



Particle size and shape modification of hydroxyapatite nanostructures synthesized via a complexing agent-assisted route



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ARTICLE INFO

Article history:

Received 30 October 2013

Received in revised form 3 March 2014

Accepted 3 April 2014

Available online 13 April 2014

Keywords:

Nanostructures
Complexing agent
Hydroxyapatite

ABSTRACT

In this work, hydroxyapatite (HAP), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, nanostructures including nanorods, nanobundles and nanoparticles have been prepared via a simple precipitation method. In the present method, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ were used as calcium and phosphorus precursors, respectively. Besides, the Schiff bases derived from 2-hydroxyacetophenone and different diamines were used as complexing agents for the in situ formation of Ca^{2+} complexes. The formation mechanism of 0-D and 1-D nanostructures of HAP was also considered. When the complexing agents could coordinate to the Ca^{2+} ions through N and O atoms to form the $[\text{CaN}_2\text{O}_2]^{2+}$ complexes, HAP nanoparticles were generated. On the other hand, nanorods and nanobundles of HAP were obtained by forming the $[\text{CaN}_2]^{2+}$ as well as $[\text{CaO}_2]^{2+}$ complexes in the reaction solution. This work is the first successful synthesis of pure HAP nanostructures in the presence of Schiff bases instead of using the common surfactants.

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1. Introduction

Within the last four decades, the use of specially designed ceramics for the repair of damaged parts of the body has improved the quality of life. Excellent biocompatibility, ability to promote cellular functions, and osteoconductivity are the remarkable properties of bioceramics [1, 2]. The bioceramics can be divided into two large groups: bioinert and bioactive ceramics [3]. The bioinert ceramics have almost no influence on the surrounding living tissues like ZrO_2 and Al_2O_3 . In contrast, the bioactive ceramics like calcium phosphates are able to bond with the living tissues.

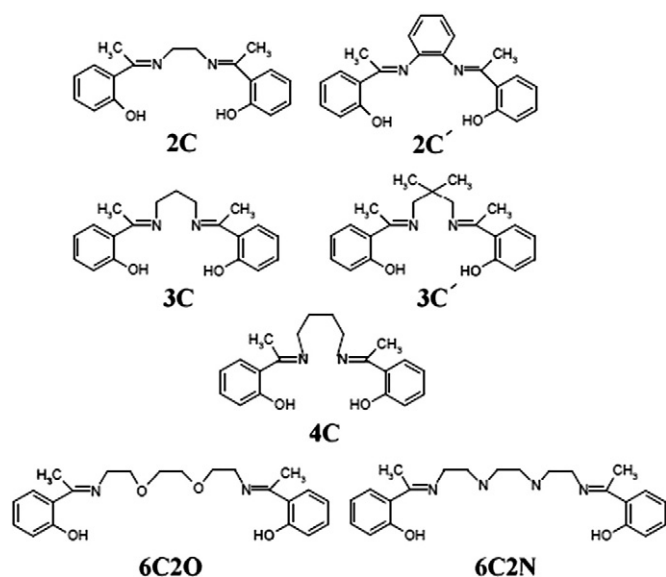
Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; Ca/P (molar ratio) = 1.67) is one of the most attractive calcium phosphates due to its clinical applications. Since HAP has excellent biocompatibility and surface active properties with living tissues, it has become one of the most important materials for artificial bone and tissue engineering [4,5]. Besides the biological applications of HAP as bone and tooth implants, porous materials based on hydroxyapatite are good candidates for drug delivery systems [6,7]. In bioanalytical chemistry, HAP columns for the separation of ribonucleic acid (RNA) and deoxyribonucleic acid (DNA) in biological samples [8], and biocompatible fluorescent probes based on terbium-doped HAP nanoparticles are widely used [9]. In addition, HAP is known

as an efficient catalyst because of its interesting properties such as ion-exchange ability, adsorption capacity, non-toxicity, acid–base properties, and thermal stability [10,11]. For example, the removal of Pb^{2+} ions from aqueous solution by hydroxyapatite [12], the removal of Congo red (CR) dye from aqueous solution by hydroxyapatite–chitosan composite [13], the transesterification of soybean oil by hydroxyapatite loaded with strontium [14], and 1-hexene hydroformylation by a high surface area hydroxyapatite as a support for $\text{Rh}(\text{CO})_2(\text{acac})$ were developed [15]. Recently, the use of HAP nanoparticles in protein adsorption for fibrinogen and bovine serum albumin was also reported [16].

Up to now, many kinds of chemical synthesis methods for the preparation of HAP nanostructures such as hydrothermal [16], sol–gel [17], sonochemical [18], precipitation [19], microemulsion [20], microwave [21], mechanochemical [22], and surfactant-assisted approach [23] have been introduced. Among the present methods, precipitation approaches provide several advantages such as production of homogeneous and nano-sized grains with narrow particle size distribution, excellent reproducibility, high yield, low synthesis temperature from room temperature to 200 °C, and facile control of the reaction conditions [24]. Despite these advantages, the crystal growth of the nuclei formed in the initial stages may take place during the precipitation process in the reaction solution [25]. This phenomenon leads to the generation of nanocrystals with higher dimensions. One strategy to overcome this drawback is the use of complexing agents or surfactants, which can arrest the crystal growth. So far, numerous size-controlled synthesis methods based on the precipitation approach by using the common surfactants including polyethylene glycol, triethanolamine

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Scheme 1. Chemical structure of the as-synthesized Schiff bases.

