Recent Progress in
Nanocomposites

Rich Falcon

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Edited by **Rich Falcon**

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Preface

Every book is a source of knowledge and this one is no exception. The idea that led to the conceptualization of this book was the fact that the world is advancing rapidly; which makes it crucial to document the progress in every field. I am aware that a lot of data is already available, yet, there is a lot more to learn. Hence, I accepted the responsibility of editing this book and contributing my knowledge to the community.

This book brings forth the experiences of experts from different scientific spheres across the world on their encounters with various aspects of nanocomposite science and its uses. It documents latest findings and advancements in nanocomposites through study and research. The book elucidates the applications of nanocomposites in water treatment, super capacitors, anticorrosive and antistatic applications, and other such applications. It also sheds light on multipurpose nanocomposites, photonics of dielectric nanostructures and electron scattering in nanocomposite materials.

While editing this book, I had multiple visions for it. Then I finally narrowed down to make every chapter a sole standing text explaining a particular topic, so that they can be used independently. However, the umbrella subject sinews them into a common theme. This makes the book a unique platform of knowledge.

I would like to give the major credit of this book to the experts from every corner of the world, who took the time to share their expertise with us. Also, I owe the completion of this book to the never-ending support of my family, who supported me throughout the project.

Editor

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New Frontiers in Mechanosynthesis: Hydroxyapatite – and Fluorapatite – Based Nanocomposite Powders

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Additional information is available at the end of the chapter

1. Introduction

Mechanosynthesis process is a solid state method that takes advantage of the perturbation of surface-bonded species by pressure or mechanical forces to enhance the thermodynamic and kinetic reactions between solids. Pressure can be applied via conventional milling equipment, ranging from low-energy ball mills to high-energy stirred mills. In a mill, the reactants are crushed between the balls and wall (horizontal or planetary ball mill, attritor, vibratory ball mill), or between rings or ring and wall (multi–ring media mill) (Bose et al., 2009). These processes cause the creation of defects in solids; accelerate the migration of defects in the bulk, increase the number of contacts between particles, and renew the contacts. In these circumstances, chemical interaction occurs between solids (Avvakumov et al., 2002). This procedure is one of the most important fields of solid state chemistry, namely, the mechanochemistry of inorganic substances, which is intensively developed; so that, a large number of reviews and papers published on this subject in the last decades (Silva et al., 2003; Suryanarayana, 2001; De Castro & Mitchell, 2002). The prominent features of this technique are that melting is not essential and that the products have nanostructural characteristics (Silva et al., 2003; Suryanarayana, 2001; De Castro & Mitchell, 2002). In the field of bioceramics, high efficiency of the mechanochemical process opens a new way to produce commercial amount of nanocrystalline calcium phosphate-based materials. A review of scientific research shows that the mechanosynthesis process is a potential method to synthesis of nanostructured bioceramics (Rhee, 2002; Silva et al., 2004; Suchanek et al., 2004; Tian et al., 2008; Nasiri–Tabrizi et al., 2009; Gergely et al., 2010; Wu et al. 2011; Ramesh et al., 2012).

On the other side, bioceramics play a vital role in several biomedical applications and have been expanding enormously the recent years (Adamopoulos & Papadopoulos, 2007). Among different forms of bioceramics, particular attentions have been placed to calcium phosphates-based powders, granules, dense or porous bodies, and coatings for metallic or polymeric implants due to their excellent biocompatibility and osteointegration properties (Marchi et al., 2009). It is well known that hydroxyapatite (HAp: $Ca_{10}(PO_4)_6(OH)_2$) is a major mineral component of bones and teeth (Zhou & Lee, 2011). Therefore, synthetic HAp has been extensively utilized as a bioceramic for maxillofacial applications owing to its excellent osteoconductive properties (Adamopoulos & Papadopoulos, 2007). Besides this field, in a variety of other biomedical applications calcium phosphates have been used as matrices for controlled drug release, bone cements, tooth paste additive, and dental implants (Ramesh-babu et al., 2006). Nevertheless, HAp intrinsic poor mechanical properties (strength, toughness and hardness), high dissolution rate in biological system, poor corrosion resistance in an acid environment and poor chemical stability at high temperatures have restricted wider applications in load-bearing implants (Fini et al., 2003; Chen et al., 2005).

