



## 超临界水中含碳酸根羟基磷灰石的快速连续合成

于文利<sup>1</sup> 林长春<sup>1</sup> 洪 流<sup>1</sup> 赵亚平<sup>\*,1</sup> 饶群力<sup>2</sup>

(<sup>1</sup>上海交通大学化学化工学院, 上海 200240)

(<sup>2</sup>上海交通大学分析测试中心, 上海 200240)

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### Rapid and Continuous Synthesis of Carbonated Hydroxyapatite in Supercritical Water

YU Wen-Li<sup>1</sup> LIN Chang-Chun<sup>1</sup> HONG Liu<sup>1</sup> ZHAO Ya-Ping<sup>\*,1</sup> RAO Qun-Li<sup>2</sup>

(<sup>1</sup>School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240)

(<sup>2</sup>Instrumental Analysis Center, Shanghai Jiao Tong University, Shanghai 200240)

**Abstract:** Carbonated hydroxyapatites (CHA) were rapidly and continuously synthesized in supercritical water by using a tubular reactor. The effects of reaction time and the ratio of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  on the apatite structure were investigated by using XRD, FTIR and TEM. Results showed that 30 seconds were enough to produce fully crystalline CHA nano-rods, ca. 20×70 nm in size, at 380 °C and 24 MPa. When the ratio of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  was not less than 1, the  $\text{CO}_3^{2-}$  ions mainly substituted for  $\text{PO}_4^{3-}$  in apatite structure; but  $\text{CO}_3^{2-}$  ions could react with  $\text{Ca}^{2+}$  to form  $\text{CaCO}_3$  phase when the ratio of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  was less than 1.

**Key words:** carbonated hydroxyapatite; supercritical water; continuous synthesis

Carbonated hydroxyapatite (CHA,  $\text{CO}_3\text{-Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) is a general name for hydroxyapatite (HA) containing carbonate ions ( $\text{CO}_3^{2-}$ ), which partially substitute for phosphate ions ( $\text{PO}_4^{3-}$ ) and/or hydroxide ions ( $\text{OH}^-$ ) in apatite structure. Due to its structural similarity to inorganic component of human hard bone and its adjustable bioresorbability, CHA has been regarded as a bioresorbable biomaterial used in hard bone repairing as well as local drug delivery system<sup>[1-3]</sup>.

CHA has been prepared by several methods including solid phase reaction, wet chemical reaction, microwave synthesis, etc. Lafon et al.<sup>[4]</sup> successfully obtained  $\text{PO}_4^{3-}$ -substituted CHA by using a wet chemical

synthesis and also got  $\text{OH}^-$ -substituted CHA by using a solid phase reaction. Murugan et al.<sup>[5]</sup> synthesized CHA by using a microwave synthesis method, finding that  $\text{CO}_3^{2-}$  substituted for  $\text{PO}_4^{3-}$  as well as  $\text{OH}^-$ . However, these previous methods usually took a batch-type production mode involving several steps such as precipitation and high-temperature treatment, making it difficult to control precisely the same quality of the as-synthesized products between batches, and the CHA reported in the literatures usually occurred as agglomerated particles. So it is desirable to develop novel methods for production of CHA with high quality.

Supercritical water<sup>[6]</sup> has recently gained interest

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\*通讯联系人。E-mail: ypzhaos@sjtu.edu.cn

第一作者: 于文利, 男, 35 岁, 博士, 讲师; 研究方向: 超临界流体技术与纳米材料。

as a green and controllable media for synthesizing inorganic nano-particles with high quality. Due to its rapid mass transfer rate, it could provide a rapid mixing, nucleation and crystallization environment within a tubular reactor, integrating traditional precipitation and high temperature treatment process into one continuous process.

In this report, we describe a rapid and continuous synthesis of crystalline, phase pure CHA nano-rods in supercritical water. The effects of reaction time and the ratio of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  on the apatite structure were investigated.

