Thermal Stability of Electrochemical-Hydrothermal Hydroxyapatite Coatings

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Abstract

Dense, uniform hydroxyapatite (HA) coatings were synthesized by hydrothermal crystal growth onto titanium substrates that were electrochemically seeded with HA nanocrystals. The HA was also doped with yttrium and/or fluoride during the hydrothermal reaction. The resulting HA coatings have a unique morphology consisting of crystal domains aligned with the crystallographic *c*-axis oriented normal to the surface of the coating. At elevated temperatures, the HA coatings were found to slowly decompose via dehydroxylation to β -tricalcium phosphate (β -TCP). Thermal decomposition negatively impacts the mechanical stability of the coating and can negatively impact performance *in vivo* due to the higher solubility of β -TCP relative to HA. It is shown that thermal decomposition of HA membranes can be avoided by adding water vapor to suppress dehydroxylation during thermal processing, or by doping the membrane with fluoride during hydrothermal synthesis. Thermal decomposition of HA coatings to β -TCP was characterized by X-ray diffraction and scanning electron microscopy. Coatings of HA or yttrium-doped HA were found to be unstable in dry air above 600 °C, but stable in a steam atmosphere at 900 °C. Coatings doped with fluoride or co-doped with yttrium and fluoride were also thermally stable in dry air at 900 °C. Therefore, the unique HA coating morphology and composition can be maintained during post-synthesis thermal processing or high temperature applications.

Keywords:

Hydroxyapatite, Hydrothermal, Thermal stability, Fluoride

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1. Introduction

Hydroxyapatite (HA) is a crystalline phase of calcium phosphate having the stoichiometric formula of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ with either monoclinic or hexagonal crystal symmetry [1]. The mineral component of teeth and bone tissue consists of HA that is partially substituted with other atoms at the calcium, phosphate, and hydroxyl positions in the crystal lattice [2, 3]. Given its structural and compositional similarity to natural bone mineral, synthetic HA has been extensively studied as a bone substitute, orthopedic implant coating, and drug delivery carrier [4–11]. Hydroxyapatite is a brittle material, so it is often applied as a coating on metal for load bearing applications. The HA coating provides bioactivity, corrosion resistance, and biocompatibility, while the metal provides mechanical strength. A variety of coating methods are available, including plasma spray, sol-gel synthesis, biomimetic approaches, and electrochemical crystallization [12–17]. The chemical composition and morphology of the coating varies greatly depending on the synthesis conditions. Coatings are typically polycrystalline with randomly oriented crystal domains, and may contain impurities of other amorphous or crystalline calcium phosphate phases. Synthetic HA crystals are often nonstoichiometric in which the relative amounts of calcium, phosphate, and hydroxyl groups vary while the HA crystal structure is maintained. In addition, HA is readily doped with other ions that greatly affect the physical, chemical, optical, and electrical properties of the material. For example, doping with strontium, magnesium, and other ions has been shown to enhance bone growth near the HA surface [18, 19]. Fluoride doping increases chemical and structural stability [20–22]. Europium doping creates fluorescent HA crystals [23]. Yttrium doping has been shown to enhance high temperature proton conductivity of HA ceramics [24, 25].

Recently, a novel multi-stage coating method was developed that combines electrochemical and hydrothermal crystallization [26, 27]. A very short electrochemical crystallization is carried out in the first stage in order to seed a metal surface with HA nanocrystals. In the second stage, extended hydrothermal crystal growth onto the seeded substrate results in a dense coating. The electrochemical-hydrothermal method results in a unique HA coating morphology in which all of the crystal domains are aligned with the crystallographic *c*-axis normal to the metal surface. During the hydrothermal crystallization step, the coating may be doped with carbonate, magnesium, yttrium, and other ions [28, 29]. The method was shown to be superior to electrochemical synthesis alone in producing uniform coatings [27]. The unique morphology of the coating was shown to enable enhanced high temperature proton conductivity and permanent electrical polariza-

tion [25, 26, 30]. Unlike other coating methods, the surface is exclusively covered by crystallographic *c*-planes. The control of the HA crystal plane exposed to surrounding fluid may prove valuable in biomedical applications [31].

