# CONTENTS

**Acknowledgements**  
iv-vi  

**Abstract**  
vii-viii  

**Table of Contents**  
ix  

**List of Tables**  
x-xv  

**List of Figures**  
xiv-xix  

**Preface**  
1-3  

**Chapter 1: Fundamentals and Literature Review**  
4-61  

1.1 Nano Instigation  
4  

1.2 Calcium Phosphate as Nanomaterials  
6  

1.3 Preparation of Nanostructures of Different Shapes  
16  

1.4 Synthesis of Calcium Phosphate Nanoparticles  
23  

1.5 Microemulsion – Fundamental Aspects and Literature Review  
38  

**Chapter 2: Materials and Methods**  
62-72  

2.1 Chemicals  
62  

2.2 Experimental Section  
62  

2.3 Characterization  
67  

**Chapter 3: Effect of Wet Chemical Processing Routes on the Nanomorphologies of Calcium Phosphate**  
73-92  

3.1 Introduction  
74  

3.2 Results  
80  

3.3 Discussion  
85  

3.4 Conclusions  
91
<table>
<thead>
<tr>
<th>Chapter 4: Ca/P Ratio Controlled Phase Morphology of Calcium Phosphate Nanomaterials via Emulsion Using Mixed Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Introduction</td>
</tr>
<tr>
<td>4.2 Results and Discussion</td>
</tr>
<tr>
<td>4.3 Conclusions</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Chapter 5: A Novel Route for the Synthesis of Single Crystaline Defect Free Hydroxyapatite</td>
</tr>
<tr>
<td>5.1 Introduction</td>
</tr>
<tr>
<td>5.2 Results and Discussion</td>
</tr>
<tr>
<td>5.3 Growth Mechanism</td>
</tr>
<tr>
<td>5.4 Conclusions</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Chapter 6: Synthesis of Nanocrystalline Calcium Phosphate in Microemulsion-Effect of Nature of Surfactants</td>
</tr>
<tr>
<td>6.1 Introduction</td>
</tr>
<tr>
<td>6.2 Results</td>
</tr>
<tr>
<td>6.3 Mechanism of Calcium Phosphate Crystallization Process in Microemulsion</td>
</tr>
<tr>
<td>6.4 Conclusions</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Chapter 7: Microemulsion Mediated Synthesis of Brushite Nanoparticles: Effect of Temperature</td>
</tr>
<tr>
<td>7.1 Introduction</td>
</tr>
<tr>
<td>7.2 Results</td>
</tr>
<tr>
<td>7.3 Discussion</td>
</tr>
<tr>
<td>7.4 Conclusions</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Chapter 8: Conclusions</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Bibliography</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Appendix</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 1.1 : Broad Classification of Biomaterials Pertaining to Their Properties.

Table 1.2 : Types of Bioceramics with Respect to Their Tissue Reaction.

Table 1.3 : Ca/P Molar Ratios, Chemical Formulas, and Solubilities a of Some Calcium Orthophosphate Minerals.

Table 1.4: Crystallographic Data of Calcium Orthophosphates.

Table 1.5: Surfactants which are often used in microemulsion-mediated nanoparticles synthesis.

Table 1.6: Dimensions and characteristics of different emulsion systems.

Table 2.1: Chemicals and their role & properties.

Table 2.2: Composition of Emulsion Reaction Systems

Table 2.3: Composition of Single Surfactant and Mixed Surfactant Systems

Table 2.4: Composition of Microemulsion Systems.

Table 6.1: Assignment of IR Absorption Bands (cm⁻¹).

Table 7.1: Assignment of IR Absorption Bands (cm⁻¹).
LIST OF FIGURES

Figure 1.1 : Impression of the position of nanoscale dimensions among different objects that are already known.

Figure 1.2 : Illustration of the overall free energy $\Delta G$ as a function of the growth particles size $r$.

Figure 1.3 : Schematic representation of the concentration of molecularly dissulfed sulfur before and after nucleation as a function of time. $C_{RN}$ is the concentration for a given nucleation rate $R_N$. Reprinted from ref 18. Copyright 1950 American Chemical Society.

Figure 1.4 : Schematic representation (free-energy and diameter axes do not have numerical values) of energetics of two different polymorphs as a function of particle radius. Differences in critical nucleus size and activation energy and crossover in phase stability of nanoparticles are shown. Taken from ref. 215.

Figure 1.5 : Schematic illustration of a surfactant.

Figure 1.6 : Schematic representation of a spherical micelle.

Figure 1.7 : Schematic representation of the shape of the surfactant self-assemblies for various values of the packing parameter.

Figure 1.8 : Schematic representation of (a) oil droplet in an oil-in-water microemulsion and (b) of a water droplet in a water-in-oil microemulsion.

