The F content in sol–gel derived FHA coatings: an XPS study

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Abstract

Fluoridated hydroxyapatite (FHA) coatings have good bioactivity and small solubility in body fluid and thus have good potential as alternative for pure hydroxyapatite (HA) in bioactive applications. Bioactivity and solubility are sensitive to fluorine content in the coatings. In this work, Ca(NO3)2, P2O5 and HPF6 are used to prepare FHA coatings. The fluorine content of the coatings is characterized by means of X-ray photoelectron spectroscopy (XPS) analysis and a pF-meter with a fluorine-sensitive electrode. The XPS results of the F/Ca ratio are in good agreement with the HPF6/Ca ratio designed in the dipping sol when F/Ca is below 0.2. The F/Ca ratio saturates at 0.2 as fluorapatite forms. Upon saturation of F in FHA, the extra fluorine is believed to vaporize and evade the coating as HF formed from the reaction between CaF2 and the acidic P-containing groups. For the same reason, the fluorine content in the coating is also affected by the Ca/P ratio in the dipping sol.

1. Introduction

Human bone is a composite of collagen and calcium phosphate. Thus, efforts on materials development for bone repair are focused on calcium phosphates which provide good biocompatibility. Of them, hydroxyapatite (HA) is the most hopeful since its similarity to natural bones [1] in both crystalline structure and chemical composition. In many cases, HA is applied as coating on biomedical metal and thus integrates the coating’s bioactivity with the metal’s mechanical properties [2]. Although such implant materials have good performance during the early fixation period, its long-term performance could deteriorate by the relatively large dissolution of HA in body fluid [3,4].

Substitution of (OH)− by F− results in the formation of fluoridated hydroxyapatite (FHA). This lowers HA’s solubility and promotes bioactivity and thus is widely used in prevention of dental caries [5]. Recently, many researchers focus on the application of FHA as bioactive coatings to provide both early fixation and long-term performance [6–8]. In comparison to pure HA, in vitro results have shown that FHA coatings could provide lower dissolution [7,9], better apatite-like layer deposition, better protein adsorption [10], comparable or better cell attachment [7,11,12] and improved alkaline phosphatase activity [12] in cell culture. However, these advantages of FHA coatings are sensitive to fluorine content. Sol–gel deposition provides easy control of chemical composition at relatively low heat treatment temperature [9,13] and thus is employed in this study to produce FHA coatings. X-ray photoelectron spectroscopy (XPS) and a pF-meter with a fluorine-sensitive electrode are used to characterize the fluorine content in the coating and to establish the relationship between the F content in the coating and that in the dipping sol.

2. Experimental

In preparation of the dipping sols, calcium nitrate tetrahydrate (Ca(NO3)2 · 4H2O, GR, Merck) was dissolved
in ethanol (GR, Merck) to form the 2mol/L “Ca-precursor”; ethanol was gradually poured into phosphor pentoxide (P₂O₅, GR, Merck), and the solution was refluxed for 24 h as the “P-precursor.” Then, the Ca- and P-precursor were mixed with various amount of H₃PO₄ (GR, Merck) for six ratios of H₃PO₄/Ca (1:90 through 6:90) and five compositions of Ca/P (1.50–2.00). These solutions were further refluxed for 24 h to be the “dipping sols.”

Titanium alloy substrates (Ti6Al4V, 20×30×1 mm) were polished down to #1200 grade SiC paper. The substrates were rinsed in double distilled water and ultrasonically washed in acetone for 10 min. After drying, the substrates were dipped in the sols (50 ml) and slowly drawn out at a speed of 3 cm/min. The sol-coated substrates were then immediately transferred into an oven at 150 °C and held for 15 min to dry up before transferring to a firing oven at 600 °C. The firing occurred at 600 °C for 15 min. This dipping–drawing–drying–firing process was repeated for five times for desired coating thickness.

The coatings were characterized by X-ray diffractometry (XRD; RIGAKU, D-Max, RA, 2°/min, 0.02° per step) for phase identification. For chemical bonding and chemical group identification, the coatings were scratched off the Ti-alloy substrate, mixed with KBr powders and compressed into pellets for Fourier transformed infrared analysis (FTIR; NICOLET, Avatar 360). X-ray photoelectron spectroscopy (XPS; AXIS HSi 165 Ultra, Aluminum mono, 1 eV per step) was used for fluorine content analysis at the surface of the coating. In addition, a pF-meter was also used to characterize the bulk fluorine content in the coating: the scratched-off coatings were weighed and dissolved in a diluted acid. The acidic solution was analyzed for fluorine using a pF-meter (PH-2, Hangzhou Huaguang) with a fluorine-ion-sensitive electrode (PF-1, Shanghai Kangning).

