



Surface modification of zinc-containing hydroxyapatite by tartaric acid



Thouraya Turki^a, Masseoud Othmani^a, Christophe Goze Bac^b,
Férid Rachdi^{b,*}, Khaled Bouzouita^c

^a Laboratoire de Physico-Chimie des Matériaux, Faculté des Sciences de Monastir, 5019 Monastir, Tunisia

^b Laboratoire Charles Coulomb, UMR 5221 CNRS/UM2, Université Montpellier 2, Place E. Bataillon, 34095 Montpellier, France

^c Institut Préparatoire aux Etudes d'Ingénieur de Monastir, Tunisia

ARTICLE INFO

Article history:

Received 31 March 2013

Received in revised form 5 June 2013

Accepted 2 July 2013

Available online 7 August 2013

Keywords:

Hydroxyapatite

Zinc

Grafting

Tartaric acid

ABSTRACT

The surface of Zn-substituted hydroxyapatites ($\text{Ca}_{(10-x)}\text{Zn}_x(\text{PO}_4)_6(\text{OH})_2$, with $0 \leq x \leq 2$, $\text{Ca}_x\text{Zn}_x\text{HA}$) modified by tartaric acid was investigated by various techniques. XRD powder patterns revealed that synthesized samples were single phase of HA with broadened XRD reflections. FTIR and (^{13}C , ^1H and ^{31}P) MAS NMR measurements confirmed the grafting of the tartaric acid on the apatite surface. Chemical analysis showed that for ZnHA the grafted acid amount increases with the increase of the acid concentration in the starting solutions, while for HA, it remained constant, indicating more reactivity for ZnHA surface. A mechanism of surface modification is proposed based on the obtained results.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Over the last three decades, hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA) is widely used in various biomedical applications, mainly in orthopedics and dentistry, due to its chemical composition, biocompatibility and osteoconductivity [1–3]. However, the development of materials, which resemble as closely as possible the bone, is still a major challenge that the scientific researchers attempt to overcome. Indeed, the bone can be regarded as a natural composite material composed of two main phases, an organic component (collagen) and a mineral component acting as a reinforcement phase. This latter phase is mainly constituted by HA, which is nonstoichiometric, calcium deficient and containing several species such as Na^+ , Sr^{2+} , Mg^{2+} , Mn^{2+} , F^- , Cl^- , CO_3^{2-} etc. [4,5]. These species play an important role on its physical and biological properties such as crystallinity, solubility and biological response [6–8]. Therefore, many hydroxyapatites substituted by one or more of the preceding species have been synthesized and characterized.

Among the previous ions, Zn is believed to be involved in more than 200 enzymes [9]. Furthermore, this element is known to have a beneficial effect on bone growth and bone mineralization [10–12], and might play a role on the osteoblastic and osteoclastic activities [13,14]. Also, it decreases the inflammatory response [15]. For

these reasons, many researches have been interested in preparing Zn-substituted HA [16,17]. However, despite the numerous studies that have been devoted to the incorporation of Zn into the HA structure, the substitution limit of this element and its location into the apatite structure are subjects of controversy. In an early work [18], we have synthesized zinc-containing HA. The XRD analysis indicated that Zn could substitute Ca up to 20 at%, while the Rietveld refinement showed that Zn was statically distributed between the two cationic sites.

In addition to its property to accommodate a wide variety of substitutions, HA shows a great ability to fix different substances onto its surface paving the way for many other applications. Thus, the modified materials have potential use in biomedical applications such as prosthetic devices [19] and orthopedic and dental implants [20]. Also, there are used as support for catalysts [21], adsorbent of rare earths and heavy metals for water purification [22] or in chromatography to purify and separate proteins and enzymes [23]. Different processes of fixation have been proposed, based on the interactions between the metallic or phosphate ions of the apatitic surface and the anionic or cationic groups of the organic molecules, e.g. carboxylic [24–26], alkylphosphonic [27] and amino acids [28], alcohol [29], polymers [30] and organosilanes [31]. Moreover, several studies showed the possibility of ionic exchange between phosphate ions of the apatite and organic ions such as R-PO_4^{2-} , R-SO_4^{2-} and R-COO^- [32,33]. For other authors, the organic moieties can replace the OH group of the apatitic structure [34,35].