Figure 1.9 : A series of phase diagrams of a ternary system transform from Winsor I (a, b) via Winsor III (c to e) to Winsor II (f, g). The dark triangles are three-phase regions. Tie lines indicate the compositions of the equilibrium phases of the two-phase regions: S, W and O stand for surfactant, water and oil, respectively.
Figure 1.10: Schematic diagram illustrating the phase behavior of an oil/water/surfactant system [modified from Moulik and Paul, 1998].

Figure 1.11: Schematic phase prism in terms of temperature and composition [redrawn from Schubert and Kaler, 1996].

Figure 1.12: Schematic pseudo-binary phase diagram at $\alpha = \alpha_1$ as a function of temperature and surfactant weight fraction $\gamma$ [redrawn from Schubert and Kaler, 1996].

Figure 1.13: Schematic section of phase prism of a ternary mixture surfactant/oil/water at constant surfactant weight fraction $\gamma$ ($\gamma_1 < \gamma < \gamma_2$). [Redrawn from Schwuger et al., 1995].

Figure 1.14: Different methods of nanoparticle synthesis in microemulsions: (a) One microemulsion method: Energy triggering method and (b) One-microemulsion method plus reactant method. Cations: A,N, Anions: B,M [redrawn from Osseo-Asare and Arriagada, 1990].

Figure 1.15: Schematic of a collision between two reverse micelles with dissimilar cores. The micelles form a short-lived dimer, as some surfactants molecules are released into the oil phase and the contents of the micellar cores are exchanged.

Figure 1.16: Schematic representation of the course of concentration C during microemulsion and bulk phase precipitation in case of batch operation [redrawn from Schmidt, 2000].

Figure 2.1: Geometrical illustration of crystal planes and Bragg’s law.

Figure 3.1: Illustration of the dependencies of the nucleation rate $B$, growth rate $G$ and the mean particle diameter $d_{pm}$ on the supersaturation (redrawn from Nyvilt et al., 1985).

Figure 3.2: The FTIR spectrum of calcium phosphate nanoparticles obtained from (a) chemical co-precipitation; (b) reverse microemulsion and (e) emulsion process.
Figure 3.3 : The XRD data of calcium phosphate nanoparticles obtained from (a) chemical co-precipitation; (b) reverse microemulsion and (c) emulsion process.

Figure 3.4 : TEM images of calcium phosphate nanoparticles obtained from (a) chemical co-precipitation and (b) reverse microemulsion.

Figure 3.5 : TEM images of calcium phosphate nanoparticles obtained from (c) emulsion process.

Figure 3.6 : Mechanism for the formation of hollow nanospheres.

Figure 4.1 : The FTIR spectra of calcium phosphate nanoparticles obtained from the system (a) E₁, (b) E₂, (c) E₃, (d) E₄ & (e) E₅.

Figure 4.2 : The XRD pattern of calcium phosphate nanoparticles obtained from the system (a) E₁, (b) E₂, (c) E₃, (d) E₄ & (e) E₅.

Figure 4.3(a, b): FETEM micrographs of the sample obtained from the system E₂.

Figure 4.3 : Magnified FETEM micrograph (c) and lattice fringes (d) of the sample obtained from the system E₂.

Figure 4.4 (a, b): FETEM micrographs of the sample obtained from the system E₃.

Figure 4.4 : Magnified FETEM micrograph (c) and lattice fringes (d) of the sample obtained from the system E₃.

Figure 4.5 (a, b): FETEM micrographs of the sample obtained from the system E₄.

Figure 4.5 (c): Lattice fringes of the sample obtained from the system E₄.

Figure 4.6 (a, b): FETEM micrographs of the sample obtained from the system E₅.

Figure 4.6 (c): Lattice fringes of the sample obtained from the system E₅.

Figure 5.1 : The FTIR spectrum of single crystal calcium phosphate nanoparticles.
Figure 5.2: The XRD pattern of single crystal calcium phosphate nanoparticles.

Figure 5.3(a, b): FETEM micrographs of single crystal hydroxyapatite nanorods synthesized by emulsion route.

Figure 5.3(c, d): Magnified FETEM micrographs of single crystal hydroxyapatite nanorods synthesized by emulsion route.

Figure 5.3(e, f): Magnified lattice of single crystal hydroxyapatite nanorod synthesized by emulsion route.

Figure 5.4: Schematic illustration showing the formation of single crystal hydroxyapatite nanorods.

