Characteristics and properties of hydroxyapatite derived by sol–gel and wet chemical precipitation methods

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Abstract

The synthesis of crystalline hydroxyapatite (HA) nanoparticles with expected microstructure is of primary importance because the process directly relates to the phase purity, morphology, and particle size of the final HA particles. In this work, different morphologies of HA powders were prepared via wet precipitation (HA–Wp) and sol–gel synthesis (HA–Sg) methods. The results showed that pure HA powders were successfully obtained via the two different methods, in which HA–Wp presented smaller crystallite size in accordance with the larger specific area compared with HA–Sg powders. A high surface area of 97.4 m\textsuperscript{2}g\textsuperscript{-1} was obtained in HA-Wp powder, whereas that of HA–Sg powder was 9.0 m\textsuperscript{2}g\textsuperscript{-1}. Upon calcinations at 800–1000 \degree C, the calcined powders were found to be Ca-deficient apatites as HA–Wp and HA–Sg powders decomposed to the secondary phase of \(\beta\)-TCP at 900 \degree C and 1000 \degree C, respectively. Microstructural analysis showed significant difference in terms of HA morphologies produced via the two methods. The HA-Wp powder consisted of nanoscale needle-like structures with soft agglomerated particles, whereas HA–Sg powder exhibited nanoglobular-like structures with hard agglomerated particles. The characteristics of nanocrystalline HA powder obtained from wet chemical precipitation is known to exhibit high surface activity as a bone substitute material.

Keywords: A. Calcination; Sol–gel synthesis; Microstructure; Hydroxyapatite

1. Introduction

During the last several decades, HA \([\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]\) has attracted considerable attention for use in orthopedics and dentistry because of its structural and compositional similarity with natural bone. HA has been primarily used to form sintered body and polymer composites [1] as replacements for bone and periodontal defects [2,3], dental materials [3,4], and maxillofacial implants [2]. In fact, its biocompatibility and ability to bond with surrounding tissues of HA have been experimentally proven to be superior to any other biomaterial [5]. However, most synthetic apatites are formed via high temperature processes, resulting in a well-crystallized structure, which presents little or no activity toward bioresorption [6]. HA solubility increases from crystalline to amorphous and reduces crystal size, which are more advantageous in clinical applications [7]. Hence, in recent years, interest in the synthesis of nanosized HA with grain size less than 100 nm has increased because of its high surface activity and enhanced bioresorption [5]. Moreover, this ultrafine structure is similar to the mineral found in hard tissues and can readily promote osteointegration and subsequent bone tissue formation [5]. In addition, given its greater surface area, nanocrystalline HA exhibits improved

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sinterability at lower temperatures resulting in a high density body couple with enhanced mechanical properties [6–12] suitable for biomedical applications.

In HA synthesis, precise control of crystal growth presents the utmost challenge because it directly relates to the size and geometric shape of the final particles [5]. These primary characteristics are widely documented to majorly affect mechanical properties, biocompatibility, and bioactivity. For example, HA bioceramics with conventional microstructure cannot be used for load-bearing orthopedic and dental application because of their poor mechanical reliability [5]. Paz et al. [13] reported the formation of HA via biomimetic and wet chemical precipitation with spherical (~23 nm) and needle-like (~23 nm in width and ~62 nm in length) morphologies, respectively. They concluded that the morphology, crystallinity, and size distribution of the resulting nanoparticles were strongly dependent on the synthesis method. Evis and Webster [9] also found that crystalline HA with uniform morphology was obtained by increasing the ageing times to 100 h because the particles with non-uniform morphologies redissolve and recrystallize into a more ordered form during the ageing process. The authors also found that the morphology of the particles has an effect on the HA phase stability [9].