According to the literature (Jallot et al., 2005), the biological and physicochemical properties of HAp can be improved by the substitution with ions usually present in natural apatites of bone. In fact, trace ions substituted in apatites can effect on the lattice parameters, the crystallinity, the dissolution kinetics and other physical properties (Mayer & Featherstone, 2000). When OH^- groups in HAp are partially substituted by F^-, fluoride-substituted HAp (FHAp: $Ca_{10}(PO_4)_6(OH)_{2-x}F_x$) is obtained. If the substitution is completed, fluorapatite (FAp: $Ca_{10}(PO_4)_6F_2$), is formed. When fluoride consumed in optimal amounts in water and food, used topically in toothpaste, and mouth rinses, it increases tooth mineralization and bone density, reduces the risk and prevalence of dental caries, and helps to promote enamel remineralization throughout life for individuals of all ages (Palmer & Anderson, 2001). It is found that the incorporation of fluorine into HAp induced better biological response (Rameshbabu et al., 2006). On the other hand, the incorporation of bioinert ceramics and addition of appropriate amount of ductile metallic reinforcements into calcium phosphate-based materials has demonstrated significant improvement in structural features as well as mechanical properties. Therefore, improvements on structural, morphological, and mechanical properties of HAp ceramics have been tried by a number of researches (Cacciotti et al., 2009; Schneider et al., 2010; Farzadi et al., 2011; Pushpakanth et al., 2008; Rao & Kannan, 2002; Viswanath & Ravishankar, 2006; Gu et al., 2002; Ren et al., 2010). These studies have shown that such characteristics of HAp might be exceptionally strengthened by various methods such as making nanocomposites, use of different sintering techniques, and adding dopants. In the field of nanocomposites, an ideal reinforcing material for the HAp-based composites, which satisfies all of the requirements, has not yet been found. Thus, synthesis and characterization of novel nanostructured calcium phosphate-based ceramics provided the key target for current research. In most researches (Enayati–Jazi et al., 2012; Rajkumar et al., 2011; Choi et al., 2010), calcium phosphate-based nanocomposites were prepared using multiple wet techniques which ordinarily comprise of several step processes. Over the past decades, the mechanochemical synthesis has been extended for the production of a wide range of nanostructured materials (Suryanarayana, 2001), particularly for the synthesis of nanocrys-

talline calcium phosphate-based ceramics (Rhee, 2002; Suchanek et al., 2004; Tian et al., 2008; Nasiri–Tabrizi et al., 2009; Gergely et al., 2010; Wu et al. 2011; Ramesh et al., 2012). The advantages of this procedure remains on the fact that melting is not necessary and the powders are nanocrystalline (Silva et al., 2007).

In this chapter, a new approach to synthesis of HAp- and FAp-based nanocomposites via mechanochemical process is reported. The effect of high-energy ball milling parameters and subsequent thermal treatment on the structural and morphological features of the nanocomposites were discussed in order to propose suitable conditions for the large scale synthesis of HAp- and FAp-based nanocomposites. Powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and energy dispersive X-ray spectroscopy (EDX) techniques are used to provide evidence for the identity of the samples. Transmission electron microscopy (TEM), Field-Emission Scanning Electron Microscope (FE-SEM), and scanning electron microscopy (SEM) are also utilized to study of the morphological features of the nanocomposites. Literature reported that the size and number of balls had no significant effect on the synthesizing time and grain size of FAp ceramics, while decreasing the rotation speed or ball to powder weight ratio increased synthesizing time and the grain size of FAp (Mohammadi Zahrani & Fathi, 2009). On the other hand, our recent experimental results confirm that the chemical composition of initial materials and thermal annealing process are main parameters that affect the structural features (crystallinity degree, lattice strain, crystallite size) of the products via mechanochemical method (Nasiri-Tabrizi et al., 2009; Honarmandi et al., 2010; Ebrahimi-Kahrizsangi et al., 2010; Fahami et al., 2011; Ebrahimi-Kahrizsangi et al., 2011; Fahami et al., 2012). Consequently, the present chapter is focused on the mechanochemical synthesize of HAp- and FAp-based nanocomposites. In the first part of this chapter, an overview of recent development of ceramic-based nanocomposites in biomedical applications and mechanochemical process are provided. The other sections describe the application of these procedures in the current study. The effects of milling media and atmosphere to prepare novel nanostructured HAp-based ceramics are studied. Moreover, mechanochemical synthesis and characterization of nanostructured FAp-based bioceramics are investigated.

