEM observation

Figure 5 shows the TEM images of FeHAp prepared in this study. FeHAp00 (Fig. 5a) was composed of the aggregation of needle-like crystals. All most of FeHAp01 (Fig. 5b) was also composed of the similar needle-like crystals as that of FeHAp00. Only a little other no-needle-like crystals (plate like) contained around the needle-like crystals which seemed to be aggregated due to the adhesiveness of the no-needle-like crystals. Ratio of the no-needle-like crystals to the needle-like crystals increased with the increase of iron (Fig. 5c, d), especially FeHAp50. Considering all of the TEM images, it could be supposed that the needle-like crystals were FeHAp and the no-needle-like crystals were the precursor of FeHAp which was more poor in crystallinity since the precipitates were obtained at a low temperature (323 K). Therefore, FeHAp decreased with the increase of iron and this indicated that the crystal growth of FeHAp was effected by the presence of iron. In FeHAp50A, three kinds of particles were observed. The three kinds of particles included the needle-like crystal, the no-needle-like crystal and a new type crystal. In the new type crystal, the iron content was higher than that of the other two. It suggested that iron compounds as impurity were co-precipitated in FeHAp50 as same as that indicated from its XRD patterns at various temperatures.

3.3 Photo-absorption properties

Figure 6 shows the UV–vis diffuse reflectance spectra of FeHAp00, FeHAp01 and FeHAp10. FeHAp00 does not show photo-absorption in the UV and visible light regions. However, both of FeHAp01 and FeHAp10 clearly show photo-absorption in the UV light region and the photo-absorption intensity of FeHAp10 is obviously stronger than that of FeHAp01. Furthermore, there is a red shift in the UV–vis diffuse reflectance spectrum of FeHAp10 compared with that of FeHAp01. These results indicated that

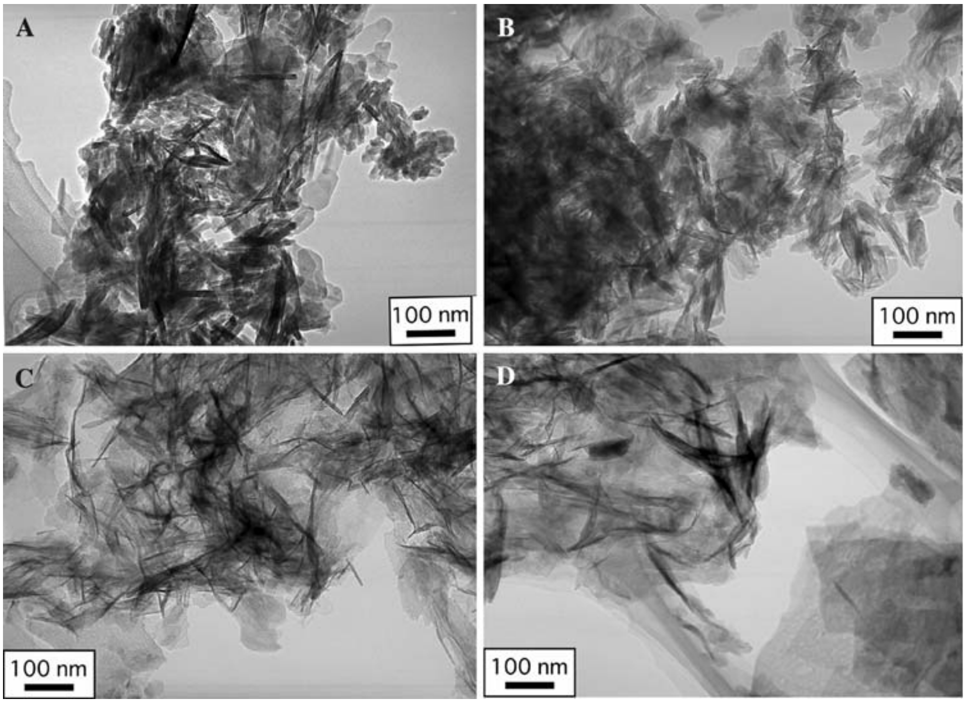

Fig. 5 TEM images of FeHAp samples

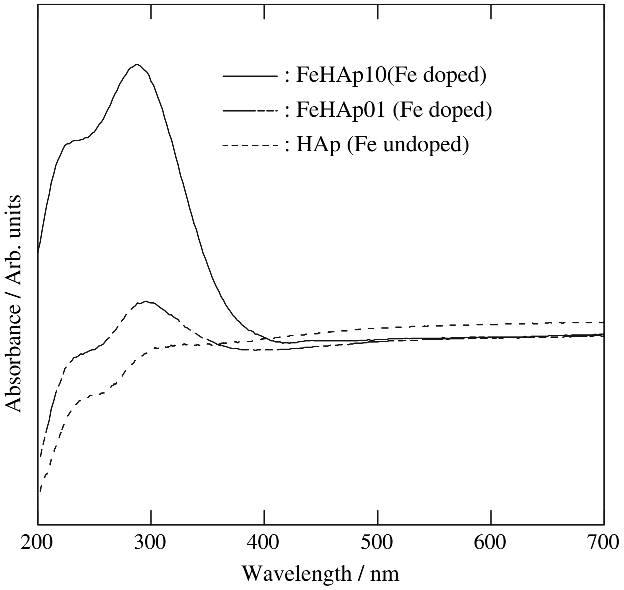

Fig. 6 UV–vis diffuse reflectance spectra of FeHAp00, FeHAp01 and FeHAp10 samples

novel energy levels are probably formed in the wide band gaps of HAp when Fe(III) with high spin were doped into their apatite structures. The UV light could be absorbed due to the transitions from their valence bands to the novel energy levels and/or from the novel energy levels to their conduction bands. Their band gaps became narrower when Fe(III) with high spin were increased.

4 Conclusions

We prepared a small quantity of iron containing HAp by a modified pseudo-body solution at 323 K. Though FeHAp has low crystallinity, the materials with pure apatite structure were obtained (FeHAp01 and FeHAp10). Trends were suggested that their lattice parameters became larger and their crystallinity became lower when iron ions were increased. Moreover, their band structures could be modified and novel energy levels are probably formed in the wide band gaps of HAp when iron were substituted into their apatite structures. Compared with that of FeHAp00, FeHAp01 and FeHAp10 could obviously absorb UV light and the intensity became stronger with the increasing iron content. So, the above results would be very helpful to understand the behavior of trace iron element contained in bones and teeth and also benefit the development of novel biomaterials and novel catalytic materials for environmental purification and industrial application.

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