In general, the raw materials used to synthesize HA originate from commercial chemicals and natural sources. Naturally sourced HA involve extraction via heat treatment of animal cortical bones (bovine, pig, etc.) and natural waste (egg shell, clamshell) [14], as well as conversion from marine coral derivates [15] to natural HA with acceptable porosity. HA preparation methods can technically be categorized into four groups, namely, dry methods (solid state synthesis, and mechanochemical method), wet chemistry methods (wet chemical precipitation, hydrolysis method, sol–gel, hydrothermal, emulsion method, and sonochemical method), high-temperature processes (combustion, pyrolysis), and combination procedures (hydrothermal–mechanochemical, hydrothermal–hydrolysis). Each method has been exclusively documented with their own advantages and significant results over the others. HA powders with various morphology, stoichiometry, and level of crystallinity can be obtained depending on the method of synthesis. Among these routes, wet chemistry methods, i.e., precipitation and sol–gel, present advantages of precise control over the morphology and size of the particles. Thus, these methods are the most promising for the synthesis of nanosized HA with expected morphology [5].

Wet chemical precipitation and sol–gel methods have been widely used to obtain HA with different particle morphologies. These methods have traditionally been used in the synthesis of materials for implants and are the part of the wet chemistry techniques. Sol–gel synthesis method involves the formation of a colloidal sol, which will subsequently turn into a gel [16]. This method requires no special energy conditions for the formation of the desired compound; thus, the synthesis of ceramic materials could be carried out at room temperature [16]. However, sol–gel synthesis requires a strict control of process parameters and an intimate contact mixing at molecular level (because of the slow reaction between Ca and P precursors in the sol phase) to obtain highly pure, nanosized powder with homogeneous composition. Meanwhile, wet chemical precipitation requires a special pH value control condition for precipitation to occur because the degree of neutralization of phosphoric acid is pH dependent [5]. Moreover, the morphology (shape and size) of nanoparticles obtained via this method is highly sensitive to reactant addition rate [13], in which a lower addition rate of acid will result in a large particle size.

Therefore, although wet chemical precipitation and sol–gel methods have been classified as the simple routes employed in producing HA [17,18] and are able to produce high-purity HA [19], the production of HA nanoparticle with expected morphology via these method remain challenging mainly because of the raw materials used for synthesis.

This paper reports the comparison of the characteristics of nanocrystalline HA powders synthesized via wet chemical precipitation and novel sol–gel synthesis by using different raw materials. The different morphologies and size of powders obtained were evaluated via various physico–chemical techniques, such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM) analyses. In addition, the thermal stability of synthesized powders upon calcination was also studied via XRD analysis.

2. Experimental procedures

2.1. Powder synthesis via wet chemical precipitation

Pure HA powder was produced via a simple wet chemical precipitation method [20]. Calcium hydroxide, Ca(OH)$_2$ (98% purity, R&M Chemicals), and orthophosphoric acid, H$_3$PO$_4$ (85% purity, Merck), were used as Ca and P precursors with a molar ratio of 10:6. Initially, 0.6 mol of H$_3$PO$_4$ (400 mL) was added dropwise (9 drops to 10 drops per 10 s) into 1.0 mol of Ca(OH)$_2$ solution (750 mL) with vigorous stirring. During the titration process, the pH of the mixture was monitored and maintained above 10.5 by adding ammonium (NH$_4$) solution (85% concentration, J. T. Baker). Once titration was completed, the solution was continuously stirred for at least another 5–6 h. The precipitate was then left for ~12 h at room temperature before being filtered and washed using distilled water. The filtered precipitate was dried in an oven at 60 °C for 24 h. The dried cake was then crushed and sieved to obtain well-defined HA powder, hereafter referred to as HA-Wp powder.

