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Rapid synthesis of hollow nano-structured hydroxyapatite microspheres via microwave transformation method using hollow $CaCO_3$ precursor microspheres

Hongguang Chen[a,*], Senlin Leng[b,*]

[a]*Shanghai Nanotechnology Promotion Center, Shanghai 200237, China*
[b]*Institute of Physics and Electronics Engineering, Tongren University, Tongren 554300, China*

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Abstract

Hollow nano-structured hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HAp] microspheres were rapidly synthesized via microwave transformation of a sacrificial hard-template of similarly structured calcium carbonate ($CaCO_3$) hollow microspheres in Na_3PO_4 aqueous solution. Results showed that the microwave process significantly increased transformation efficiency. Pure hollow HAp microspheres could be obtained within ultra-short-period of 30 min via the microwave transformation process, in comparison to over 48 h in the traditional hydrothermal transformation method. These studies suggest that the microwave assisted hard-template transformation process is an effective approach to synthesize HAp with high efficiency. The resulting hollow nano-structured HAp microspheres may have applications in drug-delivery and serve as materials for chemical and environmental applications.

Keywords: Hydroxyapatite; Hollow microspheres; Microwave; Ultrafast synthesis; Hard-template transformation

1. Introduction

Recently, the fabrication of materials with three-dimensional (3D) architectures has been attracting increased attention due to their unique chemical, physical, biological and environmental properties and potential applications in advanced functional materials [1–3]. Therefore, the search for new strategies for the control of 3D architecture materials has garnered much interest. Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HAp] has been widely used in biomedical materials, chemical and environmental engineering and industrial and technological fields [4–12]. The performance of HAp in these applica tions depends greatly on its morphology and 3D architecture [1,3,4]. Hollow nano-structured HAp microspheres have attracted interest due to their high specific surface area, large hollow volume and novel 3D hierarchical architecture. These properties allow for the improvement of surface adsorption and reaction activity, incorporation of higher drug dosage and better controlled release rates [4,13,14].

Until now, many methods have been developed to synthesize hollow nano-structured HAp microspheres. The assembly approach using amino acids [15], surfactants, polymers, DNA, proteins and chelators as assistants or templates is a popular strategy to synthesize the hollow HAp microspheres [4,16–18]. For example, Qi et al. reported a DNA-templated hydrothermal synthesis of HAp nanosheet-assembled hollow microspheres [14]. Solvothermal synthesis is another facile method to fabricate hollow HAp microspheres. Ma and Zhu prepared the hierarchically nano-structured HAp hollow microspheres assembled from nanorods using water and *N*,*N*-dimethylformamide (DMF) as mixed solvents [17]. The microwave/sonication-surfactant combination techniques were also developed to

*Corresponding authors: Tel./fax: 86 21 64101616 223/54290007.
E-mail addresses: hgchen@snpc.org.cn (H. Chen), lengsenlin@sohu.com (S. Leng).

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rapidly synthesize hollow HAp microspheres using chelate reagents as template or using creatine phosphate as an organic phosphorus source [19,20]. However, a large amount of the assistant reagents and templates, costly phosphorus sources, and even unhealthy organic solvents are required in these reported methods. Most recently, Lin et al. developed a novel hydrothermal transformation method to fabricate hollow HAp microspheres using the similarly structured $CaCO_3$ microspheres as hard-templates [1]. However, the hydrothermal process is time-consuming, usually requiring dozens of hours for the complete transformation of $CaCO_3$ into HAp. Recently, the use of microwave energy to heat chemical reactions had attracted increasing attention for its successful application in organic syntheses, polymer chemistry, material sciences and nanotechnology. Usually, the microwave dielectric heating dramatically reduces the processing time, increases product yield and enhances material properties, when compared with conventional heating methods [21].

In the present study, a microwave-assisted transformation process was applied to rapidly synthesize hollow nanostructured HAp microspheres using similarly structured $CaCO_3$ microspheres as hard-templates. The effects of microwave irradiation on the resulting material characteristics were investigated in comparison with the conventional hydrothermal transformation method.

