

Low temperature synthesis and characterization of carbonated hydroxyapatite nanocrystals



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ARTICLE INFO

Article history:

Received 30 January 2016

Received in revised form

18 March 2016

Accepted 18 March 2016

Available online 21 March 2016

Keywords:

Bioceramics

Hydroxyapatite

Nanoparticle

Carbonate

Bone regeneration

X-ray diffraction

ABSTRACT

Carbonate substituted hydroxyapatite (CHA) nanorods were synthesized via coprecipitation method from aqueous solution of calcium nitrate tetrahydrate and diammonium hydrogen phosphate (with urea as carbonate ion source) in the presence of ammonium hydroxide solution at 70 °C at the conditions of pH 11. The obtained powders were physically characterized using transmission electron microscopy (TEM), X-ray powder diffraction analysis (XRD), and FTIR and Raman spectroscopy. The particle size was evaluated by Dynamic light scattering (DLS). The chemical structural analysis of as prepared sample was performed using X-ray photoelectron spectroscopy (XPS). After ageing for 12 h, and heat treatment at 1000 °C for 1 h, the product was obtained as highly crystalline nanorods of CHA.

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1. Introduction

Hydroxyapatite (HA), $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ bioceramic has received much attention as bone implants material because it is chemically similar to the biological apatite. It is being extensively used in bone regeneration [1] as it bonds physiochemically to bone and stimulates bone formation that is essential for implant osteoconduction and osseointegration. Bioactive and osteoconductive properties of hydroxyapatite make it a good synthetic bioceramic [1,2].

The structure of regular bone has a varying carbonate content from 4–8% besides trace elements (Na^+ , Mg^{2+} , K^+ , F^- , Cl^-) [3–5]. Due to the presence of carbonate in natural bone, the need to synthesize carbonated HA has acquired great importance among researchers [6]. It is also reported that the solubility and resorption of carbonated hydroxyapatite is greater than pure HA resulting in an increased concentration of calcium and phosphate at the site of bone formation [7]. The replacement of hydroxide and phosphate ions by carbonate, forms A and B type carbonated hydroxyapatite

respectively [8]. The B-type carbonate reduces the crystallinity and improves the solubility in the apatite lattice (both in vitro and in vivo tests) [9].

A widespread research is being carried out to synthesize nanocrystals of CHA due to their rapid solubility and stimulation of bone growth rate [10]. In some studies carbonate substitution was carried out in air and CO_2 environment [11] while in some by controlling temperature and HCO_3^- concentration, two precipitation variables acicular and spheroidal crystals were synthesized [8]. For dental and orthopedic-applications, nanosized substituted hydroxyapatite was prepared by using CO_3^{2-} and F^- by aqueous precipitation method [12].

In this paper, coprecipitation synthesis was used for the production of carbonate substituted HA nanoparticles at low temperature and atmospheric pressure. The aqueous solutions of calcium nitrate tetrahydrate and diammonium hydrogen phosphate with Urea ion were slowly mixed at 70 °C in the pH range 11. It was observed that nanoparticle properties are largely dependent on reaction parameters such as particle size and shape, selection of conditions such as the temperature, reaction pH, and variation in Ca:P ratio.

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2. Materials and methods

Calcium nitrate tetrahydrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 99%] and diammonium hydrogen phosphate [$(\text{NH}_4)_2\text{HPO}_4$, 98%] were purchased by SigmaAldrich. Urea [$(\text{NH}_2)_2\text{CO}$, 99%] and ammonium hydroxide solution (NH_4OH , 28%) were purchased by VWR International. Deionised water was used throughout all experiments.

2.1. Synthesis procedure

2.1.1. Carbonate(CO_3^{2-})-substituted hydroxyapatite

Carbonate substitution reactions were carried out by using coprecipitation method in this study. In the first step, 0.25 M of calcium nitrate were dissolved in 250 mL deionised water and the pH of this solution was maintained to pH 11 by adding 15 mL neat ammonium hydroxide solution. Urea was added to diammonium hydrogen phosphate and this solution was then slowly added to calcium nitrate solution at 70 °C under constant stirring. A $\text{Ca}:[\text{PO}_4^{3-} + \text{CO}_3^{2-}]$ molar ratio of 1.67 was adjusted in all precursor solutions. The aqueous suspension obtained by this process was aged for 12 h. It was anticipated that carbonate substitutes phosphate ion in HA lattice leads to B-type carbonate substitution. The wet residue obtained was washed, centrifuged and dried in oven at 90 °C overnight.

2.2. Characterization

2.2.1. Chemical analysis

Chemical analysis of CHA samples was carried out using K-Alpha X-ray photoelectron spectrometer (Thermo Scientific) with two chamber vacuum. It uses a monochromated Al K- α source ($E = 1486.6$ eV) with maximum power of 72 W. The vacuum chamber pressure was at a pressure of $\sim 3 \times 10^{-8}$ Torr. The spectrum involved an energy of 150 eV for survey scans. The detector is a 128 channel sensitive detector. The XPS spectra were processed using Casa™ software.

