

Self-assembled dahlia-like cadmium hydrogen phosphate hydrate nanostructures as templates for cadmium hydroxyapatite hexagonal prisms

Hamed Arami, Mahyar Mazloumi, Razieh Khalifehzadeh, Aidin Lak, S.K. Sadrnezhaad*

Materials and Energy Research Center, P.O. Box 14155-4777, Tehran, Iran

Received 31 May 2007; received in revised form 6 August 2007; accepted 26 August 2007

Communicated by H. Fujioka

Available online 31 August 2007

Abstract

Cadmium hydroxyapatite (Cd-Hap, $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$) and cadmium hydrogen phosphate hydrate ($\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$) nanostructures with average crystallite sizes of about 38 and 44 nm, respectively, were prepared through a simple chemical process. The formation mechanism and characteristics of the $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ precipitates prior to the hydrothermal process and Cd-Hap during the hydrothermal treatment were investigated with XRD, SEM, TEM and BET analyses. It was found that self-assembled dahlia-like $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ nanostructure precipitates were formed due to interlace of preliminary nanosheets prior to the hydrothermal process, while nanostructure Cd-Hap hexagonal prisms were prepared after 15 h of hydrothermal treatment.

© 2007 Elsevier B.V. All rights reserved.

PACS: 81.07.-b; 81.20.ka; 61.46.+w

Keywords: A1. Nanostructures; A2. Growth from solutions; B1. Cadmium compounds; B1. Nanomaterials

1. Introduction

Calcium hydroxyapatite (Ca-Hap, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), which is the major prototype compound of biological apatites in the endoskeleton of the vertebrates [1], is tolerant to cationic and anionic substitutions [2]. Various cation-exchanged hydroxyapatites have been synthesized through the replacement of divalent ions such as Sr^{2+} [3], Ba^{2+} [4], Pb^{2+} [5], Cu^{2+} [6] and Cd^{2+} [2,7]. Cadmium substitutes for calcium ions in hydroxyapatite structure, located in Ca(II) sites of apatite lattice with symmetry m at $z = \frac{1}{4}$ or $\frac{3}{4}$ [8] resulted in formation of Cd-Hap phase [2,7].

Several researchers have investigated the formation of cadmium hydroxyapatite (Cd-Hap), and determined its crystal structure [9], thermal behavior [10,11] and IR spectra [12]. Yasukawa et al. [13] prepared well-crystallized and needle-like cadmium hydroxyapatite particles via a

two-step wet chemical method utilizing acetamide to control the pH of the solution. They prepared cadmium hydrogen phosphate hydrate ($\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$, Cd₅-P) precursor after 1 day aging followed by 1–7 days aging for transformation into the Cd-Hap needles. Ropp et al. [11] have also reported that Cd₅-P is the stable cadmium phosphate precipitate over a wide range of temperature, concentration and pH values, and its conversion to the Cd-Hap requires several weeks. Zhu et al. [14] have investigated the hydrothermal formation of Cd-Hap and showed that cadmium apatite formed from intermediate phases of Cd₅-P and $\text{Cd}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ in the low and high pH reaction media, respectively. They reported that the morphology of the Cd-Hap crystals varied from stubby hexagonal prismatic to rod-like in shape with the increase in pH value of the phosphate solution.

In this work, the detailed growth mechanism of the room-temperature precipitation of the self-assembled dahlia-like Cd₅-P phase and its hydrothermal transformation to prismatic cadmium hydroxyapatite phase was investigated.

*Corresponding author.

E-mail address: arami@merc.ac.ir (S.K. Sadrnezhaad).