2.2. Powder synthesis via sol–gel synthesis

Sol–gel synthesis was also employed to synthesize HA by using Ca (NO$_3$)$_2$·4H$_2$O and di-ammonium hydrogen phosphate [(NH$_4$)$_2$HPO$_4$] as starting precursors. Ethylenedinitrilotetraacetic acid (Titriplex II) was used as the chelating agent to prevent immediate precipitate formation, and urea was used as a gelling agent. A 500 mL portion of ammonium solution (25% solution, Merck) was used to alter the pH. Initially, 0.6 mol Titriplex II was dissolved in ammonia solution at 60 °C with vigorous stirring. An aqueous solution of 0.5 mol Ca (NO$_3$)$_2$·4H$_2$O and 0.3 mol (NH$_4$)$_2$HPO$_4$ were then added into the Titriplex suspension, followed by adding 0.75 mol urea. The mixture was subsequently

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refluxed at 100 °C for 3–5 h with stirring until a gel was obtained. This gel was then dried at 340 °C for 3 h to ensure complete organic and inorganic substance removal. The HA obtained via this method is hereafter known as HA–Sg powder.

Both as-synthesized HA-Wp and HA–Sg after drying the powders were subjected to calcination at different temperatures of 800–1000 °C at a ramp rate of 10 °C/min for 2 h. The thermal stability of the powder was investigated for their phase stability.

### 2.3. Powder characterization

Phase analysis by X-ray Diffraction (XRD) (EMPYREAN, PANalytical, Netherlands) of the samples was carried out at room temperature using Cu-Kα as the radiation source at a scan speed of 0.5° per minute and a step scan of 0.02°. The crystalline phase compositions were identified with reference to the standard JCPDS Card no. 01-074-0565 for hydroxyapatite (HA) available in the system software. The crystallite size of the as-synthesized powders was calculated by using Scherrer’s formula [18].

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were conducted on the as-synthesized HA-Wp and HA–Sg before drying powders in ambient air by using the TG/DTA instrument (Perkin Elmer, Pyris Diamond TG/DTA) with 5 °C/min heating rate from room temperature up to 1000 °C. This method was used to determine the phase stability and reaction temperatures of the produced HA powders. Measurements of the molecular radicals were carried out via the attenuated total reflectance (ATR) method of the FTIR spectrometer (Perkin Elmer FTIR, Spectrum 100 Series) in the mid-infrared range (400 cm⁻¹ to 4000 cm⁻¹). The powders were directly placed onto the holder, and 16 scans were performed at a resolution of 4 cm⁻¹.

The as-synthesized powder morphology was evaluated via FESEM (JEOL, JFM 6700 F, Japan). Images at a significantly higher resolution were recorded via TEM (JEOL, JEM-2100 F, Japan). For TEM observation, the HA powder suspension was prepared by mixing the HA powder with ethanol (95%, Merck) solution followed by sonication for 30 min. A drop of the suspension was applied onto a copper grid and visualized via TEM. The specific surface areas of the powders were measured via nitrogen adsorption method by using the Brunauer–Emmett–Teller (BET) surface area analyzer (Quantachrome Instruments, Autosorb-1). The samples were outgassed at 350 °C for 3 h prior to BET measurement.

### 3. Results and discussion

The XRD patterns of the as-synthesized HA-Wp and HA–Sg powders after drying the powders from the two methods are presented in Fig. 1. All patterns matched with the JCPDS Card no. 09-0432 for hydroxyapatite. Fig. 1 also shows that both powders were purely crystalline HA phase. However, significant differences in crystallinity degree and peak width between HA-Wp and HA–Sg powders were observed. The primary peaks of HA at (211), (112), and (300) from HA-Wp powder shows broadened peaks, whereas HA–Sg powder depicts sharp reflections that represent the higher crystallinity degree of this powder. In this work, the sharp peaks of the HA–Sg powder could be due to the higher temperature applied for the drying process (340 °C) compared with that of the HA-Wp powder (60 °C). Fathi et al. [21] reported that the crystallinity and crystallite size of HA powder synthesized via the sol–gel method depended on calcination temperature, in which the degree of crystallinity increased with calcination temperature.

