JOURNALOF

Ceramic Processing Research

# Preparation of nanorod hydroxyapatite by combination of chemical precipitation and microwave technique

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Nanorod hydroxyapatite powders were synthesized using  $H_3PO_4$  and  $Ca(OH)_2$  as precursor materials via a combination of chemical precipitation and microwave techniques route. Effects of various reactive solvent, heating mode of microwave and microwave time on phase stability and morphology of as-prepared hydroxyapatite were investigated based on orthogonal design. The results suggested that when the reactive solvent was pure water, uniform, no agglomerated rod-like hydroxyapatite was formed. Increasing microwave time improved the crystallinity and morphology of rod-like hydroxyapatite, significantly. Heating mode of microwave had a profound influence on the shape, dispersibility and morphology of nanorod hydroxyapatite. Continuously heating by microwave was better for synthesis of nanorod hydroxyapatite. Phase stability of high energy metastable hydroxyapatite brought by microwave route was improved by low temperature presintering.

Key words: Hydroxyapatite, Rod, Microwave route, Phase stability.

#### Introduction

Hydroxyapatite (HA) and related calcium phosphate ceramics have been widely used as bone fillers and implant materials for many years due to their close resemblance with the mineral phase of natural bone [1]. Natural apatite in bone has elongated crystals incorporated into collagen [2]. Many attempts have been reported to fabricate nano- or micro-structured scaffolds to mimic structural and three-dimensional details of natural bone or teeth consisting of tiny HA crystals in the nano-regine, in order to understand the natural biomineralization process and relationship between their unique structure and physicochemical properties [3, 4]. Various techniques have been employed to prepare nano-sized HA, including precipitation [5], hydrothermal [6-7], sol-gel [8], crystal conversion [9] and microwave techniques [10]. The crystal size, shape, chemical composition, defect concentration and assemblage all depend on the manufacturing technology. It is established that the resulting microstructure and properties vary considerably from one preparation route to another. However, no one has been successful in arranging such HA nanocrystals to mimic the fine and complex structure of real bone and teeth.

Calcium phosphates exist in different forms exhibiting different crystal structures and Ca/P ratios such as HA, octacalcium phosphate, tricalcium phosphate ( $\beta$ -TCP), dicalcium phosphate dehydrate (DCP) and dicalcium

phosphate. HA is having non-biodegradable property, whereas  $\beta$ -TCP is used as biodegradable bone replacement material [11]. Meanwhile, an appropriate content of  $\beta$ -TCP in HA is helpful for the growth of artificial bone and a higher content of  $\beta$ -TCP in HA have a serious influence on mechanical property and chemical stability.

In order to solve these problems, our concern in this study was focused on fabrication nanorod HA by combination chemical precipitation and microwave techniques to mimic structural and three-dimensional details of natural bone or teeth. Effects of various reactive solvent, heating mode of microwave and microwave time on phase stability, crystal size and morphology were investigated based on orthogonal design.

## **Experimental**

Commercially available  $H_3PO_4$  and  $Ca(OH)_2$  were used in the present study as raw materials to fabricate nanorod HA powder. Orthoplan table  $L_9(3^4)$  was chosen to arrange the experiment. Three factors and its corresponding levels which affect the synthesis of nanorod HA were listed in table 1. According to orthoplan table  $L_9(3^4)$ , nine experiments were conducted as the following steps, respectively.

 $H_3PO_4$  and  $Ca(OH)_2$  solutions were mixed together using continuous magnetic stirring for 2 h at room temperature according that the Ca/P ratio was fixed at 1.667. The pH was kept above 10 by the addition of ammonia. The mixtures were then put into the microwave oven, which power was 500W. The precipitations obtained were aged, filtered, dried and then sintered firstly at 500 °C, dwelled for 2 h, then heated to 1000 °C

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Levels	Mode of microwave heating (A)	Solvent	Time of microwave
1	continuously heating	water	20 min
2	intermittently	ethanol	30 min
3		ethanol: water = $3:1$	10 min

Table 1. Levels of factors for orthogonal design.

and holded for 2 h, respectively. After finished nine experiments in orthoplan table  $L_9(3^4)$ , the optimum to make nanorod HA powder was chosen. Fixed level of two factors as they were in optimum process and changed levels of the third one according to table 1, then repeated the above experimental steps, respectively.

Phase identification of the as-prepared samples was conducted via an XRD (D/max-2200PC) using Cu Ká radiation. The morphology of the samples was investigated by scanning electron microscopy (JSM-5610LV).

# **Results and discussion**

#### **Reactive solvent**

XRD patterns of as-prepared nanorod HA powder sintered at 1000 °C for 2 h with various reactive solvent is presented in figure. 1. When the reactive solvent was pure ethanol, pure HA phase couldn't be obtained and the crystallnity of HA was poor. As changing reactive solvent from pure, ethanol to the mixture of ethanol and water, intensity of HA peaks improved. When the reactive solvent was pure water, stronger intensity of HA peaks were detected, indicating that pure water was recommended to be optimum for producing pure HA with good crystalinity. It also can be found that small amount of  $\beta$ -TCP peaks were observed, which was due to decomposition of HA during microwave and subsequently sintering. It includes dehydrated and decomposition reactions and equations in this stage can be as follow.

$$2OH^{-}O^{2-} + H_2O$$
 (1)

$$Ca_{10}(OH)_2(PO_4)_6 = H_2O + 2Ca_3(PO_4)_2 + Ca_{10}(PO_4)_6O$$
 (2)

$$2Ca_{10}(PO_4)_6O \rightarrow 2Ca_3(PO_4)_2 + Ca_2P_2O_7 + 3Ca_4P_2O_9$$
 (3)

Effect of various reactive solvent on the crystallization of HA is attributed to OH<sup>-</sup>. Pure water keeps a balance of H<sup>+</sup> and OH<sup>-</sup>, while pure ethanol is difficult to ionize and only few H<sup>+</sup> can occur, which influences the ionization equilibrium of water, leading to OH<sup>-</sup> decreases [12]. Subsequently decreasing OH<sup>-</sup> affects the ratio of Ca: P: OH<sup>-</sup>, resulting in difficult to form HA. Pure water was recommended to be optimum for producing rod-like HA.