At temperatures above ~300 °C, HA becomes proton conductive via a mechanism of proton hopping along the linear columns of hydroxyl groups along the crystallographic *c*-axis [32]. The high temperature proton conductivity has led researchers to investigate novel uses of HA in applications such as sensors, ion conducting membranes, and electrets [32–35]. In dry air, it has been shown that the proton conductivity is slowly lost due to dehydroxylation [36]. The decrease in proton conductivity at high temperature can be an indirect measurement dehydroxylation, as the loss of hydroxyl groups eliminates the proton conduction paths. For HA that is deficient in calcium relative to the stoichiometric composition, dehydroxylated HA forms according to the reaction [37]:

The dehydroxylated HA will then decompose to a mixture of β -tricalcium phosphate (β - $\text{Ca}_3(\text{PO}_4)_2$, β -TCP) and stoichiometric HA:

The dehydroxylation process is accelerated the more calcium deficient the HA is, with dehydroxylation occurring as low as 500 °C [37]. Decomposition to β -TCP is detrimental for applications that exploit ion conduction of HA since the complete loss of hydroxyl groups will eliminate the proton conduction path, and the β -TCP formation will introduce grain boundaries that block proton conduction [32, 36, 38]. Dehydroxylation can also be problematic upon sintering of HA coatings for biomedical applications since the decomposition byproducts can dissolve *in vivo* faster than pure HA [39].

In the present study, calcium deficient HA and yttrium-doped HA coatings were synthesized by the electrochemical-hydrothermal method. Then two techniques were investigated for their ability to enhance high temperature stability of the coatings by suppressing dehydroxylation. Heating the coatings in a steam environment rather than dry air was used to increase thermal stability as the water

vapor can drive reaction (1) above to the left [36]. Thermal stability was also enhanced by substituting a fraction of the hydroxyl groups in HA with fluoride during hydrothermal crystallization. Fluoride-doped HA (FHA) is more resistant to decomposition to β -TCP at elevated temperatures, as the fluoride ions interfere with the dehydroxylation process [40–43]. By preventing dehydroxylation, the unique HA coating morphology obtained by electrochemical-hydrothermal synthesis can be maintained after thermal processing, potentially opening up new applications for the material.

2. Experimental Procedure

2.1. Materials

Analytical grade $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.0% purity) and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% purity) were purchased from Alfa Aesar. $(\text{NH}_4)_2\text{HPO}_4$ (>99.0% purity) was purchased from EMD. K_2HPO_4 (99.99% purity), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (99+% purity), NaCl (>99.0% purity), tris(hydroxymethyl)-aminomethane (99.8+% purity), disodium ethylenediaminetetraacetate dihydrate ($\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$) (99.0 - 101.0% purity), and NH_4F (98% purity) were all obtained from Sigma-Aldrich. 36.5-38.0% hydrochloric acid and 28.0-30.0% pure ammonium hydroxide were purchased from Mallinckrodt Chemicals. Detergent powder was purchased from Alconox. Titanium(Ti) substrates (12.5 mm x 12.5 mm and 0.89 mm thick) and platinum foil (25 mm x 25 mm and 0.127 mm thick) were purchased from Alfa Aesar. Deionized water was used for all solutions.

2.2. Electrochemical Crystallization

Titanium substrates were polished with SiC paper (800 grit) to provide surface roughness. The substrates were then thoroughly washed with Alconox detergent powder, rinsed with tap water, attached to a silver wire by tightly wrapping the wire through a drilled hole in the substrate, sonicated in an ethanol/acetone (volume ratio = 1:1) solvent for 30 minutes, and then rinsed with deionized water.

An electrolyte solution was prepared containing NaCl (138 mM), CaCl_2 (1.25 mM), K_2HPO_4 (0.828 mM), and tris(hydroxymethyl)-aminomethane (50 mM) in 125 mL deionized water. The solution was adjusted to pH 7.2 using hydrochloric acid. The electrolyte solution was then heated to 95 °C. During heating, the solution was covered to minimize evaporative loss of water. The substrate and a platinum plate were held parallel to each other with a fixed distance of separation of 10 mm. The substrate and platinum plate were connected to the negative

100 and positive outlets, respectively, of a direct current power supply (Instek GPS-
101 3030D) and immersed in the electrolyte solution. The electrochemical reaction
102 was carried out for 5 minutes at a constant current density of 12.5 mA/cm² (rela-
103 tive to the platinum plate area), then rinsed off with deionized water and dried in
104 air.