Broader peaks translate to a higher value of FWHM, which indicates smaller crystallite size [22,23]. In other words, HA obtained via the wet precipitation method had a smaller crystallite size compared with that obtained from sol–gel synthesis. This result was further confirmed by the crystallite size calculated using Scherrer’s formula. The mean crystallite sizes for HA-Wp powder were 19.9 and 44.9 nm, which correspond to the (211) and (112) peaks of HA, respectively. Meanwhile, for the HA–Sg powder, the crystallite sizes that correspond to the (211) and (112) planes were 51.2 and 59.8 nm, which are considerably larger than those of the HA-Wp powder.

The smaller crystallite size of HA-Wp was also supported by the specific surface area results obtained from the BET measurement. The surface areas of HA-Wp and HA–Sg powders were 97.4 and 9.0 m² g⁻¹, respectively. As a result, the powder reactivity of HA-Wp could be significantly enhanced because of the smaller crystallite size, which consequently increases the specific surface area to volume ratio [24]. In addition, the HA-Wp powder characteristic also more likely correlates to the properties of bone mineral crystal, namely, low crystallinity with an extremely large surface area [25,26].

The effect of calcination at different temperatures of 800 °C, 900 °C, and 1000 °C on HA phase stability was also conducted on the HA-Wp and HA–Sg after drying the powders. According
to Pattanayak et al. [27], calcination at different temperatures (200–1000 °C) of HA powder synthesized via precipitation technique revealed that the crystalline HA phase was stable up to 600 °C prior to its transformation into crystalline TCP. A similar result was also obtained by Salimi et al. [28] and Fathi et al. [21] at a temperature of 600 °C in the thermal stability observation of HA synthesized via the sol–gel technique. Meanwhile, Sahu et al. [29] found that HA powder obtained via sol–gel synthesis maintained its phase stability after calcination at 750 °C. Hence, in this work, the temperature range from 800 °C to 1000 °C was selected for calcining HA, taking into account that the possibility for HA decomposition to other phases, primarily β-TCP phase, can only be obtained after calcinations at T > 700 °C [8,21].

The XRD patterns of the calcined HA are shown in Fig. 2. Both powder maintained pure HA crystalline phase at 800 °C. HA-Wp powder decomposed to tricalcium phosphate (TCP) from 900 °C, as indicated in Fig. 2(b), in which β-TCP was presented along with HA phase. Moreover, the fraction of β-TCP phase increased upon calcinations at 1000 °C, as shown in Fig. 2(c). On the other hand, pure HA from sol–gel synthesis was stable at 900 °C (Fig. 2(e)) and started to decompose to TCP at 1000 °C, as seen in Fig. 2(f).

The decomposition of HA powders into β-TCP phosphate is a characteristic of Ca-deficient HA powders [30–33]. However, if the decomposition forms α-TCP as the secondary phase instead, this formation could not be attributed to non-stoichiometric HA. Instead, the formation could be due to the formation of an intermediate phase, oxyapatite, which shows the gradual loss of the radical OH\(^{-}\) (dehydroxylation) when heated at atmospheric conditions [19]. According to Fathi et al. [21], pure HA powder derived from the sol–gel was only obtained after the powder was subjected to calcination at 600 °C, whereas the powder could be decomposed into β-TCP and CaO at 700 °C [21,26]. However, in the present work, the characteristic of pure HA was achieved by as-synthesized HA–Sg after drying the powder at a relatively low temperature of 340 °C (Fig. 1). Meanwhile, Sooksaen et al. [24] indicated that HA powders calcined beyond 800 °C showed the presence of CaO when HA nanopowders were synthesized via wet chemical process by using Ca(NO\(_3\))\(_2\)·4H\(_2\)O and (NH\(_4\))\(_2\)HPO\(_4\) as Ca and P precursors. CaO is actually an impurity in most HA derived via sol–gel, which is due to the decomposition of calcium nitrate that remains either partially reacted or unreacted in the gel during the sintering process [15,22,26]. However, in the present study, CaO was not detected by XRD until 1000 °C for both HA-Wp and HA–Sg powders.

