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, together 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 ratio was adjusted to fit the equation (Ca+Zr)PO₄=1.87. Several samples were made, varying the amount of Zr in solution, so the samples were denoted as HAp+x%H₂O₂ where x = 0, 1, 5 and 10 at %. Firstly, solutions of Ca(NO₃)₂ and PO₄ were made, mixed and precipitated with 25 % NH₄OH. 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 efficiency is determined by ICP-AES analysis. Particles size and morphology is characterized through electron microscopy, FE-SEM and TEM. Sintering studies were performed in heating microscope.

RESULTS AND DISCUSSION

XRD analysis: pure HAp

ICP-AES chemical analysis: Synthesis efficiency = 80 %

FTIR spectroscopy analysis:
- pure HAp for 1 and 5 at.%, but at 10 at.% probable formation of ZrO₂.
- disordering of crystal structure with increase of Zr⁺⁺⁺⁺ content is noticed from lowering intensity of OH stretching vibration mode around 3570 cm⁻¹.

Sintering studies:
- pure HAp/Zr sintered around 1100 °C
- with increase of Zr content, sintering temperature increase.
- sample HAp10/Zr shows retardation in sintering around 800 °C, probably due to the presence of some amount of ZrO₂, according to FTIR results.

CONCLUSIONS

1. This type of chemical precipitation method can be successfully applied for the synthesis of new material, Zr-doped HAp nanoparticles. 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 causes 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 ZrO₃ could be supposed in the HAp10/Zr.
4. Sintering studies suggested that increased content of Zr slows down densification and increases sintering temperature.

10 nm

100 nm

Table 1. Characteristic vibration appeared in FTIR spectra.

<table>
<thead>
<tr>
<th>Vibration Mode</th>
<th>Grouping</th>
<th>Coordinate</th>
<th>Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH Stretching</td>
<td>HAp</td>
<td>HAp</td>
<td>3620</td>
</tr>
<tr>
<td>OH Stretching</td>
<td>HAp+1%Zr</td>
<td>HAp+1%Zr</td>
<td>3570</td>
</tr>
<tr>
<td>OH Stretching</td>
<td>HAp+5%Zr</td>
<td>HAp+5%Zr</td>
<td>3570</td>
</tr>
<tr>
<td>OH Stretching</td>
<td>HAp+10%Zr</td>
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<tr>
<td>OH Stretching</td>
<td>HAp+15%Zr</td>
<td>HAp+15%Zr</td>
<td>3570</td>
</tr>
</tbody>
</table>

Electron microscopy analysis:
- HAp10%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.