3. Results

After the dipping–drawing–drying–firing process was repeated for five times, the thickness of the coatings is around 1.5 μm. Fig. 1 plots two XRD patterns of FHA coatings at H₃PO₄/Ca=1:90 and 6:90. These patterns were typical of all six coatings from H₃PO₄/Ca=1:90 through 6:90 (with a step of 1:90): peaks ascribed to (112), (211), (300) and (002) pertaining to apatite phase were observed; there was no trace of CaO, β-TCP or CaF₂. FTIR results in Fig. 2 confirmed the existence of PO₄³⁻ (962, 1040, 1092, 601 and 569 cm⁻¹), OH⁻ (1640 and 3450 cm⁻¹) and CO₃²⁻ (1400 and 1450 cm⁻¹) chemical groups. The widened OH bands located at 1640 and 3450 cm⁻¹ could be attributed to the moisture adsorption in KBr salt, which overlapped the stretch band of OH in apatite structure. Fig. 3 shows the fluorine content (in terms of F/Ca) in the coating obtained by the pF-meter method and that by the XPS method as a function of the F-concentration in the sol (in terms of H₃PO₄/Ca). A few observations are worth noting: (1) the two curves have the same trend, but the XPS results are higher than that of the pF-meter method; (2) at low concentration, fluorine content in the coating increased in

![Fig. 1. Typical XRD patterns of FHA coatings derived from sols with different H₃PO₄/Ca ratio.](image-url)
a linear manner. At above HPF₆/Ca ≥ 4:90, a saturation of F in the coating occurred; (3) from the XPS results for the low F cases, the F content in the coating roughly matches that in the sol. This can be seen by multiplying the x axis by 6 to give F/Ca of 0.07, 0.13, 0.20, 0.27, 0.33 and 0.40, and then comparing with the F/Ca ratio in the coating (the y axis); (4) the increase of fluorine in the coating continues with increase of fluorine in the sol until F/Ca in the coating reaches about 0.2. After that, increasing of the F-concentration in the sol does not promote more incorporation of F in the coating (the F/Ca ratio in the coating becomes almost constant).

4. Discussions

4.1. Discrepancy in F/Ca data

As noted in Fig. 3, the fluorine content obtained by the pF-meter method, which could be termed as the bulk composition, is appreciably lower than that obtained by XPS. The discrepancy may have come from the following two aspects: first, the pF-meter method gives the chemistry as weight percentage. The scratching process (using another piece of Ti-alloy substrate) may have resulted in the inclusion of substrate materials from the coating–substrate interface in the scratched-off coatings. Although the amount of such inclusion may be very limited, the total amount of the scratch-off coatings was only in the magnitude of a few hundredths of a gram, thus the resulting error in the weight of the coating may not be very small. Second, the F/Ca ratio of the coatings was calculated from the weight percentage that was obtained through molecular weight of HA (Ca₁₀(PO₄)₆(OH)₂). However, in the firing process, possible substitution of PO₄³⁻ or OH⁻ [14] by CO₃²⁻ took place, thus the resultant coating chemistry deviated from pure stoichiometry. For instance, the existence of CO₃²⁻ was observed in the FTIR results (cf. Fig. 2); that further aggravated the weight calculation error. In XPS analysis, however, no weight information was used in assessing the F/Ca ratio, and the CO₃²⁻ substitution of PO₄³⁻ or OH will not affect the F/Ca ratio. Therefore, XPS data would be much more accurate, although it only gives information on the surface. However, both data give similar changing trends between the F/Ca ratio in the coatings and the HPF₆/Ca ratio in the dipping sols: at first, the fluorine content in the coatings increased against
HPF6/Ca ratio and then leveled off. Such results indicate that there is a fluorine limitation in the FHA coatings.

4.2. F-limit in the coating

A pure hydroxyapatite has a stoichiometric formula in the form of Ca10(PO4)6(OH)2. With fluoridation, F− replaces some of the (OH)− and forms Ca10(PO4)6Fx(OH)2−x, that is the so-called fluoridated hydroxyapatite (FHA). In the extreme case, fluorine replaces all the OH group and thus forms fluorapatite Ca10(PO4)6F2 or FA. In an HA, F/Ca=0 since there is no fluorine. In an FHA, the F/Ca ratio varies from 0 to 0.2. In a pure FA, F/Ca=2:10=0.2, that is the stoichiometric limit.

