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Original Research

Microstructural features of flower like Fe brushite☆

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ABSTRACT

The iron doped brushite (Fe-DCPD) nano particles were synthesized via co-precipitation method with Fe concentrations ($0 \le x \le 1$) in steps 0.2. The influence of iron concentration on the crystallinity, particle shape, morphology, optical, magnetic and electrical properties was investigated. The results showed that iron doping content is the crucial factor in the variation of physical properties. The particle shape changed from spheres at x = 0.2 to be fiber network at x = 0.8. The saturation magnetization (M_s) increased from 0.4 (emu/g) at x = 0.2 to 1.6 (emu/g) at x = 0.8 which is considered more than four times with a considerable decrease of coercive field.

1. Introduction

Calcium phosphates (CaPs) bioceramics have elevating interest in materials science studies [1–4]. They display excellent biocompatibility, bioactivity and osteoconductivity, little toxicity, suitable biodegradable rate and also direct chemical bonding with bones or bone regeneration properties attributed to the close chemical similarity with the mineral constituent of natural bone and teeth of human body [5–7]. Therefore, they can be used in tissue engineering, treatment of bone diseases and controlled drug delivery systems [3,8,9].

There are many phases of CaPs that show resorbable and non-resorbable behavior of ceramics and cements [10,11]. Among Several synthetic types of CaPs, hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$), brushite (DCPD, $CaHPO_4{\cdot}2H_2O$) have been the most extensively studied apatites owing to their similarity to the mineralized matrix of natural bone [12]. They can be obtained by chemical reactions depending on the pH value; brushite can be produced in acidic mediums [13,14].

Bioceramics that contain HAP have a low resorption rate as a result of their poor solubility at a physiological pH level [10,15]. On the other hand, brushite has raised considerable interest in the last decades due to its metastability under physiological conditions and can be resorbed more quickly than stable HAP owing to its higher solubility [10,16,17]. In addition, brushite is also considered as a precursor material in the preparation of other CaPs bioceramics [18]. So far, DCPD has been used as many functional materials, such as the abrasive component of tooth paste, a feed additive, and water treatment compounds [19–21].

Iron (Fe) is one of an essential trace element in hard tissues. It is an essential micronutrient for various biological processes and it is an important component of metalloproteins. In human body, about 60–70% of iron is present in haemoglobin as circulating erythrocytes. In the intestinal lumen, iron exists as ferrous and ferric salts [22]. Since Fe^{2+} ions can substitute Ca^{2+} ions in DCPD, they affect the physical, biological properties of DCPD [23,24]. In addition, small amounts of iron were found to have positive impact on the biomedical properties of DCPD [25–28]. In addition, Fe-DCDP illustrates better bioactivity, haemocompatibillity, osteointegration and was found to show little cytotoxicity when compared with pure phase of DCDP [29–31].

In addition, magnetic nanoparticles are being increasingly attention for drug-delivery agents, and contrast agents for magnetic resonance imaging (MRI) as well as heat mediators for hyperthermia-based cancer therapy and many other exciting biotechnological applications [23]. The pure phases of CaPs don't show magnetic properties. However, magnetic ions (Fe, Co, Ni, etc.,) were incorporated into CaPs, exhibit magnetic properties [23,32]. Therefore, combining bioceramics with magnetic properties, one can get the multifunctional material which can carry out hyperthermia therapy and local drug delivery such as a multifunctional Fe-DCPD scaffold to repair the bone defect and also, to avoid the re-development of the tumor [11].

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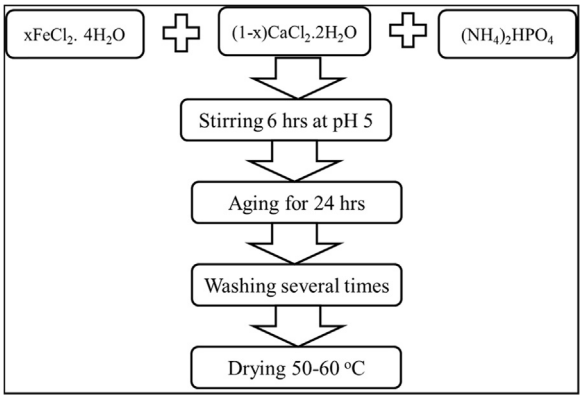

Fig. 1. Block diagram for the preparation steps of Fe-DCPD by co-precipitation method.

