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Mechanochemically-assisted synthesis and characterization of Zr-doped hydroxyapatite

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INTRODUCTION

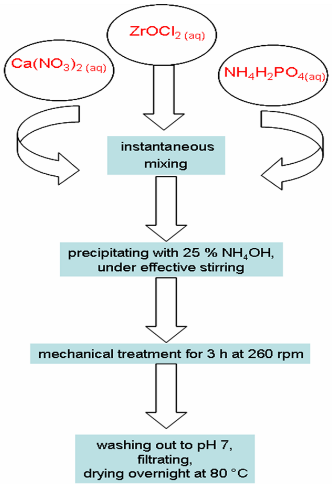
Hydroxyapatite (HAp) bioceramics attract researches' interests over the decades as a candidate for ideal bone tissue reconstruction material. Its excellent biocompatibility and bioactivity, originating from chemical similarity to the mineral part of the bones, make this material perennial fountain of inspiration and application of wide range of experimental approaches to improve its properties, mainly that of mechanical nature. Doping the crystal lattice of HAp with various ions, while preserving pure apatite crystal structure, seems promising way for alteration of its biological and mechanical properties.

The aim of this study was to investigate capability of mechanical treatment on formation of Zr-doped hydroxyapatite nanopowders.

EXPERIMENTAL PART

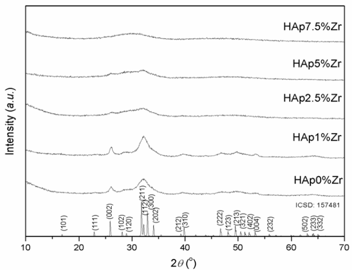
The synthesis is performed in planetary ball mill (Retsch, PM 4). Firstly, solutions of Ca^{2+}, PO_4^{3-} and Zr^{4+} were made, mixed and precipitated with 25 % NH_4OH. The starting precursors ration was adjusted to fit the equation (Ca+Zr)/P=1.67. Several samples were made, varying the amount of Zr in solution, so the samples were denoted as HAp x% Zr, where x =0, 1, 2.5, 5 and 7.5. All step-by-step synthesis is shown in the right flowchart. Mechanical treatment is done in agate vials with alumina ball under 260 rpm rotation speed for 3 h.

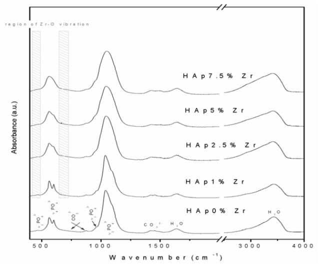
Phase composition of materials is determined by XRD method, while presence of characteristic functional groups and middle-range arrangement is measured by FTIR spectroscopy, Chemical composition and Zr incorporation efficacy is determined by ICP-AES analysis. Particle size and morphology is characterized through field emission electron microscopy, FE SEM. Further thermal treatment is done for 1 h at 1000 °C to check the thermal stability of the prepared materials.

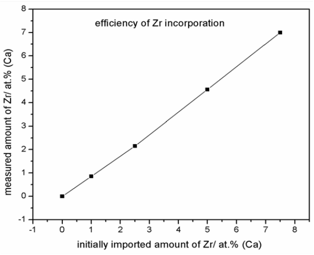

$ZrOCl_{2\,(aq)}$
$Ca(NO_3)_{2\,(aq)}$
$NH_4H_2PO_{4(aq)}$
instantaneous mixing
precipitating with 25 % NH_4OH, under effective stirring
mechanical treatment for 3 h at 260 rpm
washing out to pH 7, filtrating, drying overnight at 80 °C

RESULTS AND DISSCUSION

as-prepared materials

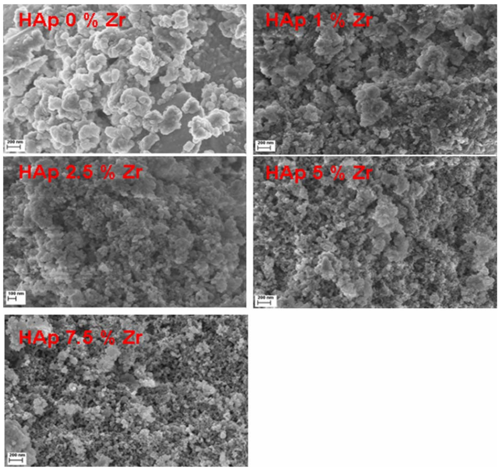






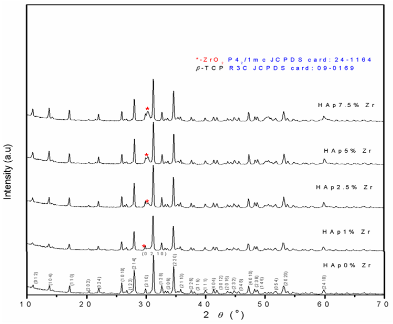
XRD patterns of as-prepared materials show that the present reflections are very broad and but their positions correspond to that of pure HAp crystal phase. This implies a short range order and low crystallite size of HAp prepared through this method. It could be observed that crystal arrangement is influenced by the presence of Zr^{4+} ions, yielding to greater disordering with increase in Zr content. While the sample HAp1% Zr resembles pure HAp0% Zr, further addition of Zr^{4+} destructs apatite crystal structure and sample HAp7.5% Zr is totally amorphous material, with only one observable reflection in the location of the most intense HAp reflections.

IR spectra of the prepared sample reveal that the present vibrations are that of pure HAp, mainly from PO_4^{3-}, CO_3^{2-} and H_2O. As well as XRD patterns suggested lost of long range ordering with increase of Zr content, IR spectra consist of broad bands and high amount of bounded water. It should be noted that there are no characteristic OH^- vibration mode around 3600 cm^{-1} which indicates crystal lattice disordering. However, here can be observed that it is inherently connected to the synthesis method, and is further enhanced, which can be seen from the disappearance of O-P-O double degenerated bending mode around 602 cm^{-1}. Also, there are intensive bands corresponding to the carbonate ions incorporated into crystal lattice of HAp. Their presence could be consequence of the fact that synthesis is performed in the air conditions, as well as the possibility of material high affinity for carbonates because of misbalanced electro-neutrality upon Zr^{4+} incorporation.



Electron micrographs of the prepared powders show that they are consisted nanometer primary particles, more or less agglomerated. It can be observed that there is morphology change upon addition of Zr. The particles became less agglomerated and obviously smaller, decreasing in size from about 100 nm for HAp0%Zr to 30 nm for HAp7.5%Zr. Moreover, the samples containing Zr ions have significantly different morphology, being composed of porous structures applicable in various domains.

materials after calcinations 1h at 1000°C



Thermal treatment of the prepared materials improved crystallinity and yielded to complete transformation of the initial apatite crystal phase into β-TCP, also important material in the field of hard tissue reconstruction.

Thermal instability originates from low Ca/P ratio, according to ICP-AES analysis being away from stoichiometric 1.67. Also, under thermal treatment tetragonal ZrO_2 crystal phase appeared, which could suggests extraction of Zr from HAp crystal lattice. However, possibility to obtain composite of β-TCP and ZrO_2.

CONCLUSIONS

From the presented results, it can be concluded that this mechanochemically-assisted approach can be successfully used for synthesis of amorphous Zr-doped hydroxyapatite. Increase in Zr content resulted in crystal structure disordering. IR analysis revealed that only hydroxyapatite vibrations mode existed, with strong bands of incorporated carbonate ions. From the electron microscopy results, it can be seen that there are significant difference in particle size and morphology, meaning that materials with incorporated Zr possess smaller particles with porous-like morphology.