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FACILE SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTURED CARBONATED HYDROXYAPATITE MICROSPHERES

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Nanostructured carbonated hydroxyapatite microspheres consisting of nanorods and nanosheets have been synthesized by a facile hydrothermal method using as starting material porous vaterite $CaCO_3$ microspheres prepared by a fast chemical coprecipitation method in the presence of alginate. The pertinent structural, morphological and textural properties were investigated by FTIR, SEM and N_2 adsorption at 77K. Results showed that the porous vaterite $CaCO_3$ microspheres were successfully converted into nano-structured hydroxyapatite carbonated microspheres with a particle size between 4 and 5 μm and BET specific surface area of 28.9 m^2/g.

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1. Introduction

Nanosized calcium phosphates (CaPs) materials can mimic the dimensions of calcified tissues components, and thus be utilized as biomaterials due to their excellent biocompatibility, biological activity and strong ion exchange capacity [1, 2]. The most widely used member of the CaPs family is hydroxyapatite (HA) [3]. Carbonates are among the most abundant components in bioapatite. Nanosized carbonate apatites (CHA) are typically synthesized by demanding chemical-processing routes, including wet chemical precipitation, co-precipitation, emulsion methods, sol–gel synthesis, mechanochemical methods, mechanochemical–hydrothermal reactions, and microwave precipitation [3].

In the present work, we focus on the development of nano-structured carbonated HA microspheres easily synthesized by a hydrothermal treatment of vaterite $CaCO_3$ microspheres in an aqueous solution containing phosphate ions.

2. Experimental

$CaCO_3$ samples were synthesized for the first time (to the best of our knowledge) via a fast precipitation method in the presence of alginic acid sodium salt biopolymer (Sigma-Aldrich) at room temperature in aqueous solutions. Calcium chloride ($CaCl_2$) (Fluka) and sodium carbonate anhydrous (Na_2CO_3) (Panreac) were used as precursors for the preparation of synthetic sorbents. Alginic acid sodium salt was dissolved in solution with its concentration of 0.8g/100ml solution of $CaCl_2$. In a typical synthesis, 100 mL of water containing 2.66 g $CaCl_2$ and 0.8 g of alginic acid sodium salt were added in a Berzelius beaker, under vigorous stirring for 30 min. Then 100 mL of water containing 2.12 g Na_2CO_3 (Panreac) was injected quickly into the above mixed solution. The resultant mixture was continuously stirred for another 40 min, after which the products were filtered and washed with deionized water several times, and dried at 90°C for 18.5 h.

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5.0 g of NaH_2PO_4 (Riedel-de Haën AG) was dissolved into 15 ml of deionized water, followed by the addition of CCMs (0.6 g). The mixture was transferred to a Teflon-lined stainless steel autoclave with 30 ml capacity and hydrothermal reaction took place at 140 °C for 28 h. After the hydrothermal treatment, the autoclaves were cooled down naturally and the obtained HA microspheres (CCHAs) were filtered off, washed with deionized water, and then dried at 60 °C for 72 h for characterization.

The powder X-ray diffraction (PXRD) patterns of the samples were recorded on a Rigaku R-AXIS IV Imaging Plate Detector mounted on a Rigaku RU-H3R Rotating Copper Anode X-ray Generator (λ = 1.54 Å).

SEM images of the developed materials were obtained using a Jeol JSM 7401F Field Emission Scanning Electron Microscope (SEM). The materials were subjected to gold coating prior to SEM imaging.

