Chemical Engineering Journal 252 (2014) 173–184

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Simple morphology-controlled fabrication of hydroxyapatite nanostructures with the aid of new organic modifiers

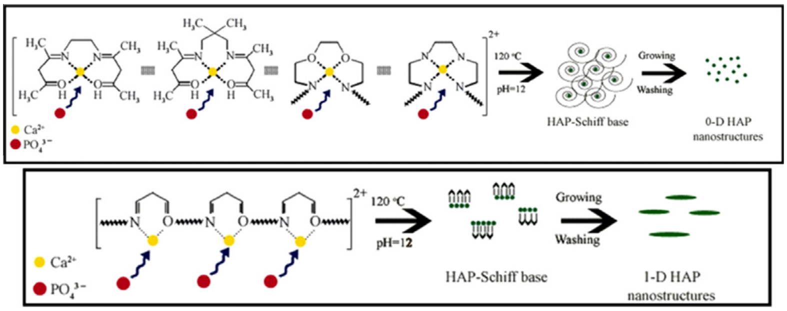
Fatemeh Mohandes [a], Masoud Salavati-Niasari [b,*]

[a] *Department of Inorganic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, P. O. Box 87317-51167, Islamic Republic of Iran*
[b] *Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box 87317-51167, Islamic Republic of Iran*

HIGHLIGHTS

- Hydroxyapatite nanostructures have been prepared by a simple precipitation method.
- To control shapes of the products, chelating ligands based on Schiff bases were used.
- The Schiff bases derived from acetylacetone were applied as novel chelating ligands.
- Different morphologies of hydroxyapatite nanostructures have been formed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 January 2014
Received in revised form 23 April 2014
Accepted 6 May 2014
Available online 14 May 2014

Keywords:
Nanostructure
Calcium phosphate
Chelating ligand
Hydroxyapatite

ABSTRACT

A novel precipitation route has been developed for the synthesis of hydroxyapatite (HAP) nanostructures with the aid of various Schiff bases. To control size and shape of HAP nanostructures, the Schiff bases derived from acetylacetone (Hacac) and different diamines were used as chelating ligands for the *in situ* preparation of Ca^{2+} complexes. In this method, $Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_2HPO_4$ were applied as calcium and phosphorus precursors, respectively. Moreover, the formation mechanisms of zero-dimension (0-D) and one-dimension (1-D) nanostructures of HAP were considered. When the Ca^{2+} ions could coordinate to the Schiff bases to form the $[CaN_2O_2]^{2+}$ and $[CaN_4]^{2+}$ complexes, HAP nanoparticles were generated. On the other hand, nanobundles and nanorods of HAP were obtained by forming the $[CaNO]^{2+}$ complexes in the reaction solution. This work is the first successful synthesis of pure HAP nanostructures in the presence of various Schiff bases.

