Advanced Powder Technology xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Synthesis of hollow structural hydroxyapatite with different morphologies using calcium carbonate as hard template

Xu Xia [a], Jiwei Chen [a], Juan Shen [a,b,*], Di Huang [c], Peizhen Duan [a], Guohong Zou [a]

[a] School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China
[b] State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, PR China
[c] College of Mechanics, Taiyuan University of Technology, Taiyuan 030024, PR China

ARTICLE INFO

Article history:
Received 10 July 2017
Received in revised form 9 March 2018
Accepted 13 March 2018
Available online xxxx

Keywords:
Calcium carbonate
Conversion
Hydroxyapatite
Hydrothermal treatment
Formation mechanism

ABSTRACT

Hydroxyapatite (HAp) with hollow structure was successfully synthesized by hydrothermal process of as-prepared calcium carbonate used as a hard template and calcium sources in a diammonium phosphate solution. Calcium carbonate was fabricated by precipitation, which possessed different morphologies such as balls, rods and blocks through regulating the amount of citric acid. The synthesized powders were characterized by X-ray diffraction (XRD), Fourier transform infrared spectrograph (FT-IR), field-emission scanning electron microscope (FESEM) and high-resolution transmission electron microscopy (HRTEM) and nitrogen adsorption–desorption. Results indicated that different morphologies calcium carbonate could convert to hollow structural HAp with the higher BET surface area and the mesopores. Hydrothermal temperature and hydrothermal time play a slight role on transition percentage. As hydrothermal temperature and hydrothermal time increased, the conversion rate of calcium carbonate to hydroxyapatite increased. The possible formation mechanism of hydroxyapatite was preliminarily investigated. The resultants of HAp are interesting materials for drug delivery and sustained-release.

1. Introduction

Recently, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) with specific morphologies has been attractive to chemists and material researchers because the performance of HAp depends greatly on its morphology and structure [1]. Therefore, the development of new technology used to control morphologies and structures has been a hot topic. Various shapes of hydroxyapatite including nanowire [2], rod-shaped structure and flower-like structure [3,4] have been synthesized and used as functional biomaterials for bone tissue engineering applications [5]. For example, Kumar and Girija [4] have obtained flower-like HAp nanostructure from eggshell. Zhang et al. [6] have successfully fabricated rod-shaped HAp with mesoporous structure by a hydrothermal method using Pluronic block co-polymer F127 as the template. These kinds of hydroxyapatite are potential candidates in medical application such as bone implant materials [5]. However, to our knowledge, the preparation of HAp with atypical morphology has only rarely been reported.

Various approaches have been used to synthesize HAp, including coprecipitation [7–9], sol-gel [10–12], microwave-assisted synthesis method [13,14], glass conversion method [15–17], template-directed method [18,19] and hydrothermal reaction [20–22], et al. The template-directed method is divided into soft and hard template, which have been shown to be an interesting approach for fabricating HAp with various morphologies [23]. Hard templates-directed method has a stronger restrictive effect on the preparation of nanostructures, and can exactly control the morphologies and sizes of nanomaterials. Therefore, hard-template synthesis approach can get corresponding morphologies and sizes of HAp by controlling various templates. Besides, it is found that calcium carbonate could be converted to HAp under hydrothermal treatments according to literatures [24,25]. Chen et al. [26] fabricated hollow nano-structured hydroxyapatite microspheres *via* microwave transformation method using hollow $CaCO_3$ precursor microspheres. Holopainen et al. [27] found that $CaCO_3$ fibers could be converted to nanocrystalline hydroxyapatite fibers by treatment in a dilute phosphate solution. Hence, calcium carbonate is an ideal template used to synthesize HAp without post-treatment of hard template.

* Corresponding author at: School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China.
E-mail address: juanshen@swust.edu.cn (J. Shen).

https://doi.org/10.1016/j.apt.2018.03.021
0921-8831/

Table 1
Different reaction conditions for preparation of hydroxyapatite.

Samples	$(NH_4)_2HPO_4$ (mol)	$CaCO_3$ (mol)	Hydrothermal temperature (°C)	Hydrothermal time (h)
S1	0.0024	0.0040	140	20
S2	0.0024	0.0040	140	30
S3	0.0024	0.0040	140	48
S4	0.0024	0.0040	180	20
S5	0.0012	0.0020	140	20
S6	0.0048	0.0080	140	20

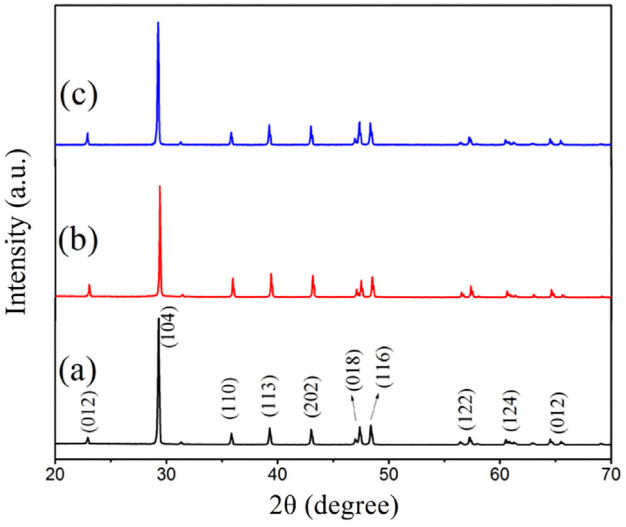

Fig. 1. XRD patterns of as-prepared $CaCO_3$: (a) balls; (b) rods; (c) blocks.

