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CHEMICAL PRECIPITATION SYNTHESIS AND CHARACTERIZATION OF Zr-DOPED HYDROXYAPATITE NANOPOWDERS

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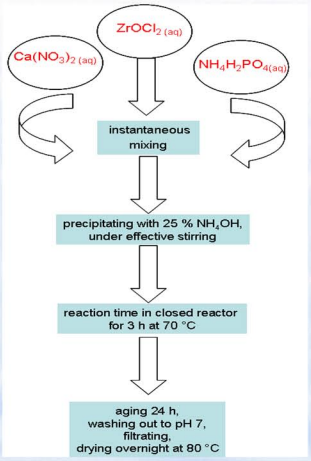
INTRODUCTION

The great importance of hydroxyapatite in the field of biomaterial science inspires researchers to investigate various approaches to adjust and improve existing and to find out new useful properties of this class of materials. Doping of original hexagonal apatite crystal structure with a number of ions has been shown to improve phase stability, mechanical and electrical properties, as well as its biological applicability. Fabrication of Zr-HAp materials could be significant for mechanical properties improvement, teeth implant color adjustment, altogether with conserved bioactivity and without cell toxicity.
In this study, simple chemical precipitation is used to synthesize zirconium-doped hydroxyapatite, Zr-HAp, with 0, 1.0, 5.0 and 10.0 at.% of Zr. Phase purity was investigated by XRD, particles morphology by electron microscopy, while middle range arrangement and presence of different functional groups through FTIR spectroscopy studies. Efficiency of Zr-ions incorporation is checked by ICP-AES chemical analysis.

EXPERIMENTAL PART

The synthesis is performed in the way of simple chemical precipitation in the reflux conditions. 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, 5 and 10 at.%. Firstly, solutions of Ca^{2+}, PO_4^{3-} and Zr^{4+} were made, mixed and precipitated with 25 % NH_4OH. Reaction was performed for 3h at 70 °C. All step-by-step synthesis is shown in the right flowchart.
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 electron microscopy, FE SEM and TEM. Sintering studies were performed in heating microscope.

Synthesis procedure

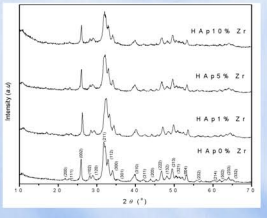


CONCLUSIONS

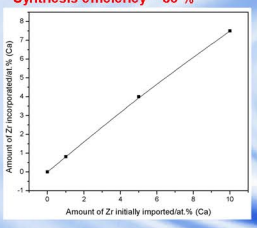
1.This type of chemical precipitation method can be successfully applied for the synthesis of new material, Zr-doped HAp nanopowders. The synthesis conditions, under closed reaction atmosphere, and precipitation with dropwise addition of ammonia solution, contributed to elongated particles' morphology of initial system.
2. Addition of Zr caused morphological, structural and chemical alterations in the system.
3. While XRD analysis did not revealed the presence of another phases, according to FTIR results, some traces of ZrO_2 could be supposed in the HAp10%Zr.
4. Sintering studies suggested that increased content of Zr slows down densification and increases sintering temperature.