Regardless, the small amount of β-TCP present in HA would be beneficial. Notably, Ca-deficient apatite presents better bioreosorable properties than stoichiometric HA because the compound promotes strong and fast bonding to natural bones by rapid resorption [22]. TCP is known to be a resorbable bioceramic for drug delivery because of its high resorption rate in the body [9]. In several clinical cases, bone implants are desired to replace new bone. However, a high content of β-TCP would result in a very high rate of resorption in the human body and, consequently, deterioration in the mechanical properties of the artificial bone replacements [24]. Given that HA is considered to be nonsoluble in the physiological environment [34], we therefore believed that the presence of a low intensity of β-TCP could optimize the resorption of HA [24].

Fig. 3 shows the FTIR spectra of the as-synthesized HA-Wp and HA–Sg powders. The FTIR spectra exhibited the typical characteristic bands of the calcium hydroxyapatite compound, namely, the existence of phosphate and hydroxyl groups. The characteristic bands of the phosphate group, PO\(_4\)\(^{3-}\), can be seen at ~1086, ~1025, ~960, ~595, ~555, and ~465 cm\(^{-1}\). In addition, the broad OH\(^{-}\) group band was detected at the range from 3200 cm\(^{-1}\) to 3600 cm\(^{-1}\) and at 630 cm\(^{-1}\). The IR spectra also showed a

![Fig. 2. XRD patterns of calcined HA powders at respective temperatures derived from wet chemical (HA-Wp) and sol–gel (HA–Sg) synthesis.](image)

![Fig. 3. FTIR spectra of as-synthesized HA powders obtained from (a) wet chemical precipitation (HA-Wp) and (b) sol–gel (Sg) synthesis.](image)
broad and a bending mode corresponding to the carbonyl group, CO$_3^{2-}$, at 1300 cm$^{-1}$ to 1600 cm$^{-1}$ and at $\sim$ 875 cm$^{-1}$. This result may be due to the partial substitution of carbonate groups from the environment for OH$^-$ and PO$_4^{3-}$ in the lattice of synthetic hydroxyapatite [35] and/or the adsorbed species remaining from aqueous precipitation [36]. However, the carbonate ions are expected to disappear from the apatite structure at a high temperature, i.e., during heat treatment, as reported previously in FTIR studies [31,37].

The TG/DTA curves of the as-synthesized powders obtained via chemical precipitation and sol–gel synthesis are presented in Fig. 4. Thermal analysis of the synthesized HA-Wp powder (Fig. 4(a)) shows a slight weight gain of $\sim$ 1% as heating occurred. This result could be associated with the early carbonation process [25]. However, this process is believed to be disrupted by the desorption of water molecules, as depicted by the weight loss of about $\sim$ 5 wt% from $\sim$ 60 $^\circ$C to $\sim$ 195 $^\circ$C. This phenomenon corresponds well with the endothermic peak in the DTA curve. Absorbed water was presented as a structured hydrated surface layer, which is a highly desirable condition for the enhancement of surface reactivity and maturation process of HA powders [38]. Subsequently, the exothermic reaction took place and continued until 845 $^\circ$C. This continuous exothermic peak that corresponded with a total of $\sim$ 6.7 wt% loss could be attributed to the crystallization process of the HA powder [7]. Furthermore, the following exothermic peak starting from $\sim$ 870 $^\circ$C can be related to the initial dehydroxylation stage of HA decomposition. This phenomenon has also been reported by Martinez et al. [7], but the decomposition of Ca-deficient HA into $\beta$-TCP took place at a lower temperature of 813 $^\circ$C. This decomposition confirmed that HA-Wp powder presents similar characteristics to Ca-deficient HA [7]. Concurrently, a similar result was also observed from the XRD patterns in Fig. 2(b), in which the appearance of $\beta$-TCP for HA-Wp powder was detected at $T=900$ $^\circ$C after 2 h with 2.3% fraction of $\beta$-TCP.