2. Recent developments of ceramic-based nanocomposites for biomedical applications

Over the past decades, innovations in the field of bioceramics such as alumina, zirconia, hydroxyapatite, fluorapatite, tricalcium phosphates and bioactive glasses have made significant contribution to the promotion of modern health care industry and have improved the quality of human life. Bioceramics are mainly applied as bone substitutes in biomedical applications owing to their biocompatibility, chemical stability, and high wear resistance. However, the potential of bioceramics in medical applications depends on its structural, morphological, mechanical, and biological properties in the biological environment. The first successful medical application of calcium phosphate bioceramics in humans is reported in 1920 (Kalita et al., 2007). After that the first dental application of these ceramics in animals

was described in 1975 (Kalita et al., 2007). In a very short period of time, bioceramics have found various applications in replacements of hips, knees, teeth, tendons and ligaments and repair for periodontal disease, maxillofacial reconstruction, augmentation and stabilization of the jawbone and in spinal fusion (Kalita et al., 2007).

Today, many specialty ceramics and glasses have been developed for use in dentistry and medicine, e.g., dentures, glass-filled ionomer cements, eyeglasses, diagnostic instruments, chemical ware, thermometers, tissue culture flasks, fiber optics for endoscopy, and carriers for enzymes and antibodies (Hench, 1998). Among them, calcium phosphate-based bioceramics have been utilized in the field of biomedical engineering due to the range of properties that they offer, from tricalcium phosphates (α/β-TCP) being resorbable to HAp being bioactive (Ducheyne & Qiu, 1999). Hence, different phases of calcium phosphate-based bioceramics are used depending upon whether a resorbable or bioactive material is desired. The phase stability of calcium phosphate-based bioceramics depends significantly upon temperature and the presence of water, either during processing or in the use environment. It is found that at body temperature; only two calcium phosphates are stable in contact with aqueous media, such as body fluids. These stable phases are $CaHPO_4.2H_2O$ (dicalcium phosphate, brushite) and HAp at pH<4.2 and pH>4.2, respectively (Hench, 1998). At higher temperatures, other phases, such as α/β-TCP and tetracalcium phosphate ($Ca_4P_2O_9$) are present. The final microstructure of TCP will contain β or α-TCP depending on their cooling rate. Rapid cooling from sintering temperature gives rise to α-TCP phase only, whereas slow furnace cooling leads to β-TCP phase only. Any moderate cooling rate, in between these two results mixed phase of both β and α-TCP (Nath et al., 2009).

One of the primary restrictions on clinical use of bioceramics is the uncertain lifetime under the complex stress states, slow crack growth, and cyclic fatigue that result in many clinical applications. Two creative approaches to these mechanical limitations are use of bioactive ceramics as coatings, and the biologically active phase in composites. Because of the anisotropic deformation and fracture characteristics of cortical bone, which is itself a composite of compliant collagen fibrils and brittle HAp crystals, the Young's modulus varies ~ 7–25 GPa, the critical stress intensity ranges ~ 2–12 MPa.m$^{1/2}$, and the critical strain intensity increases from as low as ~ 600 J.m^{-2} to as much as 5000 J.m^{-2}, depending on orientation, age, and test condition. On the contrary, most bioceramics are much stiffer than bone and many exhibit poor fracture toughness (Hench, 1998). Therefore, the only materials that exhibit a range of properties equivalent to bone are composites. For this reason, many attempts have been made to improve the mechanical properties as well as structural features through the incorporation of ceramic second phases (Viswanath & Ravishankar, 2006; Evis, 2007; Nath et al., 2009; Ben Ayed & Bouaziz, 2008). These studies have shown that the mechanical properties of HAp and fluoridated HAp might be exceptionally strengthened by composite making technique.