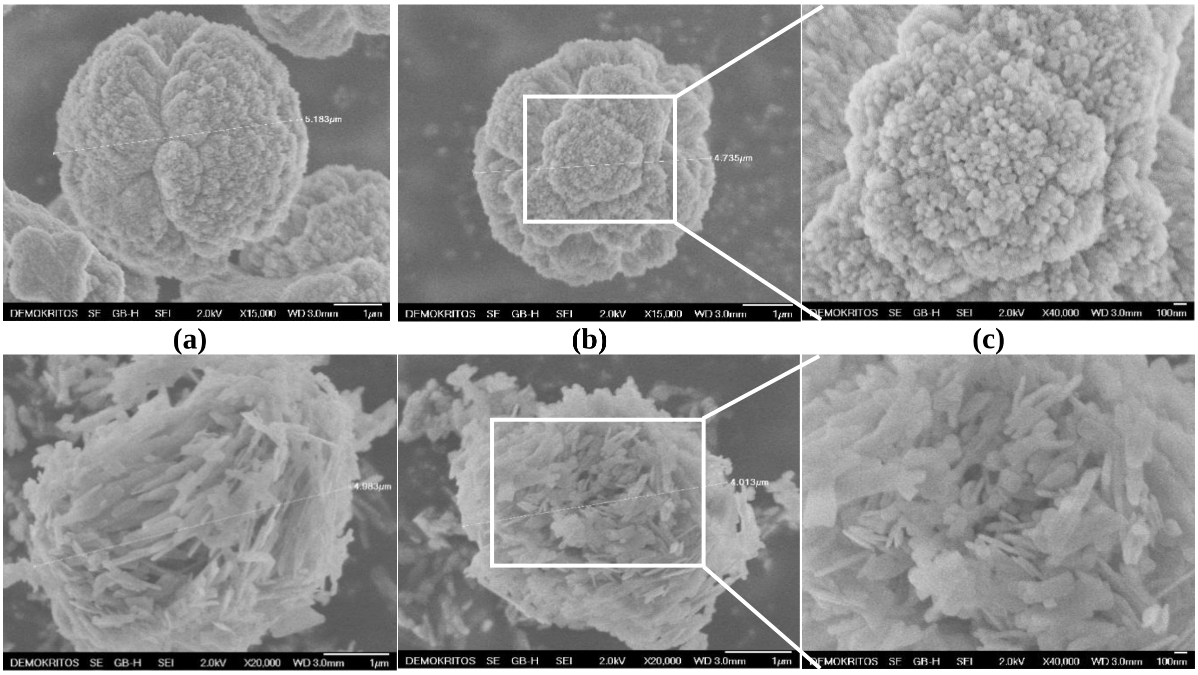
The nitrogen adsorption/desorption isotherms at 77 K were measured in an automated volumetric system (AUTOSORB-1, Quantachrome Instruments). Prior to measurement, the samples were outgassed at 250 °C for 12 h.

The infrared spectra (IR) spectra were obtained using a Thermo Scientific Nicolet 6700 FTIR equipped with a N_2 purging system and a LN2-cooled wide range Mercuric Cadmium Telluride detector.

3. Results and discussion

The SEM images of the starting material (Fig. 1(a-c)) show monodisperse porous vaterite $CaCO_3$ spheres with “flower” morphology with diameter of ca. 5μm.

SEM images of the formed material (Fig. 1 (d-e)) after hydrothermal treatment of vaterite $CaCO_3$ microspheres in an aqueous solution containing phosphate ions show nanosheets/nanorods assembled into nano-structured HA microspheres with a diameter equal to 5 μm. The sizes and the morphology of the obtained HA microspheres are almost similar with that of the starting material.