Fig. 4(b) shows the TG/DTA curve for as-synthesized HA–Sg before drying via sol–gel synthesis. The first endothermic

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![Fig. 4. TG/DTA analysis of as-synthesized HA powders derived from wet chemical precipitation (HA-Wp) and sol–gel (HA–Sg before drying) synthesis.](image)

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![Fig. 5. FESEM images of as-synthesized HA powders from (a) wet chemical precipitation (HA-Wp) and (b) sol–gel (HA–Sg) synthesis.](image)
peak, which was accompanied by a weight loss of about \(\sim \) 10% and occurred at \(\sim \) 110 \(^\circ\)C, was due to the evaporation of water from the gel. Upon heating, a massive weight loss of \(\sim \) 45% was observed within the temperature range of 120–380 \(^\circ\)C. An exothermic peak at 160 \(^\circ\)C, which corresponds to 16% weight loss, is attributed to the decomposition and removal of ammonia, organic compounds, and urea. To date, no evidence regarding to the possibility incorporation of ammonia ions into the apatite structure has been found in literature. However, Morrissey et al. [35] predicted that, with any chance of ammonia ion incorporation, the occurrence is expected to be at a low level because of their large size (\(r_{\text{cationic}} = 175\) pm), thereby rendering it negligible. At \(\sim \) 230 \(^\circ\)C, the decomposition of nitrate and hydroxide occurred, as indicated by a weight loss of \(\sim \) 21% corresponding to an endothermic peak in the DTA curve. This particular endothermic peak could be suggested as the onset of nitrate decomposition [6]. At \(\sim \) 320 \(^\circ\)C, an exothermic peak was detected, which indicates the start of HA powder crystallization from its amorphous phase [36]. Martínez et al. [7] has reported on the crystallization process of HA powder that occurs from 363 \(^\circ\)C. This exothermic tendency continues up to 980 \(^\circ\)C, thereby indicating the increase in crystallinity of HA powder. A similar phenomenon had also been depicted elsewhere [25,37]. Referring to the XRD result of HA–Sg powder (Fig. 2(e)), a single pure HA phase was retained up to 900 \(^\circ\)C, which slightly decomposed to \(\beta\)-TCP at 1000 \(^\circ\)C for 2 h. Thus, no definite exothermic peak reflecting this behavior beforehand was observed. In addition, the observation resulting from this analysis also clarified the reason of drying the HA–Sg at 340 \(^\circ\)C during the sol–gel synthesis.

Fig. 5 shows the FESEM microstructure of the as-synthesized calcium phosphate powders from wet precipitation, HA-Wp (Fig. 5(a)), and sol–gel synthesis, HA–Sg (Fig. 5(b)). Different morphologies can be observed. Both HA powders were built up from nanosized particles and showed a high tendency to agglomerate. HA-Wp powders consisted of soft agglomerates, whereas HA–Sg powder appeared to be composed of hard agglomerates. In sol–gel synthesis, dispersing all agglomerates even after rigorous stirring for hours is extremely difficult [29]. Therefore, the hard agglomerate of HA–Sg powder is thought to be due to the formation of gel during the synthesis process. On the other hand, the surface-dominated properties associated with nanocrystallite particles, which caused these particles to clump together, could be a possible reason for the agglomerate behavior.

HA-Wp particles were observed to be finer than those of the HA–Sg powder. Each crystallites cluster varied between \(\sim \) 60 to 100 and 70 nm to 200 nm in diameter for HA-Wp and HA–Sg, respectively. Particle shape and size are known to significantly affect HA powder densification, sinterability, as well as its solubility upon implant. Nanosized HA possessed higher surface area and surface roughness [5], thereby resulting in better cell adhesion and bone regeneration. In addition, Zanotto et al. [39] observed that the morphology change of HA nanoparticles is also related to their crystallinity. The needle-like shape HA nanoparticles with a rough surface results in less crystalline HA, whereas the rod-like shape with a smooth surface for nanoparticles will yield a higher crystallinity [39].