2.2.2. Transmission electron microscopy

TEM images were collected using a JEOL JEM-1200EX II Electron Microscope. Digital images were taken with a side mounted AMT 2K high sensitivity digital camera. A small amount of sample (less than 10 mg) was dispersed in neat methanol and then ultrasonicated for 2 min to yield a very dilute suspension. A few drops of the resulting suspension were then placed on a carbon-coated copper grid (procured from Agar Scientific, UK), which was used as the TEM specimen. The grid was dried prior to use in the double tilt holder of the TEM. Image J software (version 5.0) was used for assessing particle sizes.

2.2.3. Dynamic light scattering

DLS measurements were taken using a Malvern Instruments Zetasizer operated in backscatter (173°) mode. The sample slurry produced (solid content $\sim 1\%$ by volume) was diluted with methanol then placed in an ultrasonic bath for 10 min to disperse the sample. Square cuvettes with a path length of nominally 10 mm were used for measurements.

2.2.4. Powder X-ray diffraction

Bruker AXS D4 Endeavour™ XRD diffractometer was used for XRD collection of all samples. The data was collected in the 2θ range from 5 to 70° with a 0.05° scanning step and a count time of 2 s per step using Cu-K α radiation ($\lambda = 1.5406$ Å). DIFFRACplus Eva™ software was used for the phase analysis of the data by spectral matching with standard patterns. The crystallite sizes were calculated by using the Debye–Scherrer equation [13].

2.2.5. FTIR spectroscopy

The functional groups present on the surface of HA were examined using Fourier Transform Infrared spectroscopy (FTIR) using a Nicolet 6700 FTIR (ThermoScientific, UK). The FTIR spectra were collected in the range $400\text{--}4000$ cm^{-1} at resolution of 4 cm^{-1} averaging 256 scans.

2.2.6. Raman spectroscopy

A Confocal Raman DXR Spectrometer (SP Thermo-Scientific) was used for analysis. The powder Sample was deposited onto 316L stainless steel block with the help of a spatula. 316 L block was wiped clean first with distilled water then with acetone prior to sample analysis. The data was gathered using 780 nm laser, 10 X Lens with the scan time of 90 s for each sample.

3. Results and discussion

A chemical analysis of as prepared CHA sample was done by using XPS analysis as shown in Fig. 1. The peaks at 134 eV corresponded to P 2p spectra of hydroxyapatite. While the binding energy values for O 1s and Ca 2p were measured as 532 and 347 eV, respectively [14]. The peak at 285 eV corresponded to C 1s spectra of carbonate substituted hydroxyapatite. The Ca/P ratio in the CHA analysed sample (1.65) was determined using XPS analysis which is found very closed to stoichiometric ratio of 1.67 in pure hydroxyapatite.

Transmission electron microscopy was used to analyse the particle size and morphology. The as prepared CHA sample synthesized using coprecipitation process had a rod like morphology as shown by TEM in Fig. 2(a) and average length along the longest axis of each particle was $\sim 110 \pm 15$ nm (200 particles sampled). TEM image was also captured for heat-treated (1000 °C, 1h) CHA samples as shown in Fig. 2 (b). It was observed that after heat treatment, particles increased in size and became more agglomerated.

Particle size distribution was also conducted for CHA sample. DLS measurements of CHA sample synthesized at 70 °C reveals average particle size of ca. 169 and PDI (polydispersity index) value of 0.231. DLS measured diameter (100–300 nm) with PDI of 0.3 or less shows good dispersion. It was also observed that DLS measurement results are in good agreement with TEM determined distributions (Fig. 3).

Powder X-ray diffraction data was obtained for the CHA sample

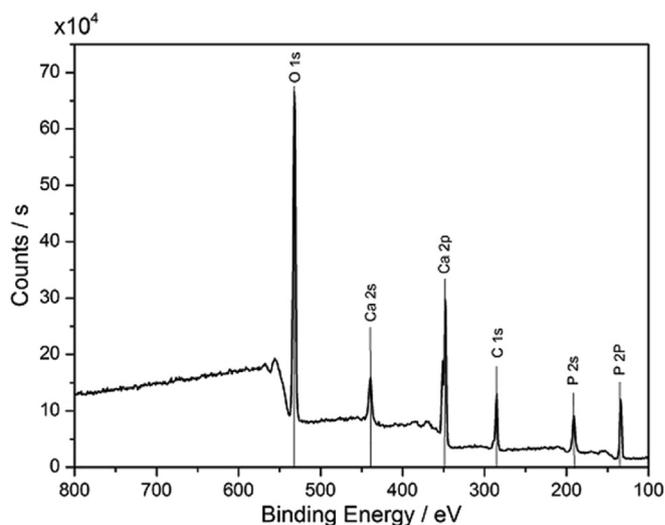


Fig. 1. XPS survey spectrum of CO_3^{2-} -substituted hydroxyapatite powders made using coprecipitation method at 70 °C.

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