* Corresponding author. Tel.: +33 611 94 05 28.

E-mail address: Ferid.Rachdi@univ-montp2.fr (F. Rachdi).

The goal of the present work is to prepare organic/inorganic hybrid materials by grafting tartaric acid ($C_4H_6O_6$) on Zn-substituted HA surface. In the text, Zn-substituted HA will be noted by $Ca_{(10-x)}Zn_xHA$, while the reacted phases will be designed by $Ca_{(10-x)}Zn_xHA-(Tacid)_n$, where Tacid correspond to the tartaric acid and n is the molar ratio with $n = n(\text{tartaric acid})/n(\text{apatite})$.

2. Experimental procedure

2.1. Powder preparation

Unsubstituted and Zn-substituted HA with the chemical formula $Ca_{(10-x)}Zn_x(PO_4)_6(OH)_2$ where $0 \leq x \leq 2$ [18] were prepared using the double decomposition method [36]. A solution of $Ca(NO_3)_2 \cdot 4H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ with different Zn/(Ca + Zn) molar ratios was added drop by drop in a solution of $(NH_4)_2HPO_4$ under N_2 bubbling. The pH of the mixed solution was maintained at 11 by a regular addition of a concentrated ammonia solution. The resulting solid phase was kept in contact with the mother solution at the boiling temperature for 1 h. Then, the precipitate was filtered, washed with hot distilled water to remove unwanted impurities and dried at $110^\circ C$ for 24 h.

Surface modification of the as-prepared powders was performed using the following method. A solution of 20 mL of tetrahydrofuran, containing tartaric acid at appropriate concentrations ($n = 5, 10, 20, 40$) was slowly added to a suspension of 1.5 g of HA in 70 mL of tetrahydrofuran maintained under vigorous stirring. Then the suspension was heated at $60^\circ C$ for 30 min. After that, 45 mL of toluene was added to the suspension, which was heated again at $150^\circ C$ for 8 h. Water resulting from the reaction was removed by azeotropic dehydration with toluene. To remove non-grafted acid, the obtained products were filtered and washed five times by tetrahydrofuran and ethylacetate, respectively. Then, the precipitate was dried at $60^\circ C$ for 24 h to remove the residual solvent [37]. The molar ratio $n(\text{acid})/n(\text{apatite})$ used were 5, 10, 20 and 40, respectively.

2.2. Sample characterization

Elemental analyses were performed at the Service Central d'Analyses, CNRS, Vernaison (France).

X-ray diffraction (XRD) analysis was carried out by means of a Philips PW 1710 powder diffractometer equipped with a diffracted beam graphite monochromator and operating with the $Cu-K\alpha$ radiation. The samples were scanned in the 2θ range from 10 to 70° with a scanning speed of 0.0011 deg/s . The average crystalline size, $D_{(hkl)}$, of the as-prepared and grafted powders was calculated using the Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the X-ray wave length of the monochromatic X-ray beam, β is the full width at half maximum and θ is the Bragg's diffraction angle.

IR spectra of the powdered samples were recorded using a Bruker Tensor 27 equipped with a diamond ATR setup in the range of $400\text{--}4000 \text{ cm}^{-1}$.

The MAS NMR analysis was conducted on 1H , ^{31}P and ^{13}C nuclei using a Bruker spectrometer Avance 300 at resonance frequencies 300.13, 121.5 and 75.4 MHz, respectively. The spinning rate of the sample at the magic angle was 2–12 kHz. 1H and ^{13}C chemical shifts were referenced to external standard of Tetramethylsilane (TMS) and ^{31}P to an aqueous solution of 85% H_3PO_4 .

