Characteristic and Formation of Hydroxyapatite Synthesized from Heat Treatment of Cuttlefish Bone

Kridsada Faksawat

Department of Physics, Faculty of Science, King Mongkut’s University of Technology
Introduction

Nano scale
1 to 100 nanometers

Shape and Size Effect
Increasing of specific surface area

Ref: http://commonsensecanadian.com
Ref: http://eng.thesaurus.rusnano.com
Hydroxyapatite

- Enhanced resorbability
- Improved densification
- Sinter ability
- Improved cell proliferation
- Improved cellular activity related to bone growth

Ref: http://oncinfo.ru
Ref: http://i.vimeocdn.com
Introduction

- Osteon
- Lamellae
- Collagen fiber
- Mineralized fibrils
- Spongy bone
- Compact bone
- Microscopic view
- Osteon canal
- Collagen triple helix
- Hydroxyapatite (Ca$_5$(PO$_4$)$_3$OH)
- Hexagonal bioactive mineral
Introduction

How do you synthesized hydroxyapatite?

- Natural material
- Chemical material

### Chemical material

- $\text{K}_2\text{HPO}_4$
  - Trace of K
- $\text{Ca}_2\text{P}_2\text{O}_7$
  - Found $\beta$ - TCP
- $\text{Na}_2\text{HPO}_4$
  - Trace of Na
- $(\text{NH}_4)_2\text{HPO}_4$
  - Odor problem

90-95% of Ca
How to synthesis of hydroxyapatite

Solid state

Ball milling

Microwave irradiation

Sol gel

H₂O/Et gelation

Precipitation

Ca²⁺ solution

PO₄³⁻ solution
Objectives

- To study phase transformation of cuttlefish bone by various sintering temperature.
- To study characteristics of hydroxyapatite synthesized from various heated cuttlefish bone by ball milling method.
- To study crystal structure, functional group and morphology of synthesized hydroxyapatite by ball milling method.
Experiment

Part 1. Temperature effect on cuttlefish bone

- 200 to 1300 °C

Part 2. Hydroxyapatite synthesis

- Ball milling method
- Vary

500 °C
900 °C
Room temperature
Experim
ent

Cuttlefish bone

Part 1

Temperature effect on cuttlefish bone

Part 1

Characterization by

Hydroxyapatite synthesis

Cuttlefish bone powder

Heated at 200 to 1300 °C

200 °C

500 °C

900 °C

1100 °C

1300 °C

Temperature effect on cuttlefish bone

Ground

200 °C

500 °C

900 °C

1100 °C

1300 °C

200 °C

500 °C

900 °C

1100 °C

1300 °C
Results & Discussion:

Part 1
Temperature effect on cuttlefish bone

Fig 1 XRD pattern of temperature effect on cuttlefish bone at various temperature.
Ball Milling Experiment:

- Vary calcium sources
  - CaO (lime phase) (for example)
  - CaCO₃ (aragonite phase)
  - CaCO₃ at 500 °C (calcite phase)

Materials:

- CaO
- (NH₄)₂HPO₄
- DI water
- Stainless steel container
- Steel ball

Reaction:

\[
CaO + 3(NH₄)₂HPO₄ + H₂O \rightarrow Ca₅(PO₄)₃(OH) + 5H₂O + 6NH₃
\]
Experim
ent:

**Part 2**

**Ball Milling**

- X-ray diffractometer: XRD
- Fourier transform infrared spectrometer: FTIR
- Scanning electron microscopy: SEM

**Characterization**

- X-ray diffractometer: XRD
- Fourier transform infrared spectrometer
- Scanning electron microscopy: SEM

**Ground until powder**

**Hydroxyapatite**

- Sample

- Dried for 48 h
Part 2

Hydroxyapatite synthesis by ball milling

Results & Discussion:

<table>
<thead>
<tr>
<th>2theta (degree)</th>
<th>CaCO$_3$ (aragonite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball milled 5 min</td>
<td></td>
</tr>
<tr>
<td>Ball milled 30 min</td>
<td></td>
</tr>
<tr>
<td>Ball milled 60 min</td>
<td></td>
</tr>
<tr>
<td>Ball milled 120 min</td>
<td></td>
</tr>
</tbody>
</table>

Intensity (a.u.)

a) Aragonite phase precursor

Fig 2 XRD pattern of synthesized hydroxyapatite from cuttlefish bone at different phase precursor by ball milling method.

5CaCO$_3$ + 3(NH$_4$)$_2$HPO$_4$ + H$_2$O

HAp $\epsilon$Ca$_5$(PO$_4$)$_3$OH + 4H$_2$O + 5CO$_2$

Pure hydroxyapatite phase at milling time 60 min

According to JCPDS file NO. 09-0432

Hydroxyapatite phase

Hexagonal
Part 2
Hydroxyapatite synthesis by ball milling

Results & Discussion:

Fig 2 XRD pattern of synthesized hydroxyapatite from cuttlefish bone at different phase precursor by ball milling method.

5CaCO₃ + 3(NH₄)₂HPO₄ + H₂O → Ca₅(PO₄)₃OH + 4H₂O + 5CO₂

Hydroxyapatite and CaCO₃ phase appeared at milling time 5 to 120 min.

According to JCPDS file NO. 09-0432, Hydroxyapatite phase is hexagonal.
Results & Discussion:

Fig 2 XRD pattern of synthesized hydroxyapatite from cuttlefish bone at different phase precursor by ball milling method.

5CaO + 3(NH₄)₂HPO₄ + H₂O → HAp ⁶Ca₅(PO₄)₃(OH) + 5H₂O

Pure hydroxyapatite phase at milling time 5 min

According to JCPDS file NO. 09-0432

Hexagonal
Part 2
Hydroxyapatite synthesis by ball milling

Results & Discussion:

Fig 3 FTIR spectra of synthesized hydroxyapatite from cuttlefish bone at various different phase precursor by ball milling method.
Part 2
Hydroxyapatite synthesis by ball milling

Results & Discussion:

Fig. 4 SEM image of synthesized hydroxyapatite from cuttlefish bone at various different phase precursor by ball milling method.

- Aragonite phase precursor
- Calcite precursor
- Lime phase precursor

Ball milling time: 120 min

Average particle size: 60-70 nm
Conclusions

From results of temperature effect on cuttlefish bone, Aragonite phase change to calcite phase completely and calcite phase transform to lime phase completely at temperature 500 °C and 900 °C respectively.

From results of hydroxyapatite synthesis:

- Hydroxyapatite phase appear at milling 5 minutes.
  - Hydroxyapatite phase appear completely at 60 minutes in CaCO$_3$ (aragonite phase) precursor.
  - Hydroxyapatite phase appear completely at more than 120 minutes in CaCO$_3$ (calcite phase) precursor.
  - Hydroxyapatite phase appear completely at 5 minutes in CaO (lime) precursor.


Thank you for your attention