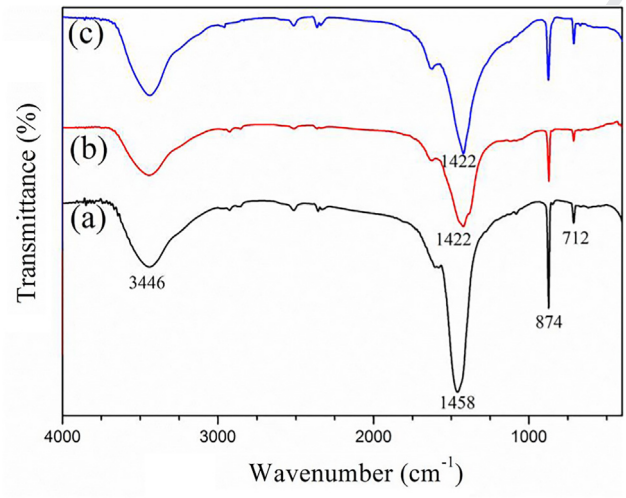

Fig. 2. FTIR spectra of as-prepared $CaCO_3$: (a) balls; (b) rods; (c) blocks.

Herein we report the successful novel preparation methodology of hollow hydroxyapatite with different morphologies, such as, ball-shape, rod-shape and block-shape. These atypically shaped particles were generated through a template-directed converted mechanism. Calcium carbonate is used as a hard template for regulating formation of hydroxyapatite with specific morphology through a hydrothermal process. In this study, calcium carbonate and citric acid as raw materials which overcame expensive cost and toxicity, and obtained products were free from contamination from other templates and surfactants. In addition, in order to improve constituent and crystallinity of HAp, the effects of reaction temperature, reaction time and the amount of reactant during the transition process were investigated. A possibly formation mechanism was proposed.

2. Materials and methods

2.1. Materials

Anhydrous sodium carbonate (Na_2CO_3, 99%), citric acid ($C_6H_8O_7$, 99%) and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, 99%) were purchased from Kelong Chemical Inc (Sichuan, China). Anhydrous calcium chloride ($CaCl_2$, 99%) was obtained from Aladdin (Shanghai, China). Deionized water was used in all experiments. All chemicals were commercially available and used as received.

2.2. Synthesis of calcium carbonate

Calcium carbonate was prepared by precipitation and the morphologies was controlled by the addition of citric acid according to the literature [28,29]. $CaCl_2$ (0.010 mol, 0.030 mol, 0.050 mol and 0.100 mol) and different amounts of $C_6H_8O_7$ were dissolved in 100 mL of deionized water at 30 °C. The amounts of $C_6H_8O_7$ were decided by the molar ratio of citric acid radical and calcium ion, which were 2:1, 1:1, 2:3 and 0, respectively, based on the molar ratio of calcium citrate (Citric acid radical/Ca ion = 2:3) . The pH was adjusted to 5.8 with NaOH solution (1.0 mol/L). Subsequently, Na_2CO_3 (0.010 mol, 0.030 mol, 0.050 mol and 0.100 mol) was dissolved into 100 mL deionized water, which was slowly added into the above solution under vigorous stirring, yielding the milky suspension of which pH was adjusted to about 12.0 by sodium hydroxide solution (1.0 mol/L), setting for 24 h after stirring for 1 h at 30 °C. The obtained calcium carbonate was rinsed with deionized water several times, and dried at 60 °C for 24 h. According to a series of experiments listed above, calcium carbonate with different morphologies was found. The reactant amounts were $CaCl_2$ (0.05 mol), Na_2CO_3 (0.05 mol) and citric acid (0.100 mol, 0.033 mol and 0 mol), which were corresponding to ball-shape, rod-shape and block-shape respectively. The fabricated calcium carbonate was used for next step reaction.

2.3. Synthesis of hydroxyapatite

0.0024 mol $(NH_4)_2HPO_4$ was dissolved in 40 mL deionized water, followed by the addition of 0.0040 mol as-prepared different morphologies of calcium carbonate. The Ca/P molar ratios of all samples were fixed at 1.67. The pH was maintained constant of 12.0 with NaOH solution in the entire process. The liquid was transferred into autoclaves and hydrothermal reaction took place at different hydrothermal conditions which are summarized in Table 1. The obtained HAp was washed with deionized water, and dried at 60 °C for 24 h.