(a) **(b)** **(c)**

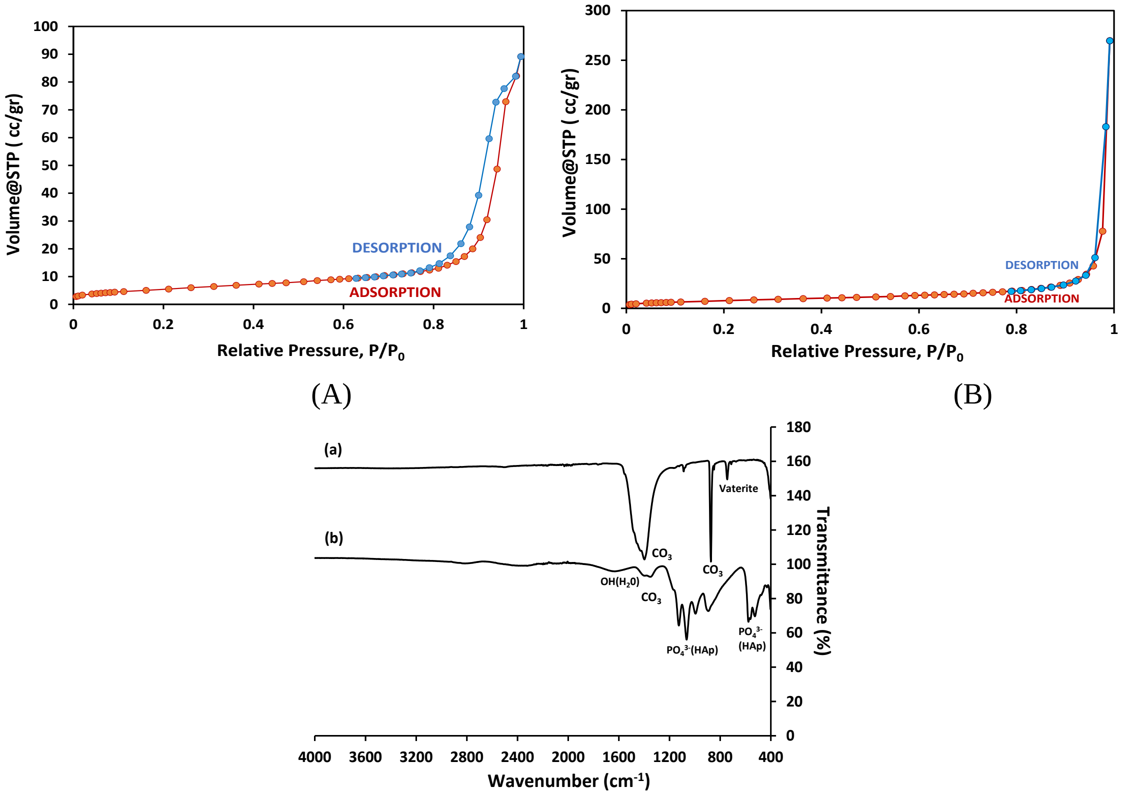
(d) **(e)** **(f)**

Fig. 1. SEM images of the porous vaterite $CaCO_3$ microspheres (a, b and c) and nano-structured carbonated HA microspheres (d, e and f)

The N_2 adsorption/desorption isotherms at 77 K of the as-prepared samples are presented in Fig. 2 (A, B). The analysis of the respective data showed a BET specific surface area of 20.42 m^2/g (porous vaterite $CaCO_3$ microspheres) and 28.9 m^2/g (nano-structured carbonated HA microspheres), respectively.

The FTIR spectrum of vaterite $CaCO_3$ microspheres powder (Fig. 2Ca) has a particularly interesting characteristic. It has a very intense broad band centered at 1394 cm^{-1} and sharp band at 872 cm^{-1}, which can be attributed to n3 (asymmetric CO stretching) mode, n2 (CO_3 out-of-plane deformation) mode and n4 (OCO bending in-plane deformation) mode vibrations, respectively. The infrared spectra at 1088 cm^{1} is attributed to n1 (symmetric CO stretching) mode of vaterite [4]. The characteristic carbonate v4 band of vaterite is at 744 cm^{-1} [5].

The FTIR spectrum of the obtained nanostructured carbonated hydroxyapatite powder is shown in Fig. 2Cb. According to literature, the first indication for the formation of hydroxyapatite is the broad band between 1064 and 1128 cm^{-1} which is attributed to the PO_4^{3-} absorption bands. The bands at 993 cm^{-1} and 526 - 578 cm^{-1} correspond to the symmetric P-O stretching vibration of PO_4^{3-} ion. The bands at 1346 and 1409 cm^{-1} are attributed to the carbonate group (CO_3^{2-}). The peak at 892 cm^{-1} was attributed to carbonate ions (CO_3^{2-}) derived from the $CaCO_3$ staring material. The characteristic peak at 1652 cm^{-1} is attributed to the bending mode of the absorbed water [6-9].



(A) (B)

(C)

Fig. 2. (A) N_2 adsorption/desorption isotherms of the porous vaterite $CaCO_3$ microspheres and (B) nano-structured carbonated HA microspheres obtained by hydrothermal treatment of calcium carbonate microspheres at 140 °C for 26 h; (C) Infrared spectra of the (a) porous vaterite $CaCO_3$ microspheres and (b) nano-structured carbonated HA microspheres.

4. Conclusions

In this work porous vaterite $CaCO_3$ microspheres were successfully converted to nano-structured carbonated HA microspheres by a hydrothermal method. The results revealed that the starting material plays an important role on the morphology, size and composition of the obtained carbonated HA microspheres. These nano-structured HA microspheres may have biomedical applications such as bone regeneration and tissue engineering.

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