## 1 Experimental

### 1.1 Synthesis of CHA

The synthesis of CHA was carried out in a continuous tubular reactor (10 mL in volume) as shown schematically in Fig.1. The reactor materials used here were 316 SS stainless steel tube (Jiangsu Nantong Hua Xing Petroleum Equipment Co., Ltd.), and the thickness of the tube wall was chosen to stand  $T_{\text{max}}=600\text{ }^{\circ}\text{C}$ ,  $P_{\text{max}}=40\text{ MPa}$ . The synthesis process was as follows. Briefly, the basic solutions of calcium nitrate ( $0.05\text{ mol}\cdot\text{L}^{-1}$ ) and ammonium phosphate ( $0.05\text{ mol}\cdot\text{L}^{-1}$ ), sodium carbonate ( $0.05\text{ mol}\cdot\text{L}^{-1}$ ) were transported by using three pumps according to the molar proportion of 10:6 (Ca: ( $\text{PO}_4^{3-}+\text{CO}_3^{2-}$ )), firstly into a simple static mixer for premixing and then into the reactor for hydrothermal reaction. The pH values of the total starting solutions were adjusted to 7 by adding  $\text{NH}_3$  or  $\text{HCl}$  (1wt%). The reaction time for every experiment could be adjusted by changing the flowrate. The resultant colloidal suspensions of CHA were quenched by water cooling system and then collected in an in-situ filter to obtain the solid particles, which were then dried at  $120\text{ }^{\circ}\text{C}$  within 1 h for analysis.

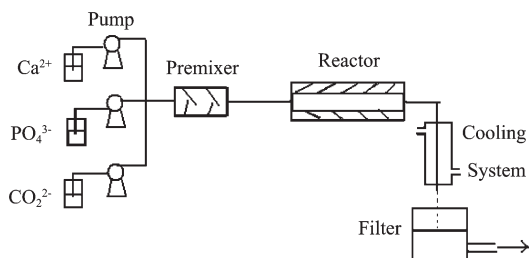


Fig.1 Continuous tubular reactor

All of the reagents used here were analytical grade and purchased from Shanghai Chemical Co. Ltd. Triply distilled water was made by our laboratory for preparation of the salt solutions mentioned above.

### 1.2 XRD analysis

The particles obtained were characterized by a Philips Powder X-ray Diffractometer (XRD) (Model PW 1800, Philips, MA, USA) with  $\text{Cu K}\alpha$  radiation source, graphite monochromator, tube voltage of 40 kV, Current of 40 mA, position scanning detector (PSC) and scanning rate of  $10\text{ s}$  over a range of  $10^{\circ}\sim 60^{\circ}$ .

### 1.3 FTIR analysis

FTIR spectra were obtained by a (Thermo Nicolet-Avatar 320 FTIR) instrument. A film was prepared by cold pressing a mixture of a sample powder with KBr in a weight ratio of 1:100. The transmittances (T) ranging from  $400\sim 4000\text{ cm}^{-1}$  were recorded.

### 1.4 TEM analysis

The morphology of the particles was investigated using a transmission electronic microscope (TEM, JEM-2010/INCA OXFORD). The as-synthesized samples were re-dispersed in water and cast in copper mesh with carbon film and dried naturally before TEM observation. The images were observed by using an acceleration voltage of 200 kV.

## 2 Results and discussion

Fig.2 shows the XRD patterns of  $\text{CO}_3^{2-}$ -substituted hydroxyapatites with  $n_{\text{PO}_4^{3-}}/n_{\text{CO}_3^{2-}}$  of 5/1 synthesized at different reaction time. It could be found that all the characteristic peaks of as-synthesized products are