2. Materials and methods

All of the applied reagents (Shanghai Chemical Co., Ltd., PR China) were analytical grade and were used without further purification in this study. The hard-template of hollow $CaCO_3$ microspheres was synthesized by chemical precipitation method according to the previous report [1]. Briefly, a 0.2 M $CaCl_2$ and 0.1 M sodium dodecyl sulfate (SDS) solution with the same volume were mixed under vigorous stirring, and then a 0.2 M Na_2CO_3 solution was rapidly added into the above mixed solution under vigorous stirring to obtain a white suspension. The reactant molar ratio of Ca/CO_3^{2-} was set at 1.0. After complete addition, the white suspension was further stirred for 2 h followed by washing eight times with distilled water and two times with absolute ethyl alcohol. After washing, the remaining liquid was separated by vacuum filtration. Finally, the obtained products (hollow $CaCO_3$ microspheres) were dried at 120 °C for 24 h.

For the microwave-assisted transformation process, the 1 g hard-templates were mixed with the 85 mL Na_3PO_4 (0.2 M) aqueous solution. Then, the mixtures were transferred to a 150 mL three-neck flat-bottomed flask and placed in a program-controlled microwave reactor (XO-SM50, Nanjing Xianou Instrument Manufacturing Co., Ltd., China). The reaction vessel was equipped with a reflux condenser and a temperature sensor. Various reaction parameters, such as the power of microwave and the reaction time, were adjustable. In a typical preparation process, the initial microwave power was set at 300 W. The temperature of the reaction system was heated to 100 °C, and the power of microwave was then program controlled between 50 and 300 W to maintain the reaction temperature. After reaction for 0, 5, 15 and 30 min, samples were cooled to room temperature; after microwave treatment, the resulting products were filtrated and washed with distilled water and anhydrous ethanol three times, respectively. The obtained products were dried at 120 °C for 24 h. For comparison, a traditional hydrothermal transformation method was applied to prepare the HAp without microwave irradiation. In this method, the 1 g precursors were mixed with the 85 mL Na_3PO_4 (0.2 M) aqueous solution. Then, the mixtures were transferred into 100 mL stainless steel autoclaves and heated at 180 °C for 0, 6, 24 and 48 h, followed by cooling to room temperature naturally. After the hydrothermal

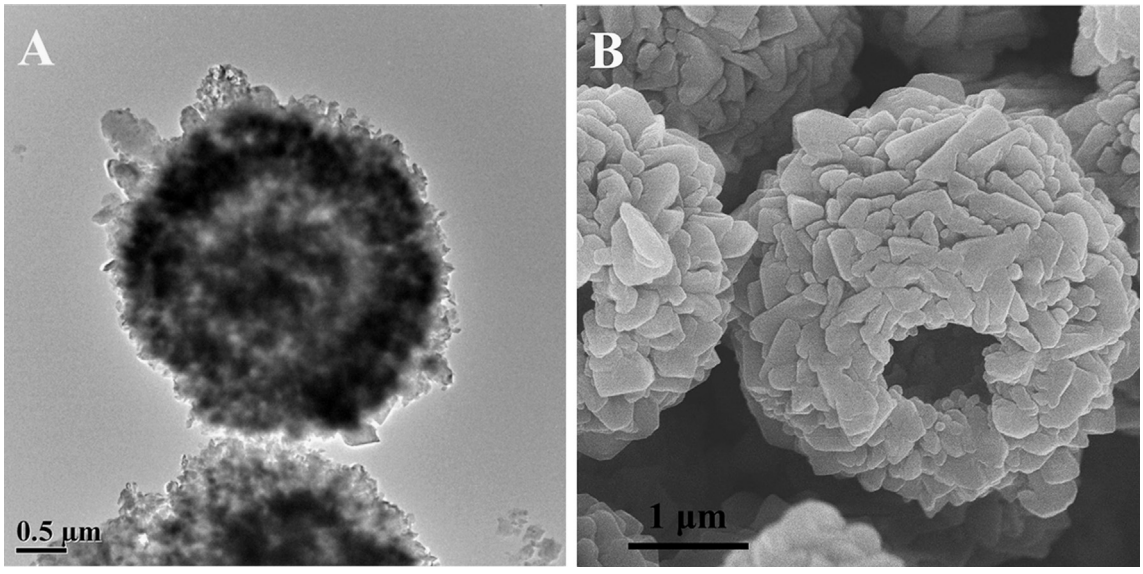

Fig. 1. FETEM (A) and FESEM (B) images of the synthetic hollow $CaCO_3$ microspheres.