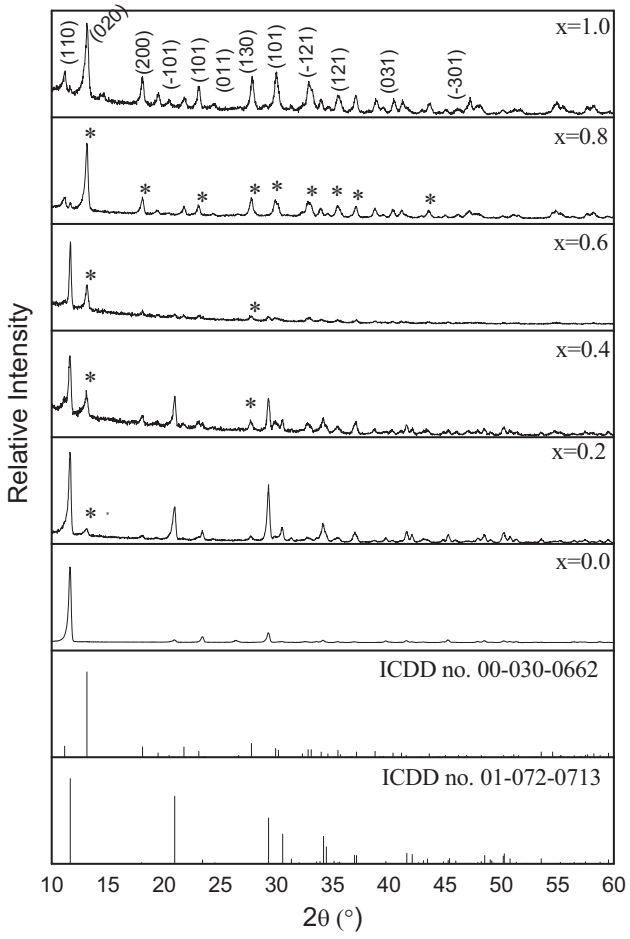

Fig. 2. XRD patterns of Fe-DCPD at different iron concentrations; (*correspond to Iron phosphate peaks).

Thus, in this piece of work, we aimed to visualize the microstructure of Fe-DCPD with different iron concentrations and evaluated their physical properties.

2. Experimental procedures

2.1. Materials and synthesis

Fe-DCPD nano particles were synthesized using co-precipitation method. Different Fe concentrations ($0 \leq x \leq 1$) in steps 0.2 were synthesized, where the precursors are iron chloride tetrahydrate (Merck) and ($CaCl_2 \cdot 2H_2O$, Merck) aqueous solutions according to the equation:

Table 1
The dependence of crystallite size of the doped iron ratio.

x	Phase	Crystallite Size (nm)
0.0	Fe-DCPD	28
0.2	Fe-DCPD	23
0.4	Fe-DCPD	35
0.6	Fe-DCPD	53
0.8	Fe-DCPD	41
1.0	Iron phosphate	74

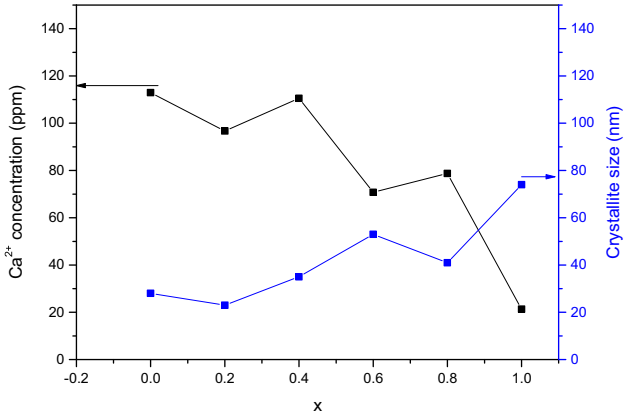

Fig. 3. Dependence of Ca^{2+} concentrations (as obtained form atomic absorption) and crystallite size on the iron content.

$$xFeCl_2 \cdot 4H_2O + (1\text{-}x)\ CalCl_2 \cdot 2H_2O + (NH_4)_2HPO_4 \rightarrow (Fe_xCa_{(1-x)})\ HPO_4 \cdot 2H_2O + 4H_2O + 2NH_4Cl \quad (1)$$

Briefly, the diammonium phosphate ($(NH_4)_2HPO_4$, Merck) was drop wisely added into the solution containing calcium and iron. The solutions kept homogeneously on a magnetic stirrer at room temperature. The pH value was maintained around 5 ± 0.1 for all samples by using diluted HCl. After several hours of the continuous stirring, the solutions were aged for 24 hrs to precipitate. The yield precipitated gels were filtered and washed several times with double distilled water and finally dried at 50–60 °C for 12 hrs. The block diagram of synthesis procedure is shown in Fig. 1.

Powder X-ray diffraction analyses were carried out to identify the formation of the samples in pure single phase using (analytical- x′ pertpro with Cu $k\alpha_1$ target, λ = 1.5404 Å, 45 kV, 40 mA, Netherlands). All the diffractograms were recorded in the range 4–70° of 2θ angles at a step size of 0.05 step time of 0.5 s. The atomic absorption data were carried out by (Perkin Elmer-Analyst 100- Germany) to determine accurately the Ca content in the samples. The surface morphology was studied using field emission scanning electron microscope (FESEM) model QUANTAFEG 250 (Netherlands). Micrographs were taken at an operating voltage of 10 kV on the powdered samples as prepared. EDX was carried out at 15 kV. The samples were ultra-sonicated in double distilled water for 20 minutes. The particle size and shape were investigated by high-resolution transmission electron microscope (HRTEM) model (JEOL / JME – 2100, Japan) operated at 200 kV of electron accelerating voltage. The magnetization (M-H) loops were performed using VSM (Lake Shore, Model-7410).

3. Results and discussion

3.1. Structural analysis

The X- ray diffraction (XRD) patterns of the powders are shown in Fig. 2. All observed peaks are coincident with the standard pattern of (ICDD no. 01-072-0713 for DCPD and ICDD no. 00-030-0662 for iron phosphate hydrate). No other diffraction peaks were observed,