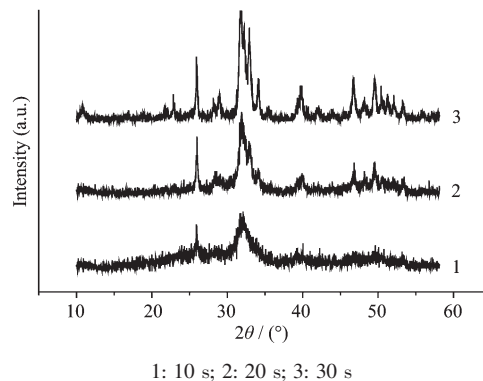


Fig.2 XRD patterns of  $\text{CO}_3^{2-}$ -substituted hydroxyapatite with  $n_{\text{PO}_4^{3-}}/n_{\text{CO}_3^{2-}}$  (5/1) synthesized at  $380\text{ }^{\circ}\text{C}$  and  $24\text{ MPa}$

similar to those of hydroxyapatite recorded in the file (PDF 9-432). On the other hand, the characteristic peaks become sharper with the increase of reaction time, indicating the increase in crystallinity of CHA, and when reaction time is 30 s, fully crystalline CHA is obtained.

The variation of CHA crystalline structure with the ratio of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  is shown in Fig.3. When the ratio is not less than 1 (sample 1, 2, 3), the as-synthesized CHA products have a similar apatite structure to pure HA (sample 0), indicating that  $\text{CO}_3^{2-}$  ions enters the lattice of hydroxyapatite by replacing  $\text{PO}_4^{3-}$  in these cases. But when the ratio is less than 1 (sample 4, 5),  $\text{CaCO}_3$  characteristic peaks are found at about  $30^\circ$ ,  $37^\circ$ ,  $44^\circ(2\theta)$  (PDF 5-586), indicating that partially  $\text{CO}_3^{2-}$  ions react with  $\text{Ca}^{2+}$  to form  $\text{CaCO}_3$  phase, leading to the coexistence of CHA and  $\text{CaCO}_3$  crystalline phase. Our result is in agreement with some previous studies<sup>[4]</sup> based on a traditional wet precipitation synthesis process when the ratio of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  is less than 1.

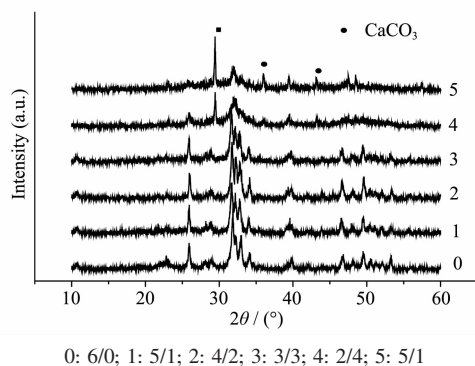


Fig.3 XRD patterns of  $\text{CO}_3^{2-}$ -substituted hydroxyapatite with different ratios of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  at  $380^\circ\text{C}$  and 24 MPa

In molecular structure of CHA,  $\text{CO}_3^{2-}$  ions could substitute for  $\text{PO}_4^{3-}$  or  $\text{OH}^-$  in apatite lattice. The  $\text{PO}_4^{3-}$ -substituted CHA has a characteristic bands around 873, 1 465, 1 412  $\text{cm}^{-1}$ , while  $\text{OH}^-$ -substituted CHA has a characteristic bands around 880, 1 545, 1 450  $\text{cm}^{-1}$  in FTIR spectra<sup>[4]</sup>. From fig.4, it could be found that the  $\text{CO}_3^{2-}$  ions mainly substitutes for  $\text{PO}_4^{3-}$  since the typical peaks of the  $\text{OH}^-$  substitution (880, 1 450 and 1 540  $\text{cm}^{-1}$ ) are not evident. This result is consistent with the previous reports that  $\text{PO}_4^{3-}$ -substituted CHA could be obtained in wet chemical synthesis<sup>[4,7]</sup>. It also