105 2.3. *Hydrothermal Crystallization*

106 A solution of Na₂EDTA·2H₂O (0.115 M) in 30 mL of deionized water was
107 stirred for 30 minutes so that it was completely dissolved. Ca(NO₃)₂·4H₂O (0.1
108 M) was then added, followed by (NH₄)₂HPO₄ (0.06 M). For yttrium doped hy-
109 droxyapatite (YHA), Y(NO₃)₃·6H₂O (0.01 M) was added. For fluoride doped
110 hydroxyapatite (FHA), NH₄F (0.02 M) was added. For yttrium and fluoride co-
111 doped hydroxyapatite (YFHA), both Y(NO₃)₃·6H₂O (0.01 M) and NH₄F (0.02 M)
112 were added. The standard HA synthesis solution had no added fluoride or yttrium.
113 The pH of each solution was raised to 10.0 with ammonium hydroxide and then
114 stirred for about 10 minutes. The electrolyte solution was then transferred to a
115 Teflon-lined stainless steel pressure vessel (Parr Item No. 4744, 45 mL internal
116 volume), and filled with approximately 30 mL solution. The substrate electro-
117 chemically coated with HA nanocrystal seeds was submerged in the solution with
118 the seed layer facing down and tilted ~45° relative to the bottom of the vessel. The
119 vessel was heated to 200 °C for 10 hours at autogenous pressure. After 10 hours,
120 the vessel was cooled to room temperature in a fume hood, and then the sample
121 was taken out, rinsed with deionized water several times, and dried in air.

122 2.4. *Thermal Processing*

123 Samples were placed into a tube furnace (Thermo Scientific, Lindberg/Blue
124 M) for 3 hours at a set point temperature of 600, 700, 800, or 900 °C. The ramp
125 rate for heating and cooling was 2 °C/minute with the heating beginning and end-
126 ing at room temperature. For samples heated in steam, a peristaltic pump (Gilson,
127 Minipuls 3) delivered a steady supply of water at a flow rate of 7 mL/minute
128 through the alumina tube containing the sample. The pump was turned on when
129 the temperature of the furnace reached 200 °C, then turned off when it cooled
130 below 200 °C.

131 2.5. *Materials Characterization*

132 The composition of HA membranes was determined by energy-dispersive X-
133 ray spectroscopy (EDX). Three spots on each sample were probed at 15 kV and

Figure 1: Electrochemically synthesized HA seed crystals: (a) side view (b) top view.

the average values and standard deviations were calculated. The crystal structure of HA was determined by X-ray diffraction (XRD) (Philips PW3020) with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) from $2\theta=20\text{--}40^\circ$ with a step rate of 0.02 degrees/second. Phase identification was made by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) files. Relative intensities were calculated using X'Pert Data Viewer software. Crystal morphology was examined using a scanning electron microscope (SEM, Zeiss-Auriga) with an accelerating voltage of 3 kV.

3. Results and Discussion

Hydroxyapatite nanocrystals were deposited onto titanium substrates through electrochemical crystallization in order to form a seeded surface to use in subsequent hydrothermal crystal growth. Figure 1 shows a typical HA layer that is formed after 5 minutes at 95 °C with an electrical current density of 12.5 mA/cm². The thickness of the HA layer is roughly 500-800 nm, while the width of each crystal is about 20-25 nm. In the side view image shown in Fig. 1(a), some of the HA was removed with a blade in order to show the film thickness and underlying substrate. The electrochemical synthesis results in a uniform coating of nanocrystals of HA. The same electrochemical seeding conditions were used for all samples. The HA nanocrystals seeds act to promote crystal growth on the titanium surface during the secondary hydrothermal crystallization step.