3. Results and discussions

3.1. Elemental analysis

The results of the chemical analysis as well as the (Ca + Zn)/P molar ratios of the as-synthesized materials are summarized in Table 1. The (Ca + Zn)/P molar ratio values suggest that HA were slightly non-stoichiometric. Also, the presence of the tartaric acid does not modify significantly the (Ca + Zn)/P molar ratio of the obtained composites.

The grafting of organic compounds on the surface of the apatite can be highlighted by carbon analysis (Table 1). In the absence of carbonate minerals in the apatite structure, as it will be shown below, the determined carbon amounts can only result from tartaric acid fixed on the particle surface. For the treated unsubstituted HA, whatever the used acid amounts, the carbon content remained constant, indicating that the acid grafted amount is independent of that initially introduced in the starting solution. However, in the case of the $CaZnHA$, for a given Zn rate, the carbon percent increased as a function of the acid concentration in the starting solution. On other hand, for a given initial concentration, the carbon percent increased as the incorporated Zn content did. With respect to the pure HA, the great affinity of acid to the Zn-substituted HA can be explained by the high reactivity of the apatite surface due to the presence of Zn, which is more electronegative than Ca, and by their SSA, greater than that of HA (Table 1). The grafting improvement of the tartaric acid on the Ca–ZnHA is in agreement with the results previously reported for this apatite modified by the lactic acid [25], Ca–NiHA modified by phosphonates [38] and Ca–CuHA modified by polyaspartic acid [26].

3.2. X-ray diffraction

The XRD patterns of the as-prepared samples are gathered in Figs. 1 and 2. All the XRD patterns showed reflections corresponding to an apatite phase, matching the JCPDS card No. 9–432 for HA. No secondary phases were detected in any of the samples. Compared to those of pure HA, the diffraction peaks of the modified HA were broader, indicating a decrease in the powders' crystallinity.

Table 1
Chemical composition (± 0.02) of Zn-substituted hydroxyapatites before and after reaction with tartaric acid.

Samples	%P _{exp}	%Ca _{exp}	%Zn _{exp}	%C _{exp}	%Tacid	(Ca + Zn)/P	(Ca/P) _{exp}	(Ca/P) _{theo}
Ca ₁₀ HA (SSA = 42.56 m ² /g)	18.40	38.89	–	–	–	1.63	1.63	1.66
Ca ₉ Zn ₁ HA (SSA = 70.73 m ² /g)	17.03	31.84	5.59	–	–	1.61	1.44	1.5
Ca ₈ Zn ₂ HA (SSA = 88.42 m ² /g)	16.61	27.77	11.34	–	–	1.62	1.29	1.33
Ca ₁₀ HA-(Tacid)10	17.19	35.77	–	1.54	4.81	1.62	1.62	1.66
Ca ₁₀ HA-(Tacid)20	16.54	34.52	–	1.54	4.81	1.61	1.61	1.66
Ca ₁₀ HA-(Tacid)40	16.67	34.87	–	1.54	4.81	1.62	1.62	1.66
Ca ₉ Zn ₁ HA-(Tacid)10	16.74	31.74	5.44	1.83	5.71	1.62	1.46	1.5
Ca ₉ Zn ₁ HA-(Tacid)20	16.74	32.07	5.43	2.20	6.87	1.64	1.48	1.5
Ca ₉ Zn ₁ HA-(Tacid)40	16.74	32.06	5.44	4.72	14.74	1.64	1.48	1.5
Ca ₈ Zn ₂ HA-(Tacid)20	14.84	25.36	10.13	4.27	13.33	1.65	1.32	1.33

Download English Version:

<https://daneshyari.com/en/article/5352575>

Download Persian Version:

<https://daneshyari.com/article/5352575>

[Daneshyari.com](https://daneshyari.com)