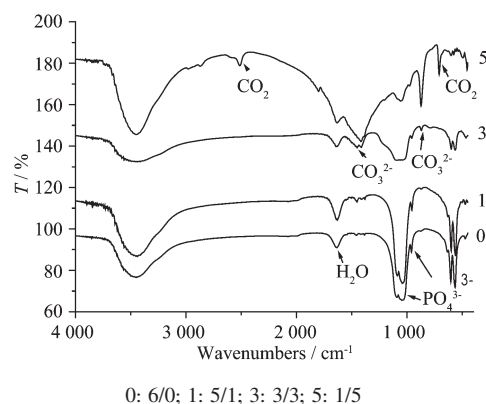


Fig.4 FTIR spectra of  $\text{CO}_3^{2-}$ -substituted hydroxyapatite with different ratios of  $n_{\text{PO}_4^{3-}}/n_{\text{CO}_3^{2-}}$

could be found that the amount of  $\text{CO}_3^{2-}$  ions increases obviously with the decrease of the ratio of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$ , which is consistent with XRD patterns in fig.3. In addition, the broad bands in the regions 1 600 and 3 200~3 600  $\text{cm}^{-1}$  corresponds to adsorbed water. The band around 2 500  $\text{cm}^{-1}$  is assigned to  $\text{CO}_2$ .

Fig.5 shows TEM images of CHA particles synthesized. It could be found that the morphology of

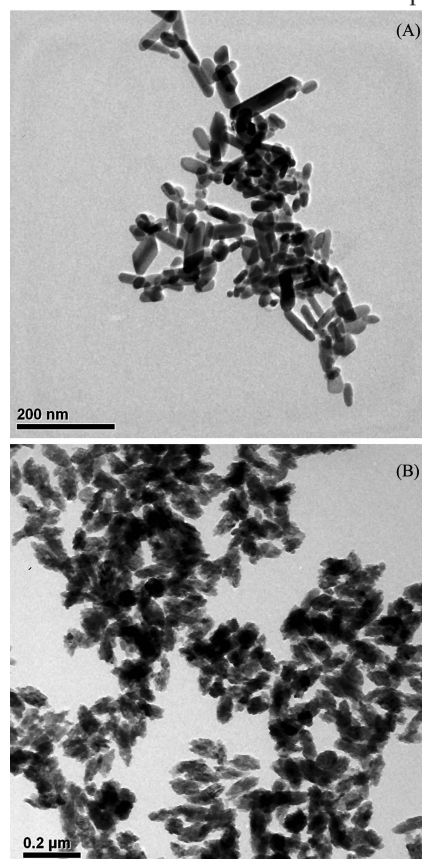


Fig.5 TEM images of CHA(A) ( $\text{PO}_4^{3-}/\text{CO}_3^{2-}$ : 5/1) and (B) ( $\text{PO}_4^{3-}/\text{CO}_3^{2-}$ : 2/4)

CHA particles varies with the ratio of  $n_{\text{PO}_4^{3-}}/n_{\text{CO}_3^{2-}}$ . The products are rod-like particles with size of ca.  $20 \times 70$  nm when the ratio of  $n_{\text{PO}_4^{3-}}/n_{\text{CO}_3^{2-}}$  is not less than 1 (typically as shown fig.5 (A)), and the particles turned into spindle-like particles when the ratio is less than 1 (fig.5(B)). This variation of morphology is possibly due to the coexistence of CHA and  $\text{CaCO}_3$  particles as indicated in its XRD patterns(Fig.3).

### 3 Conclusions

In conclusion, CHA were rapidly and continuously synthesized in supercritical water by using a tubular reactor. Results show that 30 seconds are enough to produce fully crystalline CHA nano-rods at  $380^\circ\text{C}$  and 24 MPa. When the ratio of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  is not less than 1, the  $\text{CO}_3^{2-}$  ions mainly substitute for  $\text{PO}_4^{3-}$  in

apatite structure; but  $\text{CO}_3^{2-}$  ions could react with  $\text{Ca}^{2+}$  to form  $\text{CaCO}_3$  phase when the ratio of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  is less than 1.

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