Four types of samples were synthesized by hydrothermal crystallization onto the seeded substrate: hydroxyapatite (HA), fluoride-doped (FHA), yttrium-doped (YHA), and HA co-doped with yttrium and fluoride (YFHA). Each sample was

synthesized in a single hydrothermal crystallization reaction at 200 °C for 10 hours. Hydrothermal crystallization onto the seeded substrates results in larger crystals that are aligned on the surface with the *c*-axis normal to the substrate [26]. The crystals are also easily doped during hydrothermal synthesis by adding reagents containing the desired dopant [28, 29]. The composition of the resulting samples was examined by EDX, as shown in Table 1. EDX and electron microprobe analysis confirmed the presence of yttrium and fluoride in the doped samples FHA, YHA, and YFHA. Yttrium concentration was confirmed using electron microprobe analysis since the yttrium and phosphorous EDX peaks are very close. The calcium to phosphorous (Ca:P) ratio was found to be below the stoichiometric value of 1.67 for all samples, indicating the product is non-stoichiometric calcium deficient hydroxyapatite that is typical from hydrothermally synthesis [44]. For samples doped with yttrium, the ratio (Y+Ca):P was used in Table 1 because yttrium atoms substitute for calcium in the crystal lattice.

Sample	Ca [At%]	P [At%]	Y [At%]	F [At%]	(Ca+Y):P
HA	61±0.9	39±0.9	–	–	1.54±0.06
FHA	56±1.4	34±0.1	–	9.5±1.4	1.62±0.04
YHA	54±0.9	39±0.6	6.4±0.6	–	1.55±0.04
YFHA	49±1.4	34±1.1	6.1±0.6	11±2.0	1.62±0.07

Table 1: Composition of samples as determined by EDX and EMA.

Representative side view images of all four types of samples synthesized hydrothermally onto the seeded titanium substrate are shown in Fig. 2. For the un-doped HA shown in Fig. 2(a), the crystals are ~10 μm in length and 1-2 μm in width with hexagonal facets visible on the upper surface. The longest axis of the crystals is the *c*-axis, so the SEM image indicates preferential orientation of the *c*-axis normal to the titanium substrate. With fluoride doping, the crystals are again ~10 μm in length and have a maximum width of ~2 μm, as shown in Fig. 2(b). The fluoride doped samples have flatter and more sharply defined hexagonal facets on the upper surface and a broader distribution of crystal widths with a larger fraction of the crystals smaller in width than those observed in un-doped HA. Yttrium doping suppresses growth along the *c*-axis in favor of growth perpendicular to the *c*-axis [28]. As a result, the yttrium doping results in a more dense coating, as shown in Fig. 2(c). Although some of the crystal domains are fused together, individual hexagonal facets are still visible on the upper surface. The yttrium doped crystals are wider than un-doped HA, and the coating thickness is significantly reduced to ~5 μm. The sample co-doped with yttrium and

Figure 2: Side view images of hydroxyapatite that was hydrothermally crystallized onto the seeded titanium surface: (a) hydroxyapatite (HA), (b) fluoride-doped HA (FHA), (c) yttrium-doped HA (YHA), and (d) HA co-doped with yttrium and fluoride (YFHA).

187 fluoride, shown in Fig. 2(d), reveals a similar morphology to the yttrium doped
 188 sample except that the majority of the crystal domains are fused together to form
 189 a coating that is nearly fully dense.

190 The crystal structure of the four samples shown in Fig. 2 was probed with
 191 XRD. A representative XRD pattern is shown in Fig. 3 for the un-doped HA.
 192 The most distinct feature of the XRD pattern is the very large enhancement in
 193 intensity of the (0 0 2) peak, which is consistent with the preferential orientation
 194 of the *c*-axis normal to the substrate. All other peaks were identified as belonging
 195 to HA or the underlying titanium substrate, indicating that no secondary crystal
 196 phases were present. The other three samples had similar XRD patterns, with
 197 strong enhancement of the (0 0 2) peak and all peaks were identified as belonging
 198 to either the apatite crystal structure or the titanium substrate. In the thermal
 199 stability analysis shown below, the XRD patterns of HA, FHA, YHA, and YFHA

200 samples are plotted with the (0 0 2) peak off scale in order to focus on the smaller
 201 peaks that result from the formation of secondary crystal phases upon heating.