**Fig. 1.** XRD patterns of as-prepared nanorod HA powder sintered at 1000 °C for 2 h with various solvent.



**Fig. 2.** SEM images of as-prepared nanorod HA powder sintered at 1000 °C for 2 h with (a) pure water, (b) ethanol: water = 3 : 1, (c) pure ethanol solvent.

SEM images of as-prepared nanorod HA powder with various reactive solvent sintered at 1000 °C for 2 h is shown in Fig. 2. When the reactive solvent was pure water, uniform, no agglomerated rod-like HA crystals were formed, while, when the reactive solvent was a mixture of water and ethanol, a considerable amount of rod-like HA crystals became sliced-like HA. However, when the reactive solvent was pure ethanol, rod-like morphology of mixture of HA and  $\beta$ -TCP was obtained again with more uniform and much smaller grain size than that of pure water. It was clear that reactive solvents had a significant influence on the crystal size, shape and morphology of HA.

# Microwave time

X-ray diffraction patterns of as-prepared nanorod HA powder sintered at 1000 °C for 2 h with various microware time is presented in Fig. 3. It can be seen that increasing microwave time improved the crystallinity of HA, significantly, indicating that microwave time of



**Fig. 3.** XRD patterns of as-prepared nanorod HA powder sintered at 1000 °C for 2 h with various microwave time.



Fig. 4. SEM images of as-prepared nanorod HA powder sintered at  $1000 \text{ }^{\circ}\text{C}$  for 2 h with (a) 10 min, (b) 20 min, (c) 30 min microwave time.

reactive solution had a profound influence on the crystallinity and phase stability of HA. The shorter the microwave time was, the more defects and poorer crystallinity of HA was obtained, which leaded to poor phase stability of HA. Low temperature presintering improved phase stability of HA, resulting from adjusting the crystal lattice and making high energy metastable HA change to low energy stable HA with less defects.

Fig .4. shows SEM images of as-prepared nanorod HA powder with various microwave time and then sintered at 1000 °C for 2 h. As increasing the microwave time from 10 min to 30 min, rod-like HA crystals became clearer, more regular and dispersible, indicating that the longer microwave time was, the better morphology of rod-like HA crystals were obtained. Effect of microwave time on morphology of rod-like HA crystals is contributed to reactive temperature, which changes the activation energy of grain growth in each process. With higher reactive temperature, drive force



**Fig. 5.** XRD patterns of as-prepared nanorod HA powder sintered at 1000 °C for 2 h with various mode of microwave.



**Fig. 6.** SEM images of as- nanorod HA powder sintered at 1000 °C for 2 h with (a) intermittently heating, (b) continuously heating.

along the c-axis growth of HA is much higher than that of a-axis and b-axis, resulting in increasing aspect ratio [13].

#### Heating mode of microwave

X-ray diffraction patterns of as-prepared nanorod HA powder with continuously heating and intermittently heating by microwave and then sintered at 1000 °C for 2h is shown in Figure. 5. It was clear that continuously heating by microwave was better than intermittently heating by microwave for synthesis of nanorod HA, which was contributed to various heating mode of microwave leading to different reaction temperature. Various reaction temperatures had a profound influence on nuclei and growth, which in turn affected the crystallinity and phase stability of HA.

Heating mode of microwave had a great influence on the shape, dispersibility and morphology of rod-like HA crystals as shown in Fig. 6. With heating mode of microwave changing from continuously heating to intermittently heating, rod-like HA crystals were not clear, regular and dispersible any more, which was contributed to continuously heating making the reactive temperature reach high instantly. Effect of heating mode of microwave on morphology of rod-like HA crystal was the same as that of high reactive temperature. From crystal growth perspective, growth rate of HA crystal for various crystal faces should be anistropic to obtain desired aspect ratio rods. In this case, the growth rate of HA crystal along the c-axis should be more than that is along a-axis and b-axis, leading to rod-like HA crystal morphology.

## Conclusions

In summary, factors of reactive solvent, heating mode of microwave and microwave time had a significant effect on phase stability and shape, dispersibility and morphology of rod-like HA crystals. Phase stability of high energy metastable hydroxyapatite brought by microwave route was improved by low temperature presintering. From crystal growth perspective, the growth rate of HA crystals along the c-axis controlled by reactive conditions was more than that of along a-axis and b-axis, resulting in better rod-like HA crystal morphology.

### Acknowledgments

This work was supported by National Foundation of Natural Science, China (51402179), Shaanxi Province Foundation of Natural Science (2014JM2-5076), Dr. Scientific Research Foundation of Shaanxi University of Science & Technology (BJ14-17) and Xi'an city science and technology plan (CXY1434(1)).

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