(TEA), ethylenediamine tetraacetic acid (EDTA), diethanolamine (DEA) [26], ethylene glycol [27], citric acid, sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS) [28], cetyltrimethyl ammonium bromide (CTAB) [29], and (2-ethylhexyl) sulfosuccinate (AOT) [30] have been introduced.

Herein, we report a novel precipitation route for the synthesis of pure HAP nanostructures with the aid of Schiff bases. Schiff bases, containing an imine or azomethine group ($-\text{RC}=\text{N}-$), are usually formed by the condensation of a primary amine with an active carbonyl [31]. It was reported that Schiff bases do not produce toxic materials to living organism, and they can be applied as chelating agents to generate metal complexes, which can be used in drug delivery systems [32,33]. Although the use of Schiff bases to control particle sizes and shapes of nano-sized materials has been introduced [34–36], the application of these compounds for the preparation of HAP nanostructures has not yet been reported. In this paper, we describe a novel precipitation method to synthesize HAP nanostructures. In this synthesis method, the Schiff bases derived from 2-hydroxyacetophenone and different diamines were prepared, characterized, and then used as complexing agents to produce HAP nanostructures with different morphologies. The products were analyzed by techniques such as FT-IR, ^1H NMR, XRD, FE-SEM, and TEM. By comparing the synthesis conditions of the present work and the available reports [17,29], it was found that this method has many advantages such as: simple control of morphology and particle size of HAP, fabrication of pure monophasic HAP nanostructures without using any calcination stage, and preparation of HAP nanostructures at a short time and low temperature.

Table 1
Corresponding diamines and production yield of Schiff bases.

Schiff base samples	Corresponding diamine	Yield (%)
2C	Ethylenediamine	93.0
2C'	2-Phenylenediamine	92.5
3C	1,3-Diaminopropane	92.0
3C'	2,2-Dimethyl-propylenediamine	92.8
4C	1,4-Diaminobutane	94.5
6C2O	1,8-Diamino-3,6-dioxaoctane	93.3
6C2N	Triethyltetramine	92.5

2. Materials and methods

2.1. Materials

All the chemicals with analytical grade were used as received. 2-Hydroxyacetophenone, ethylenediamine, 2-phenylenediamine, 1,3-diaminopropane, 2,2-dimethyl-propylenediamine, 1,4-diaminobutane, 1,8-diamino-3,6-dioxaoctane, triethyltetramine, calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$), sodium hydroxide (NaOH), methanol, and chloroform were purchased from Merck Co.

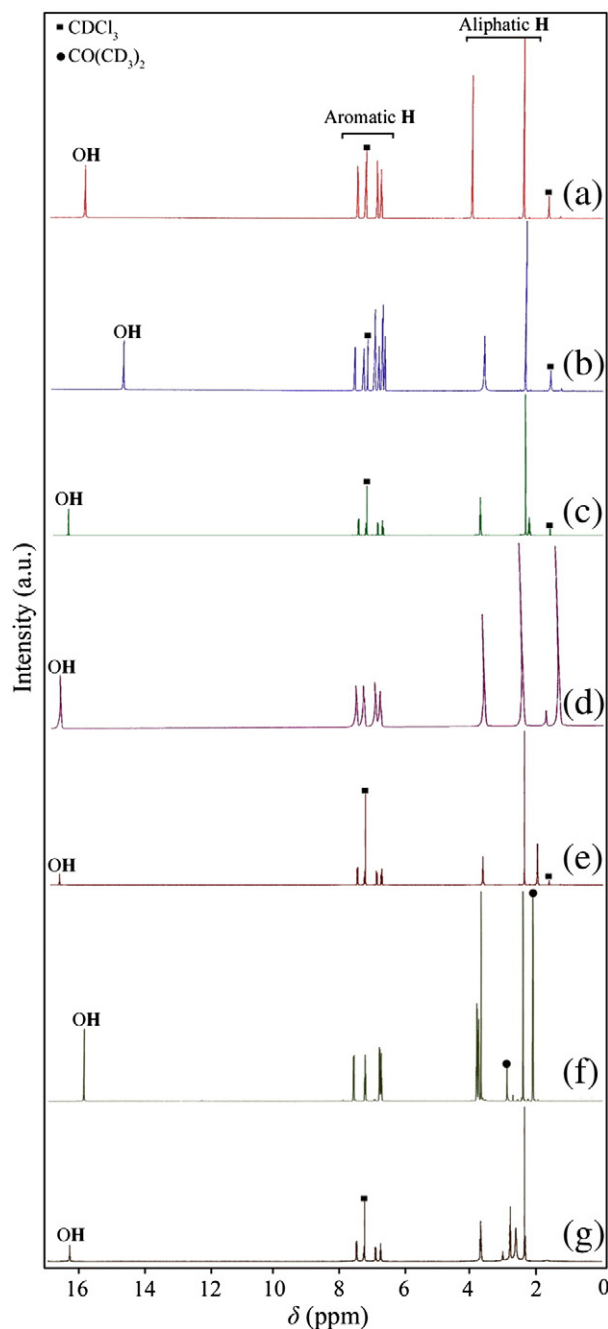


Fig. 1. ^1H NMR spectra of complexing ligands: (a) 2C; (b) 2C'; (c) 3C; (d) 3C'; (e) 4C; (f) 6C2O; and (g) 6C2N.

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