The TEM images (Fig. 6) further reveal the internal microstructures of HA-Wp and HA–Sg powders. The HA-Wp powder is in the form of nanoscale needle-like shape particles (Fig. 6(a)), whereas the morphology of the HA–Sg powder consists of globular-shaped particles (Fig. 6(b)). The HA-Wp powder morphology was in nanocrystals of soft agglomerates, with individual average particle sizes ranging from \(\sim \) 11.7 nm to 50.7 nm in length and \(\sim \) 15 nm to 25 nm in width. On the other hand, the HA powder morphology from

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### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Morphology</th>
<th>Average particle size (nm)</th>
<th>Average agglomerate size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA-Wp</td>
<td>Needle-like</td>
<td>11–51 (length), 15–25 (diameter)</td>
<td>60–100</td>
</tr>
<tr>
<td>HA–Sg</td>
<td>Globular</td>
<td>40–83 (diameter)</td>
<td>70–200</td>
</tr>
</tbody>
</table>

Fig. 6. TEM images of synthesized nano HA powder derived from (a) wet chemical precipitation (HA-Wp) and (b) sol–gel (HA–Sg) synthesis.
sol–gel synthesis (Fig. 6(b)) was highly agglomerated and confirms the presence of nanocrystals in spherical shape morphology with particle sizes from ~40.7 nm to 82.9 nm in diameter. The average size and morphology of both HA powders are summarized and presented in Table 1. The agglomeration of the primary nanoparticles was predominant via sol–gel, thereby resulting in the formation of a cluster-like morphology. Furthermore, the calculated crystallite size based on XRD data also showed that the HA-Wp powder possessed a smaller average crystallites size (~32.4 nm) compared with that derived via sol–gel HA (~60.4 nm). The particle size trend obtained via the two synthesis methods is in accordance with the specific surface area results determined via the BET method. In the present study, the surface area of the powder via wet chemical synthesis showed a higher value compared with the powder obtained via sol–gel synthesis. The needle-like particle was found to be capable of enhancing sinterability and fracture toughness [9], whereas spherical-like particles were effective in drug delivery applications [40]. In addition, HA-Wp powder is expected to present better bioactivity than the coarser particle of sol–gel HA. Biological HA crystals found in physiological human hard tissues are nanoscopic platelike or rod-like crystals that are several nanometers in thickness and tens of nanometers in length [5]. Hence, in this case, the microstructure of HA-Wp nanoparticles shows more similar characteristics to natural bone minerals than HA–Sg powder. Therefore, we deduced that HA-Wp powder with nanocrystals of needle-shape particles presents promising characteristics for its application as bone substitute material.

4. Conclusions

Two solution-based techniques for the preparation of nanoparticle HA were presented, namely, wet chemical precipitation and sol–gel synthesis methods. The characteristics of the powders were compared. Both methods present the ability to produce single-phase nanoparticle HA powders with different morphologies and particle sizes. Upon calcination, the HA-Wp powder decomposed into β-TCP at 900 °C, whereas HA–Sg started to dissociate to the secondary phase of β-TCP at 1000 °C. However, the fraction of β-TCP phase in both powders was relatively small with maximum values of 5.30% and 3.45% at 1000 °C for the HA-Wp and HA–Sg powders, respectively. Nevertheless, both powders obtained in this study were believed to behave as Ca-deficient apatite, which presents better bioresorable properties than stoichiometric HA. In terms of powder morphologies and particle sizes, the HA-Wp powder presented a smaller crystallite size and a considerably higher BET surface area of 97.4 m² g⁻¹ compared with that of the HA–Sg powder at 9.0 m² g⁻¹. The micrograph of the HA-Wp sample showed soft agglomerates of needle-like particles (average of ~31.2 nm), whereas hard agglomerates of globular-shaped particles (average of ~61.8 nm) were observed in the HA–Sg powder. Therefore, the HA powder prepared via wet-chemical synthesis with a poor crystalline structure, a smaller size of needle-like nanoparticles, as well as a large surface area, is expected to present greater reactivity than HA–Sg powder for bone substitute material because HA-Wp exhibits more similar characteristics to natural bone mineral crystals.

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