Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 39 (2013) 8995–9002

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Rod-like micelle templated synthesis of porous hydroxyapatite

Gunjan Verma[a,*], K.C. Barick[a], N. Manoj[a], A.K. Sahu[b], P.A. Hassan[a]

[a]Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India
[b]Glass and Advanced Materials Division, Bhabha Atomic Research Centre, Mumbai 400085, India

Received 7 February 2013; received in revised form 15 April 2013; accepted 28 April 2013
Available online 7 May 2013

Abstract

Use of macromolecular templates for controlling nanostructures of inorganic materials is an active area of research. In particular, oriented growth of hydroxyapatite in organic matrix is of great relevance to understand biomineralisation of bone and its potential biomedical applications. Natural bone being a composite of hydroxyapatite and collagen fibers, crystallization of hydroxyapatite in fibrous assemblies could mimic such biomineralisation. This motivated us to investigate the role of long rod-like micelles in modulating the structure of hydroxyapatite particles. In this article, we report the preparation of porous hydroxyapatite nanorods using rod-like micelles made up of a cationic surfactant cetyltrimethylammonium bromide (CTAB) and anionic hydrotrope sodium salicylate (SS) as a templating agent. The successful formation of hydroxyapatite crystals is evident from XRD, FTIR, TGA, SEM and TEM analyses. It has been observed that large hydroxyapatite nanorods of diameter ~50 nm are formed in surfactant mediated synthesis, whereas irregular shaped nanoaggregates of hydroxyapatite are obtained in the absence of surfactant. A comparative study on the porosity of hydroxyapatite clearly shows that monomodal distribution of mesopores with a peak at ~30 nm in the absence of surfactant while bimodal distribution of mesopores having maxima at ~4 nm and ~45 nm appear in hydroxyapatite prepared in the presence of surfactant template.

Keywords: Porosity; Hydroxyapatite; Rod-like micelles; Surfactant; Template synthesis

1. Introduction

Hydroxyapatite, with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$, is a biocompatible material that has been extensively studied and applied in a variety of fields due to its similarity with the mineral constituents of human bones and teeth [1,2]. Bone is a hybrid material composed of needle-shaped inorganic hydroxyapatite nanocrystals and organic collagen matrix. Its properties depend intimately on its nano-scale structures, which are dictated specifically by the collagen template. Synthetic hydroxyapatite is widely applied in biomedical engineering due to its excellent biocompatibility and bioactivity [3]. It is also used as a filler to replace amputated bone and in the reconstruction of damaged bones and tooth zones. Many prosthetic implants are coated with hydroxyapatite to promote bone growth in implant [4,5]. The textural properties of hydroxyapatite, such as pore size, pore volume, pore structure etc., are also very important in addition to their chemical composition and structure for bone-forming ability. The porous nature of biomaterials allows the in-growth of bone tissue to achieve full amalgamation with the living bones. Also the mesoporous structure makes it feasible to incorporate biologically active molecules such as drug, osteogenic agents etc. that can treat bone infection and diseases and promote bone tissue regeneration [6–10]. Significant research efforts have been devoted to synthesize hydroxyapatite with controllable properties and porous structure using various techniques such as the sol–gel method, hydrothermal reaction, precipitation method, mechano-chemical, emulsion technique, wet-chemical method as well as by using surfactants as templates [11–16]. Stupp and Braun suggested that some of the biomolecules such as proteins, glycoproteins, and polysaccharides control nucleation and growth of mineral phases and thus manipulate their microstructure and physical properties [17]. By using this concept, they synthesized apatite-based materials in aqueous solutions of organic macromolecules, including homopolymer poly(amino acids), low molar mass

*Corresponding author. Tel.: +91 22 25590288; fax: +91 22 25505151.
E-mail addresses: gunjanv@barc.gov.in, gunjangarg@yahoo.com (G. Verma).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.04.100

peptides, and synthetic polyelectrolytes. Analogous to that of biomolecules, synthetic polymers and surfactant assemblies can also drastically change the morphology and porosity of materials imparting new functional properties to them and provide new processing methods for the formation of useful objects. The self-assembly of surfactants by creating hydrophobic and hydrophilic structured domains provides an opportunity to use these systems as media for the synthesis of materials with unique properties. Recently, surfactant assemblies have been employed as templates for the synthesis of nanostructured hydroxyapatite particles. Both ionic and nonionic surfactant assemblies as well as block co-polymers have been attempted to tune the microstructure of hydroxyapatite particles [18–24].