It is found that (Kong et al., 1999) the following conditions should be satisfied to be effective as a reinforcing agent for a ceramic matrix composite material. First, the strength and the elastic modulus of the second phase must be higher than those of the matrix. Second, the interfacial strength between the matrix and the second phase should be neither too weak nor too strong. Indeed, for an appropriate interfacial strength, no excessive reaction should oc-

cur between the matrix and the second phase. Third, the coefficient of thermal expansion (CTE) of the second phase should not differ too much from that of the matrix in order to prevent micro-cracks formation in densification process. Fourth, in the case of biomaterials, the biocompatibility of the reinforcing agent is another crucial factor that should be considered. Nevertheless, an ideal reinforcing material for the calcium phosphate-based composites, which satisfies all of requirements, has not yet been found. So, some attempts have been made to develop HAp- and fluorhydroxyapatite-based composites such as HAp–Al$_2$O$_3$ (Viswanath & Ravishankar, 2006), HAp–ZrO$_2$ (Evis, 2007), HAp–TiO$_2$ (Nath et al., 2009), FHAp–Al$_2$O$_3$ (Adolfsson et al., 1999), FHAp–ZrO$_2$ (Ben Ayed & Bouaziz, 2008), poly(lactide-co-glycolide)/β-TCP (Jin. et al., 2010), polyglycolic acid (PGA)/β-TCP (Cao & Kuboyama, 2010), and HAp–CNT (Lee et al., 2011) composites. These experimental studies exhibited that interfacial reactions occurred during the high temperature processing of composites due to the large interfacial area available for the reactions. Interfacial reactions result in the formation of new phases, influence densification, mechanical properties and even degrade the biological properties of the composite in some cases which often limit their performance (Viswanath & Ravishankar, 2006). Hence, control over nanocomposite characteristics is a challenging task.

3. Mechanosynthesis of ceramic-based nanocomposites

To date, several approaches, including wet chemical methods (Mobasherpour et al., 2007; Kivrak & Tas, 1998), hydrothermal processes (Liu et al., 2006), solid–state reaction (Silva et al., 2003), and sol–gel method (Balamurugan et al., 2002), have been developed for synthesis of nanobioceramics. Among them, mechanochemical process has been extended for the production of a wide range of nanostructured materials (Suryanarayana, 2001; De Castro & Mitchell, 2002). According to literature (Bose et al., 2009), mechanochemical synthesis was originally designed for the production of oxide dispersion-strengthened (ODS) alloys. Over the past 20 years, however, the number of available mechanochemical synthesis has grown, such that Nowadays it is used for the fabrication of a wide range of advanced materials, both metallic and nonmetallic in composition. In mechanosynthesis, the chemical precursors typically consist of mixtures of oxides, chlorides and/or metals that react either during milling or during subsequent thermal treatment to form a composite powder consisting of the dispersion of ultrafine particles within a soluble salt matrix. The ultrafine particle is then recovered by selective removal of the matrix phase through washing with an appropriate solvent.

Mechanochemical approach is a very effective process for synthesizing nanocomposites with various classes of compounds: metals, oxides, salts, organic compounds in various combinations. For example, Khaghani-Dehaghani et al. (Khaghani-Dehaghani et al., 2011) synthesized Al$_2$O$_3$–TiB$_2$ nanocomposite by mechanochemical reaction between titanium dioxide, acid boric and pure aluminum according to the following reactions:

$$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O \tag{1}$$

$$3TiO_2 + 3B_2O_3 + 10Al \rightarrow 3TiB_2 + 5Al_2O_3 \tag{2}$$

Titanium diboride has an attractive combination of high Vickers hardness, electrical conductivity, excellent chemical resistance to molten nonferrous metals and relatively low specific gravity (Gu et al., 2008). However, titanium diboride has poor fracture toughness and impact strength. Thus, the composites of TiB_2 such as Al_2O_3–TiB_2 improve those mechanical properties. These nanocomposites are useful in variety of applications such as cutting tools, wear-resistant substrates, and lightweight armor (Mishra et al., 2006). Results reveal that the Al_2O_3–TiB_2 nanocomposite was successfully synthesized after 1.5 h of milling. Also, the determined amounts of structural features demonstrate that after 20 h of milling the steady state was obtained. Increasing milling time up to 40 h had no significant effect other than refining the crystallite size. The SEM and TEM observations show that increase of milling time was associated with decrease of powder particles, so that a fine structure was produced after 40 h of milling. Figure 1 shows the morphological features of the Al_2O_3–TiB_2 nanocomposite powders after 40 h of milling by SEM and TEM. It is clear that the particles exhibited high affinity to agglomerate. The agglomerates include fine particles of TiB_2 and Al_2O_3.