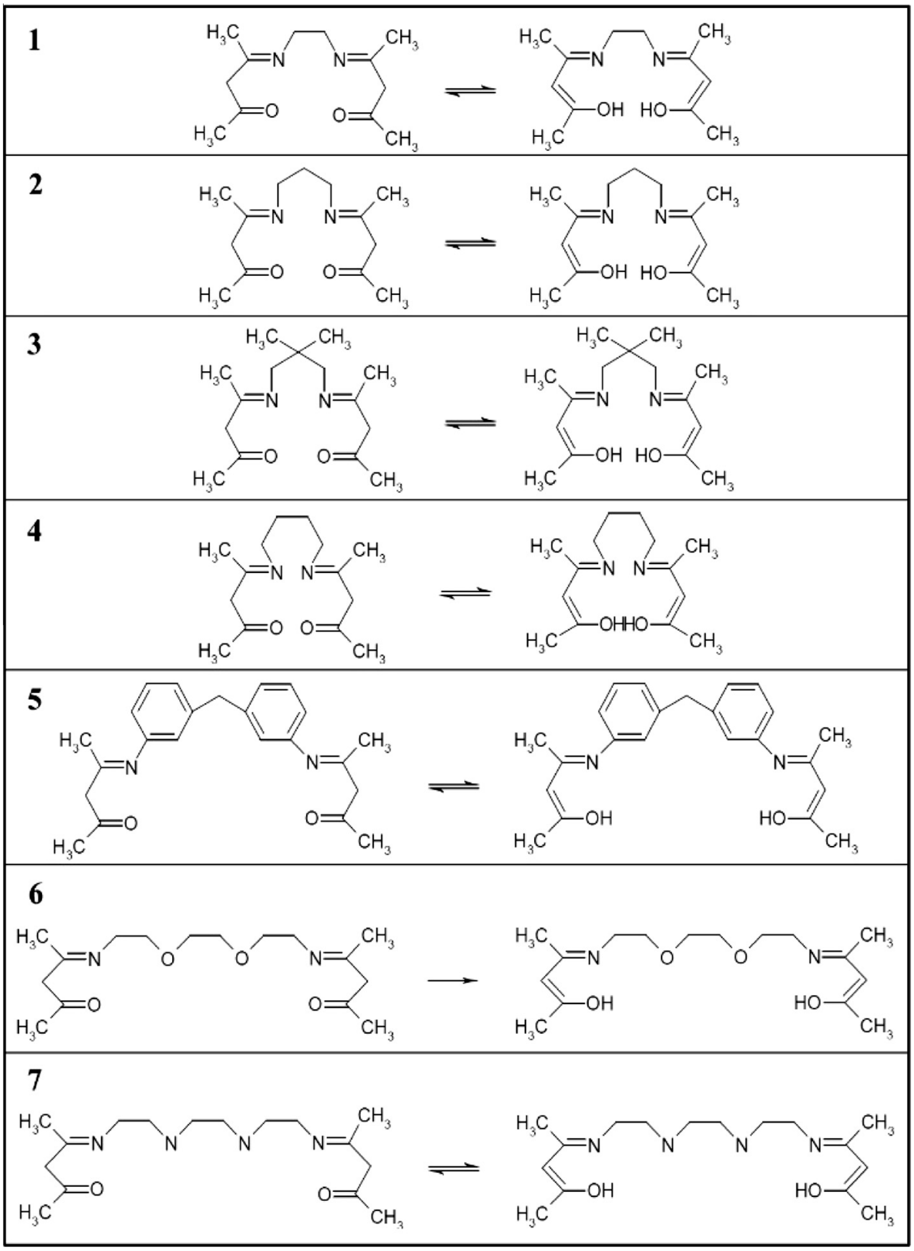
1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) is one of the most attractive calcium phosphates due to its excellent biocompatibility and surface active properties with living tissues [1]. It has become one of the most important materials for artificial bone [2,3]. It was reported that breast cancer frequently metastasizes to bone, where it leads to osteolytic bone degradation. For bone repairmen, Pathi et al. suggested a composite of HAP nanoparticles and poly (lactide-co-glycolide) [4]. Low crystalline HAP nanostructures with highly active surfaces have been used as carrier in drug and gene delivery systems. Bauer et al. studied the toxic effects of needle-like HAP particles on liver cancer cells [5]. Moreover, *in vivo* cancer hyperthermia study of magnetic hydroxyapatite nanoparticles doped by Fe^{2+} ions has been performed by Hou et al. [6]. In bioanalytical chemistry, HAP columns for the separation of ribonucleic acid (RNA) and deoxyribonucleic acid (DNA) in biological samples [7], and biocompatible fluorescent probes based on terbium-doped HAP nanoparticles are widely used [8]. In addition,

---

* Corresponding author. Tel.: +98 361 5912383; fax: +98 361 5552935.
E-mail address: salavati@kashanu.ac.ir (M. Salavati-Niasari).

http://dx.doi.org/10.1016/j.cej.2014.05.026
1385-8947/



Scheme 1. Chemical structures of the Schiff bases 1–7 and corresponding tautomers.

Table 1
Experimental results of the as-synthesized Schiff bases.

Schiff base No.	Corresponding diamine	Color and chemical state	Yield (%)
1	Ethylenediamine	Yellow solid	92.2
2	1,3-diaminopropan	Yellow solid	93.5
3	2,2-dimethyl-propylendiamine	Brown viscose liquid	–
4	1,4-diaminobutane	Yellow solid	93.8
5	4,4′-diaminodiphenylmethan	Yellow solid	93.0
6	1,8-diamino-3,6-dioxaoctane	Brown viscose liquid	–
7	Triethyltetramine	Brown viscose liquid	–

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 [9,10]. For example, the removal of Pb^{2+} ions from aqueous solution by hydroxyapatite [11], the removal of Congo red (CR) dye from aqueous solution by hydroxyapatite-chitosan composite [12], the transesterification of soybean oil by hydroxyapatite loaded with strontium [13], and 1-hexene hydroformylation by a high surface area hydroxyapatite as support for $Rh(CO)_2(acac)$ [14] were developed.

Among the presented methods for the synthesis of HAP nanostructures, precipitation approaches provide several advantages such as production of homogenous 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 [15]. 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 [16]. This phenomenon leads to the generation of nanocrystals with higher dimensions. One strategy to overcome this drawback is the use of chelating agents or surfac-