RESULTS AND DISCUSSION

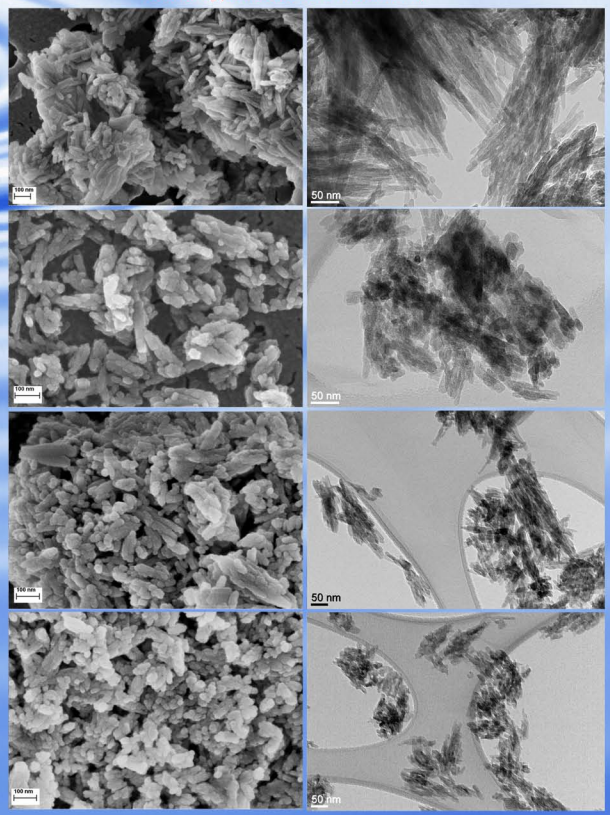
XRD analysis: pure HAp



ICP-AES chemical analysis:
Synthesis efficiency ~ 80 %



Electron microscopy analysis:
-HAp0%Zr has elongated morphology, with high aspect ratio
-the particles are softly agglomerated
-with addition of Zr, there are two effects:
1. lowering aspect ratio,
2. lowering particle size from ~100 to 50 nm,



FTIR spectroscopy analysis:
-pure HAp for 1 and 5 at.%, but at 10 at.% probable formation of ZrO_2;
-disordering of crystal structure with increase of Zr^{4+} content is noticed from lowering intensity of OH^- stretching vibration mode around 3570 cm^{-1};

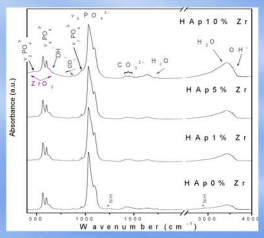


Table 1. Characteristic vibration appeared in FTIR spectra.

Assignment and vibrational modes	Band positions (cm^{-1})				
	HAp0% Zr	HAp1% Zr	HAp5% Zr	HAp10% Zr	ZrO_2 (literature data)
					351
					376
					453
ν_4 bending O-P-O, double degenerate	470$_m$,	470$_m$,	471$_m$,	471$_m$,	
ν_4 bending O-P-O, double degenerate	563$_m$, 602$_m$	564$_m$, 604$_m$	564$_m$, 604$_m$	563$_m$, 603$_m$	588
O-H libration	631$_m$	632$_m$	630$_m$	631$_m$	
ν_4 C-O	670$_m$	665$_m$	661$_m$	668$_m$	687
					789
ν_2 C-O	876$_m$,	875$_m$,	875$_m$,	975$_m$,	
ν_1 symmetric stretching P-O	962$_s$,	962$_s$,	962$_s$,	963$_s$,	
ν_3 asym. stretching P-O, triply degenerate	1034$_{vs}$, 1093$_m$	1033$_{vs}$, 1096$_m$	1032$_{vs}$, 1094$_m$	1034$_{vs}$, 1094$_m$	
ν_3 C-O	1420$_m$, 1459$_s$	1420$_m$, 1462$_m$	1421$_m$, 1454$_m$, 1480$_m$	1420$_m$, 1458$_m$, 1485$_m$	
adsorbed H_2O (bending O-H-O)	1637$_m$	1636$_m$	1637$_m$	1637$_m$	
adsorbed H_2O	3430$_{bvs}$	3245$_{bm}$, 3438$_{bvs}$	3260$_{bs}$, 3434$_{bvs}$	3270$_{bs}$, 3428$_{bvs}$	
stretching O-H	3570$_m$	3570$_m$	3570$_m$	3570$_m$	
Crystal phase	HAp	HAp	HAp	HAp+ZrO_2	tetragonal ZrO_2

Sintering studies:

-pure HAp0%Zr sintered around 1100 °C
-with increase of Zr content, sintering temperature increases;
-sample HAp10%Zr shows retardation in sintering around 800 °C, probably due to the presence of some amount of ZrO_2, according to FTIR results;