Though, anisotropic and mesoporous structures formed by incorporation of surfactants in reaction medium are reported, true templating of micelle structure has not yet been proved. This motivated us to investigate the role of long rod-like micelles in modulating the structure of hydroxyapatite particles. Moreover, a detailed comparison of morphology and porosity behavior of hydroxyapatite prepared in the presence and absence of template has not been demonstrated to the full extent. The focus of the present work is to show the role of rod-like micelle templates composed of cationic surfactant and anionic hydrotrope in tuning the nanostructures of hydroxyapatite. It is anticipated that such templates will closely resemble the biomineralisation process in bone, which is a composite of hydroxyapatite and collagen fibers. Addition of organic hydrotropes (sodium salicylate, p-toluene sulphonates etc.) to cationic surfactant solution offers a novel way to create such rod-like micelles [25–27], which could be explored as a template for material synthesis.

Herein, we report the synthesis and characterization of hydroxyapatite nanoparticles using rod-like micelles of a cationic surfactant, cetyltrimethylammonim bromide (CTAB) and anionic hydrotrope, sodium salicylate (SS) as a templating agent and the comparison of its morphology and porosity behavior with respect to the hydroxyapatite prepared in the absence of any template under similar experimental conditions. To the best of our knowledge, this is the first study in which micelles composed of surfactant and hydrotrope have been utilized as a template for the synthesis of hydroxyapatite.

2. Material and methods

2.1. Chemicals

In this study, calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$), di-sodium hydrogen phosphate (Na_2HPO_4) and cetyltrimethylammoinium bromide (CTAB) were obtained from S. D. Fine Chem. Ltd., Mumbai, India. Sodium salicylate (SS) and sodium hydroxide (NaOH) were purchased from Fluka Chemie, Buchs, Switzerland and BDH AnalaR®, E. Merck (India) Ltd., Mumbai, India, respectively. All chemicals were used as received. The nanopure water from a Millipore—Milli Q system (resistivity ~18 MΩ cm) was used to prepare aqueous solutions.

2.2. Synthesis of hydroxyapatite powders

We have prepared hydroxyapatite by precipitation followed by reflux [19]. In a typical synthesis of hydroxyapatite, 1.70 g of Na_2HPO_4 was dissolved in 100 ml of Milli Q water and pH was adjusted to 11.5 using 1 M NaOH solution. Then 4.72 g of $Ca(NO_3)_2.4\,H_2O$ was dissolved in 60 ml of Milli Q water and added dropwise to Na_2HPO_4 solution under stirring. The prepared milky suspension was refluxed at 100 °C for 2 h. The molar ratio of Ca/P was kept at 1.67 as in hydroxyapatite. The obtained precipitate was washed with Milli Q water by repeated centrifugation (at 8000 rpm for 10 min) and redispersion in water. The obtained precipitate was dried in an oven at 100 °C for 8 h and further calcined in a furnace at 550 °C for 6 h to obtain white powder of hydroxyapatite. For preparation of hydroxyapatite using surfactant as a template (HAp–CTAB–SS), 4.37 g of CTAB (120 mM) and 0.4 g of SS (25 mM) were dissolved in 100 ml Milli Q water along with 1.70 g Na_2HPO_4 followed by the same procedure as mentioned above. The obtained gel-like precipitate was separated and washed several times with water as mentioned earlier and then kept for drying in an oven at 100 °C for 8 h. It was further calcined in a furnace at 550 °C for 6 h for the removal of templates.

2.3. Characterization of micellar template

Dynamic light scattering (DLS) measurements were performed using a Malvern Autosizer 4800 (Malvern Instruments Ltd., UK) employing a 7132 digital correlator and APD detector. The light source was He–Ne laser operated at 632.8 nm with a maximum power output of 15 mW. All measurements were carried out at 30 °C using a circulating water bath. Cylindrical cell of 10 mm diameter was used in all of the light scattering experiments. The intensity of scattered light was measured five times for all the micellar solutions at a scattering angle of 130°. The autocorrelation function was obtained using a 192-channel photon correlator.

2.4. Characterization of hydroxyapatite powders

Phase analysis of the as-prepared (dried at 100 °C) and calcined hydroxyapatite (at 550 °C in air for 6 h) powders prepared in the presence (HAp–CTAB–SS) as well as in the absence (HAp) of surfactant template was carried out using powder X-ray diffraction (PXRD, Phillips PW1710) with CuKα radiation. Data were collected from 20° to 60° (2θ) with a step size of 0.02° and step time of 0.20 s. Fourier transform infrared spectra (FTIR, BOMEM MB series) were recorded in the range of 4000–450 cm^{-1} on powders prepared by the KBr-pellet technique. The weight ratio of KBr to sample was kept approximately 20:1. The thermal analysis of as-prepared samples was carried out between 30 °C and 700 °C in oxygen atmosphere by a TG-DTA instrument (Setaram Instrumentation, LABSYS 1600) at a heating rate of 10 °C/min. The morphological behavior of the as-prepared and heated (at 550 °C) samples was studied by using a scanning electron microscope (ATS 2100, SERON INC) and