Figure 3: X-ray diffraction pattern of as-synthesized HA coating on titanium. Peaks are labeled with their corresponding Miller index number. Strong enhancement of the (002) peak indicates preferential orientation of the *c*-axis normal to the Ti surface.

202 Figure 4 shows the morphological changes observed upon heating samples of
 203 HA. The unheated sample shown in Fig. 4(a) has smooth surfaces with well de-
 204 fines crystal facets. Upon heating to 600 °C in dry air for 3 hours, as shown in Fig.
 205 4(b), the crystal morphology was largely unchanged except for the appearance of
 206 a few small holes on some of the crystal facets. Increasing the heat treatment tem-
 207 perature to 700 °C in dry air results in the edges of the crystal facets becoming
 208 more rounded, and the formation of new smaller crystal grains embedded in the
 209 larger crystals, as shown in Fig. 4(c). Heating in dry air at 800 °C and 900 °C
 210 resulted in the crystals being entirely covered with new smaller crystal grains, as
 211 can be observed in Fig. 4(d) and Fig. 4(e). In contrast, Fig. 4(f) shows that HA
 212 can be heated up to 900 °C in a steam atmosphere without the crystal morphology
 213 changing. It is likely that steam suppresses the decomposition Reaction (1) via Le
 214 Chatelier's principle.

215 XRD analysis confirms that the morphological changes observed via SEM are
 216 the result of the formation of β -TCP. Figure 5 shows the XRD patterns of unheated
 217 HA in comparison to the sample exposed to steam at 900 °C for 3 hours, and HA
 218 samples exposed to dry air at 600, 700, 800, and 900 °C for 3 hours. The XRD
 219 patterns of the samples heated in steam and in dry air at 600 °C appear very similar
 220 to that of unheated HA, which is consistent with the morphology of these samples
 221 all appearing similar in Fig. 4. For the sample heated in dry air at 700 °C, a new

Figure 4: Hydroxyapatite (HA): (a) as-synthesized, (b) heated in dry air at 600 °C, (c) heated in dry air at 700 °C, (d) heated in dry air at 800 °C, (e) heated in dry air at 900 °C, (f) heated in steam at 900 °C.

peak appears that has been identified as the (0 2 10) peak of β -TCP according to JCPDS 09-0169. At higher temperatures, two additional peaks appear that have been identified as the (2 2 0) and (2 1 4) peaks of β -TCP. The intensity of the β -TCP peaks increase with increasing temperature, indicating that the fraction of HA degrading to β -TCP in dry air increases with increasing temperature. The XRD patterns also confirm that steam is effective in preventing the degradation of HA to β -TCP.

Figure 5: XRD patterns of hydroxyapatite (HA) samples: as-synthesized, heated in steam at 900 °C, and heated in dry air at 600, 700, 800, and 900 °C.

Fluoride doping is also known to enhance the thermal stability of HA [40–43]. To examine the effect of fluoride doping on β -TCP formation, several samples of FHA were subjected to the same heat treatment process used for the HA samples described above. Figure 6 shows SEM images of unheated FHA in comparison to FHA samples heated in dry air at 700, 800, and 900 °C for 3 hours. The crystal morphology is largely unchanged. The edges of the crystal facets become slightly rounded upon heating, but there is no evidence of the formation of new crystal domains. XRD results support the SEM observations, as shown in Fig. 7. For all of the FHA samples, none of the β -TCP peaks found in heat treated HA were observed. The only XRD peaks not identified as belonging to apatite were those of the titanium substrate, or TiO_2 as a result of surface oxidation of the substrate at high temperature in air. The results confirm the hypothesis that fluoride doping can enhance thermal stability of HA by preventing dehydroxylation.

Yttrium doping has been shown to significantly enhance proton conductivity of HA [24, 25]. The trivalent yttrium ion substitutes for a fraction of the divalent calcium ions in the apatite crystal lattice. As a result, some of the OH^- ions

Figure 6: Fluoride doped hydroxyapatite (FHA) samples: (a) as synthesized, and heated in dry air at (b) 700 °C, (c) 800 °C, and (d) 900 °C.