Thermodynamic studies, based on thermodynamic databases, show that the change in Gibbs free energy of the reduction of boron oxide and titanium oxide with aluminum (Eqs. (3) and (4)) is favorable at room temperature.

$$4Al + 3TiO_2 \rightarrow 2Al_2O_3 + 3Ti$$
$$\Delta G^{\circ}_{298K} = -495.488 \text{ kJ}, \ \Delta H^{\circ}_{298K} = -516.306 \text{ kJ} \tag{3}$$

$$2Al + B_2O_3 \rightarrow Al_2O_3 + 2B$$
$$\Delta G^{\circ}_{298K} = -389.053 \text{ kJ}, \ \Delta H^{\circ}_{298K} = -403.338 \text{ kJ} \tag{4}$$

It is well known if a reaction is highly exothermic, the impact of the milling balls can initiate a mechanically induced self-sustaining reaction (MSR) (Xia et al., 2008). MSR was usually observed in highly exothermic reactions. The ignition of MSR takes place after a certain activation time, during which the powder mixtures reach a critical state due to the physical and chemical changes caused by ball milling (Takacs, 2002; Takacs et al., 2006). That certain activation time depends mainly on the exothermicity of the process, the milling conditions and the mechanical properties of the raw materials. Takacs (Takacs, 2002) showed that a reaction can propagate in the form of a self sustaining process, if $\Delta H/C$, the magnitude of the heat of reaction divided by the room temperature heat capacity of the products, is higher than about 2000 K. The calculations on the system Al–B_2O_3–TiO_2 show that the value of $\Delta H/C$ is about 5110 K. Therefore, the proposed reactions occurred through an expanded MSR reaction in milled samples which led to the formation of Al_2O_3–TiB_2 nanocomposite after short milling times.
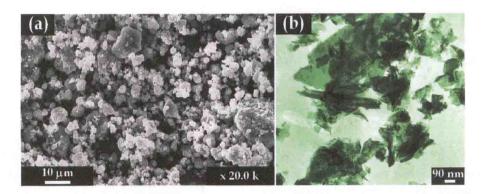
Figure 1. a) SEM micrograph and (b) TEM image of Al_2O_3–TiB_2 nanocomposite after 40 h of milling (Khaghani-Deha-ghani et al., 2011).

3.1. Mechanochemical synthesize of hydroxyapatite nanostructures

HAp and its isomorphous modifications are valuable and prospective materials in biomedi-cal applications. Therefore, a large number of studies was performed on this subject in the last decade (Rhee, 2002; Silva et al., 2004; Suchanek et al., 2004; Tian et al., 2008; Nasiri-Tabri-zi et al., 2009; Gergely et al., 2010; Wu et al. 2011; Ramesh et al., 2012). Generally, the fabrica-tion methods of HAp nanostructures can be classified into two groups: wet and dry (Rhee, 2002). The advantage of the wet process is that the by-product is almost water and as a re-sult the probability of contamination during the process is very low. On the other hand, the dry process has benefit of high reproducibility and low processing cost in spite of the risk of contamination during milling. Furthermore, the dry mechanochemical synthesis of HAp presents the advantage that melting is not necessary and the powder obtained is nanocrys-talline. The calcium and phosphorous compounds used as the starting materials in the dry process are dicalcium phosphate anhydrous ($CaHPO_4$), dicalcium phosphate dihydrate ($CaHPO_4.2H_2O$), monocalcium phosphate monohydrate ($Ca(H_2PO_4)_2.H_2O$), calcium pyro-phosphate ($Ca_2P_2O_7$), calcium carbonate ($CaCO_3$), calcium oxide (CaO), and calcium hydrox-ide ($Ca(OH)_2$), etc.

