journal

J. Am. Ceram. Soc., 91 [11] 3580–3584 (2008)
DOI: 10.1111/j.1551-2916.2008.02690.x

Rapid Formation of Mono-Dispersed Hydroxyapatite Nanorods with Narrow-Size Distribution via Microwave Irradiation

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Monodispersed single-crystal hydroxyapatite (HAp) nanorods with nearly uniform diameters and lengths of, respectively, about 25 and 100 nm were rapidly synthesized using a template-free and convenient microwave irradiation method. Precipitation of HAp occurred directly in a calcium-phosphate precursor solution containing ethylenediaminetetraacetic acid (EDTA) as a capping agent and using microwave irradiation of 900 W power and 2.45 GHz frequency as the heating source. Transmission electron microscopy observations revealed that faceted surfaces and narrow-size distribution were two interesting features of the HAp nanorods obtained. The selected area electron diffraction pattern of the nanorods obtained clearly confirmed their single crystalline nature and the growth along the basal (001) planes. Furthermore, the formation mechanism of HAp nanorods was clearly proposed, identifying the influences of EDTA and microwaves in the growth process.

I. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) is the most well-known bioceramic that has been widely used as bone and tooth implants and replacements, due to its similarity to the mineral compartment of human hard tissues.[1,2] Also, it is compatible with the biological body environment[3,4] and results in the formation of new bone cells (i.e., osteointegration).[1] Although the biological behavior of HAp is extremely favorable, its poor mechanical property is a drawback to clinical applications.[3,5,6] Therefore, in recent years, many efforts have been focused on improving the mechanical behavior of HAp bioceramics.[7,8]

Several studies confirmed that nanosize one-dimensional (1D) ceramic powders substantially improve the mechanical properties of the ceramic materials.[9,10] It has been shown that dense bioceramics with high strength and fracture toughness can be prepared using 1D HAp nanostructures (such as nanorods, nanowires, and nanofibers).[3,11] In addition, due to their interesting physical and chemical properties and their extensive biomedical applications, 1D nanobiomaterials have attracted the interest of researchers in recent years and therefore more attention has been focused toward developing effective, facile, and rapid synthetic methods for the production of these nanostructures.[5,12] Considering HAp, 1D morphologies like nanorods, nanowires, and nanofibers have been synthesized by various methods such as hydrothermal,[3] mechanochemical,[11] electrospinning,[1] chemical precipitation,[13] and microwave irradiation.[2,14]

Microwave synthesis is a mild, convenient, rapid, and efficient method for the preparation of nanostructure inorganic materials,[15,16] which results in the production of high-purity materials with small particle sizes and a narrow size distribution.[17] The prominent feature of this method is a drastical reduction of the reaction time. Several investigations have reported the formation of well-crystallized and high-purity HAp nanoarchitectures by means of microwave irradiation. Lerner *et al.*[18] reported the formation of pure HAp in 5 min from an aqueous solution using microwave irradiation. Liu *et al.*[2] and Rameshbabu *et al.*[14] also showed that the HAp nanostructures can be obtained via microwave irradiation in 30 and 15 min, respectively. Yang *et al.*[6] have prepared HAp under microwave irradiation at various durations of time from 5 to 120 min and showed that the crystallinity of the HAp increased with the time of microwave irradiation. Cao *et al.*[19] reported on microwave-assisted-solid state synthesis of HAp nanorods at room temperature. They showed that HAp cannot be obtained without microwave heating and different morphologies can be prepared by varying the microwave heating time.

In this paper, we report a facile, fast, and template-free method for the formation of monodispersed, single-crystalline HAp nanorods with a narrow size distribution under the influence of microwave irradiation and with the help of ethylene diamine tetraacetic acid (EDTA) as a capping agent to control nucleation and growth processes. The effect of EDTA on the formation mechanism of the nanorods was investigated.

II. Experimental Procedure

All the chemical reagents were analytical grade and were used without further purification. Starting materials were calcium nitratetetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, Merck, Darmstadt, Germany) and dibasic anhydrous sodium phosphate (Na_2HPO_4, Merck) as the sources of calcium and phosphate, respectively. EDTA ($C_{10}H_{16}N_2O_8$, Merck) was used as a capping agent and pH was controlled by sodium hydroxide pellets (NaOH, Merck).

In a typical synthetic method, a 50 mL solution containing $Ca(NO_3)_2 \cdot 4H_2O$ (0.1*M*) and EDTA (0.1*M*) was made and stirred at room temperature for 30 min to become fully homogenized. Then, the homogeneous solution obtained was introduced into 50 mL of Na_2HPO_4 (0.06*M*) solution. The pH of the solution was adjusted to 11 with addition of NaOH pellets. Magnetic stirring was continued at all steps of the process. After stirring for 10 min, the ready-adjusted precursor solution was placed in a microwave irradiation chamber (2.45 GHz, 900 W, TEK-3610, Tecnokit, Milan, Italy) in the continuous heating mode for 150 s. The resulting white precipitate was separated by centrifuging at 6000 rpm for 10 min. The resulting product was washed with distilled water, ethanol, and acetone several times and then dried at 60°C for 12 h.

X-ray diffraction XRD, analysis (Simens D500 diffractometer, Erlangen, Germany) was used to characterize the constituted phase of the resulting HAp powder with monochromatic Cu$K\alpha$ ($\lambda = 0.15418$ nm) radiation. Using the KBr pellet technique, Fourier transform infrared (FT-IR) spectroscopy (Bruker, Vector33, Karlsruhe, Germany) was used to identify the quality and composition of the HAp. The morphology and size of the obtained HAp was characterized by transmission electron microscopy (TEM, Philips CM200, Amsterdam, The Netherlands). Thermal analysis and phase stability of the synthesized

T. Troczynski—contributing editor

Manuscript No. 23815. Received October 4, 2007; approved August 4, 2008.
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