Figure 7: XRD patterns of fluoride doped hydroxyapatite (FHA) samples: as synthesized, and heated in dry air at 700, 800, and 900 °C.

are converted to O^{2-} to maintain charge balance in the crystal. It has been hypothesized that the ratio of $[O^{2-}]/[OH^-]$ plays a significant role in determining the conductivity [24]. Therefore, yttrium doping is of interest to create highly conductive HA membranes [25]. Unfortunately, yttrium doping was found to decrease thermal stability of HA. Figure 8 shows SEM images of unheated YHA in comparison to samples heated at 600, 700, 800, and 900 °C for 3 hours. The crystals initially have smooth facets, but numerous grain boundaries are observed starting to form on the facets at 600 °C. The new grains grow larger with increasing temperature. After heating at 900 °C, the new grains cover the entire sample and it is difficult to discern the original YHA crystals from observation of the surface of the sample. The XRD patterns confirm that these new grains are from the formation of β -TCP, as seen in Fig. 8(f). For samples heated to 700–900 °C in dry air, the (0 2 10), (2 2 0) and (2 1 4) peaks of β -TCP are observed, and the intensity of the β -TCP peaks increase with increasing temperature. It is apparent that yttrium doping decreases thermal stability, as the β -TCP grains start to form at a lower temperature and grow larger at higher temperatures than in un-doped HA processed under identical conditions.

To examine if fluoride doping may enhance thermal stability of YHA, samples co-doped with yttrium and fluoride were heated in dry air. Figure 9 shows SEM images of unheated YFHA in comparison to samples exposed to dry air at 800 and 900 °C for 3 hours. The coatings maintain the same dense morphology, with no evidence of the formation of new grains from the observation of the surface of the coating. The XRD patterns shown in Fig. 9(d) confirm that no β -TCP

Figure 8: Yttrium doped hydroxyapatite (YHA) samples: (a) as synthesized, and heated in dry air at (b) 600 °C, (c) 700 °C, (d) 800 °C, and (e) 900 °C. XRD patterns of the samples are shown in (f).

Figure 9: Yttrium/fluoride co-doped hydroxyapatite (YFHA) samples: (a) as synthesized, and heated in dry air at (b) 800 °C and (c) 900 °C. XRD patterns of the samples are shown in (d).

peaks appear in the heated samples. The results indicate that fluoride doping significantly enhances thermal stability, even when the sample is co-doped with yttrium. The data also suggest that fluoride doping may be a broadly applicable approach to increase the thermal stability of apatite materials that are doped with other elements.

4. Conclusions

Electrochemical-hydrothermal synthesis produces HA coatings with a unique morphology consisting of crystal domains aligned with the *c*-axis normal to the substrate. As a result, the surface of the coating is covered extensively with crystallographic *c*-planes. The data show that the coatings are calcium deficient in composition, and decompose at high temperature through dehydroxylation to form a mixture of β -TCP and HA. Yttrium-doped HA is known to have higher

ionic mobility than un-doped HA, but was found to be less thermally stable. The results suggest a connection between high temperature ionic mobility and thermal stability since ions are shuttled along the hydroxyl groups that are mobilized during dehydroxylation. The β -TCP grains grow to cover the coating surface. The formation of β -TCP and the introduction of grain boundaries between β -TCP and HA will hinder potential biomedical and electrochemical applications of the coatings.

Two methods were found to suppress thermal decomposition by preventing dehydroxylation that leads to β -TCP formation from calcium deficient HA: fluoride doping and added steam. The dehydroxylation reaction produces water vapor, and a steam atmosphere was found to suppress the reaction through Le Chatelier's principle. The hydroxyl groups were partially substituted with fluoride, and the presence of fluoride was found to suppress dehydroxylation. The unique coating morphology obtained through electrochemical-hydrothermal synthesis can therefore be maintained during high temperature applications and following thermal processing. The data demonstrate that fluoride doping and added steam enable the membrane morphology to be maintained at least up to a temperature of 900 °C, which exceeds the typical operating temperatures of potential electrochemical applications of HA.

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