Otsuka et al. (Otsuka et al., 1994) investigated the effect of environmental conditions on the crystalline transformation of metastable calcium phosphates during grinding. Based on the results, the mixture of $CaHPO_4$ and $Ca(OH)_2$ transformed into low-crystallinity HAp after grinding in air. Nevertheless, under N_2 atmosphere, a mixture of initial materials did not transform into HAp. After that, Toriyama et al. (Toriyama et al., 1996) proposed a method to prepare powders and composite ceramic bodies with a matrix comprising HAp. The pow-ders Was produced by the utilization of a simple and economic mechanochemical method. The composite ceramic bodies were easily obtained by simple firing of the powders at a suit-able temperature (1250 C). After sintering, the obtained products exhibited a flexural strength of more than 100 MPa in standard samples. This value is significantly higher than that usually attainable with commercially available powders (60 MPa). In another research

(Yeong et al., 2001), nanocrystalline HAp phase has been produced by high-energy mechanical activation in a dry powder mixture of CaO and $CaHPO_4$. The initial stage of mechanical activation resulted in a significant refinement in crystallite and particle sizes, together with a degree of amorphization in the starting powder mixture. A single-phase HAp of high crystallinity was attained by >20 h of mechanical activation. The resulting HAp powder exhibits an average particle size of ~ 25 nm. It was sintered to a density of 98.20% theoretical density at 1200 C for 2 h. The hardness increases almost linearly with rising sintering temperature from 900 to 1200 C, where it reaches a maximum of 5.12 GPa. This is followed by a slight decrease, to 4.92 GPa, when the sintering temperature is raised to 1300 C. Afterward, Rhee (Rhee, 2002) synthesized HAp powder by mechanochemical reaction between $Ca_2P_2O_7$ and $CaCO_3$. The two powders were mixed in acetone and water, respectively, and the single phase of HAp was observed to occur only in the powder milled in water, without the additional supply of water vapor during heat-treatment at 1100 C for 1 h. The results indicated that the mechanochemical reaction could supply enough amount of hydroxyl group to the starting powders to form a single phase of HAp. Therefore, the powder of high crystalline HAp can be obtained by the simple milling in water and subsequent heat-treatment. With the development of nanostructured materials using mechanochemical processes, nanocrystalline powders of HAp was produced in 2003 by Silva et al. (Silva et al., 2003). To produce nanocrystalline powders of HAp, five different experimental procedures in a pure dry process were utilized. For four different procedures, HAp was obtained after a couple of hours of milling (in average 60 h of milling, depending in the reaction procedure). In the preparation of nanocrystalline HAp, commercial oxides $Ca_3(PO_4)_2.xH_2O$, $Ca(OH)_2$, $CaHPO_4$, P_2O_5, $CaCO_3$ and $(NH_4)H_2PO_4$ were used in the HAp preparation. This milling process, presents the advantage that melting is not necessary and the powder obtained is nanocrystalline with crystallite size in the range of 22 nm to 39 nm. Subsequently, Silva et al. (Silva et al., 2004) synthesized nanocrystalline powders of HAp using three different experimental procedures (HAPA: $Ca(H_2PO_4)_2$ + $Ca(OH)_2$; HAPB: $Ca(H_2PO_4)_2$ + $CaCO_3$; and HAPC: $CaHPO_4$ + $CaCO_3$). Nanocrystalline HAp was obtained after 5, 10 and 15 h of milling in the reactions HAPA and HAPB, but it is necessary 15 h of milling in the reaction HAPC to obtain HAP. Moreover, in order to improve the mechanical properties of HAp calcium phosphate ceramics, with titanium (CaP-Ti) and zirconium (CaP-Zr), were prepared by dry ball milling using two different experimental procedures: CaP-Ti1: $Ca(H_2PO_4)_2$ + TiO_2; CaP-Ti2: $CaHPO_4$ + TiO_2; and CaP-Zr1: $Ca(H_2PO_4)_2$ + ZrO_2, CaP-Zr2: $CaHPO_4$ + ZrO_2. The calcium titanium phosphate phase, $CaTi_4P_6O_{24}$, was produced in the reaction CaP-Ti1. In the reactions CaP-Ti2, CaP-Zr1 and CaP-Zr2, it was not observed the formation of any calcium phosphate phase even after 15 h of dry mechanical alloying.

Nanocrystalline HAp powders were synthesized by the mechanochemical–hydrothermal method using emulsion systems consisting of aqueous phase, petroleum ether (PE) as the oil phase and biodegradable Tomadol 23–6.5 as the nonionic surfactant (Chen et al., 2004). $(NH_4)_2HPO_4$ and $Ca(NO_3)_2$ or $Ca(OH)_2$ were used as the phosphorus and calcium sources, respectively. The calcium source and emulsion composition had significant effects on the stoichiometry, crystallinity, thermal stability, particle size, and morphology of final products.