Figure 6.1: The FTIR spectrum of CP nanoparticles obtained from (a, b) Aliquat 336 based single surfactant system before (a) & after (b) calcination; (c, d) Tween 20 based single surfactant system before (c) & after (d) calcination and (e) Tween 20/ Aliquat 336 based mixed surfactant system [0.2M Ca(NO₃)₂ and 0.12M (NH₄)₂HPO₄].

Figure 6.2: The XRD data of of CP nanoparticles (a) Tween 20/ Aliquat 336 based mixed surfactant system; (b) Tween 20 based single surfactant system and (c) Aliquat 336 based single surfactant system. [0.2M Ca(NO₃)₂ and 0.12M (NH₄)₂HPO₄].

Figure 6.3: The XRD data of of CP nanoparticles obtained with Tween 20/ Aliquat 336 based mixed surfactant systems (a) 0.2M Ca(NO₃)₂ & 0.12M (NH₄)₂HPO₄; (b) 0.15M Ca(NO₃)₂ & 0.09M (NH₄)₂HPO₄ and (c) 0.10M Ca(NO₃)₂ & 0.06M (NH₄)₂HPO₄.

Figure 6.4: The XRD pattern of CP nanoparticles obtained from mixed surfactant systems with 0.15M Ca(NO₃)₂ & 0.09M (NH₄)₂HPO₄ before (a) & after (b) calcination.
Figure 6.5: TEM images of CP nanoparticles (a) Tween 20 based single surfactant system and (b) Aliquat 336 based single surfactant system. [0.2M Ca(NO$_3$)$_2$ and 0.12M (NH$_4$)$_2$HPO$_4$].

Figure 6.6: TEM images of CP nanoparticles (a) & (b) Tween 20/ Aliquat 336 based mixed surfactant system. [0.2M Ca(NO$_3$)$_2$ and 0.12M (NH$_4$)$_2$HPO$_4$].

Figure 6.7: TEM images of CP nanoparticles obtained from mixed surfactant systems with (a) 0.15M Ca(NO$_3$)$_2$ & 0.09M (NH$_4$)HPO$_4$ and (b) 0.10M Ca(NO$_3$)$_2$ & 0.06M (NH$_4$)$_2$HPO$_4$.

Figure 6.8: SEM images of CP nanoparticles (a) Tween 20 based single surfactant system; (b) Tween 20/ Aliquat 336 based mixed surfactant system. [0.2M Ca(NO$_3$)$_2$ and 0.12M (NH$_4$)$_2$HPO$_4$].

Figure 6.9: SEM images of CP nanoparticles (a) & (b) Aliquat 336 based single surfactant system. [0.2M Ca(NO$_3$)$_2$ and 0.12M (NH$_4$)$_2$HPO$_4$].

Figure 6.10: A schematic drawing showing the complementarity between the surfactant cation and phosphate anion.

Figure 6.11: Transport Mechanism. Carrier phase shown above represents the interface between the microemulsion droplets from ME-A and ME-B.

Figure 7.1: The FTIR spectrum of CP nanoparticles obtained with (a) [0.2M Ca(NO$_3$)$_2$ and 0.12M (NH$_4$)$_2$HPO$_4$], (b) 0.15M Ca(NO$_3$)$_2$ & 0.09M (NH$_4$)$_2$HPO$_4$ and (c) 0.10M Ca(NO$_3$)$_2$ & 0.06M (NH$_4$)$_2$HPO$_4$.

Figure 7.2: The FTIR spectrum of CP nanoparticles obtained at (a) 30°C, (b) 60°C and (c) 5°C. [0.15M Ca(NO$_3$)$_2$ & 0.09M (NH$_4$)$_2$HPO$_4$].

Figure 7.3: The XRD data of CP nanoparticles obtained with 0.15M Ca(NO$_3$)$_2$ & 0.09M (NH$_4$)$_2$HPO$_4$ at (a) 5°C, (b) 30°C and (c) 60°C.
Figure 7.4: TEM images of CP nanoparticles obtained from microemulsion systems with (a) 0.20M Ca(NO$_3$)$_2$ & 0.12M (NH$_4$)$_2$HPO$_4$, (b) 0.15M Ca(NO$_3$)$_2$ & 0.09M (NH$_4$)$_2$HPO$_4$. [Temperature - 30$^\circ$].

Figure 7.4: TEM images of CP nanoparticles obtained from microemulsion systems with (c) 0.10M Ca(NO$_3$)$_2$ & 0.06M (NH$_4$)$_2$HPO$_4$. [Temperature - 30$^\circ$].

Figure 7.5: TEM images of CP nanoparticles obtained from microemulsion systems at temperature (a) 60$^\circ$C and (b) 6$^\circ$C. [0.15M Ca(NO$_3$)$_2$ & 0.09M (NH$_4$)$_2$HPO$_4$].