During the refluxing process, as soon as F− is released by HPF6 hydrolysis and alcoholysis in the solution, F− reacts with Ca2+ and forms nanoscale CaF2 particles (n-CaF2) [15]. During subsequent drying and firing process, these particles react with the rest of Ca and P groups to form FHA phase. In this process, the more the F-ion in the solution, the more n-CaF2 forms, thus the greater F content in the FHA coating. An almost-linear relationship was seen in Fig. 3 as the HPF6/Ca ratio increased up to 3:90. After that, a deceleration of the inclusion of F in the coating was experienced and eventually leveled off even with further increase in F concentration in the sol. It is seen from the XPS profile (Fig. 4) of the last sample in Fig. 3 (sample at 6:90 or F/Ca=0.4 in the sol), there existed only F1s profile for F in FHA (at 684.2 eV), no trace of F1s in CaF2 (at about 686.7 eV) was seen (thus, no CaF2 phase). Therefore, although the sol contained extraneous amount of n-CaF2, fluorine in the coating only existed in the FHA phase and only up to F/Ca=0.2 (cf. Fig. 3, XPS data, last point). As such, where is the extra F?

To understand the formation mechanism in this process and answer the question of where the extra fluorine has gone, it would be useful first to examine the effect of varying Ca/P ratio. FHA coatings derived from varying Ca/P ratio in the sol (by increasing or reducing P content while keeping HPF6/Ca ratio to remain at 6:90) were analyzed by XPS and identified an undisputable decreasing F/Ca in the coating with decreasing Ca/P (Fig. 5) in the dipping sol. CaF2 phase did appear in the coatings, however, when Ca/P ratio reached a very high value, such as 2.00, as illustrated in Fig. 6, an additional F1s peak belonging to CaF2 was observed. For this sample, the F/Ca ratio in the coating reached 0.251 (Fig. 5), owing to the existence of CaF2. That the Ca/P ratio in the dipping sol significantly affected the fluorine content in the coating indicated that some form of reactions took place between fluorine and Ca or P containing groups, which consumed part of F during drying and firing process.

4.3. Fluorine-consuming hypothesis

The formation of FHA can be described from the reaction of the n-CaF2 during the drying and firing process. Let us

![Fig. 4. XPS F1s spectrum of FHA coating with HPF6/Ca=6:90 in the dipping sol.](image)

![Fig. 5. F/Ca ratio in the FHA coatings as a function of Ca/P ratio in the dipping sols (determined by XPS, with fixed F-concentration in the dipping sol: HPF6/Ca=6:90).](image)

![Fig. 6. XPS F1s spectrum of FHA coating with Ca/P=2.00 and HPF6/Ca=6:90 in the dipping sol.](image)
write FHA as $3(Ca_3(PO_4)_2)CaF_x(OH)_{2-x}$, the overall chemical process can be simplified into a two-step reaction:

$$3Ca(M_{Ca}) + 2P(M_P) \rightarrow \{i - Ca_3(PO_4)_2\}$$

$$3\{i - Ca_3(PO_4)_2\} + (x/2)(n - CaF_2) + (1 - x/2)Ca(M_{Ca}) \rightarrow Ca_{10}(PO_4)_6F_x(OH)_{2-x}$$

where $M_{Ca}$ and $M_P$ stand for the ligands coordinated to Ca and P, respectively, $i-Ca_3(PO_4)_2$ stands for the intermediate compound between Ca and P with Ca/P of 1.5, and $x \leq 2$.

Considering the point of HPF$_6$/Ca ratio in the dipping sol is equal to 3:90, which results in the formation of pure fluorapatite, the right amount of n-CaF$_2$ formed and resulted in Ca/P ratio equal to 1.5. When HPF$_6$/Ca was over 3:90, excessive n-CaF$_2$ formed, which resulted in reduction in Ca/P ratio in the sol (Ca was used in forming CaF$_2$). To take into account of the “extra” phosphor groups, the reactants in Eq. (2) can be rewritten as

$$3(n - CaF_2) + 2P(M_P) \rightarrow \{i - Ca_3(PO_4)_2\} + 6HF \uparrow$$

The intermediate compound $i-Ca_3(PO_4)_2$ further takes part in the reaction given by Eq. (2) and forms FHA. Consequently, the overall FHA formation process can be represented by

$$3(3 - x'/6)\{i - Ca_3(PO_4)_2\} + (x'/2)(n - CaF_2) + (x'/3 - 2/3)P(M_P) \rightarrow Ca_{10}(PO_4)_6F_x(OH)_{2-x} +HF \uparrow$$

where $x' \geq 2$. Since the P-containing groups are acidic, the reaction with CaF$_2$ results in volatile HF that escapes from the coating in the heating process, as shown in Eq. (3):

$$(10/3 - x'/6)\{i - Ca_3(PO_4)_2\} + (x'/2)(n - CaF_2) + (x'/3 - 2/3)P(M_P) \rightarrow Ca_{10}(PO_4)_6F_x(OH)_{2-x} +HF \uparrow$$

For HPF$_6$/Ca>3:90, $x' \geq 2$, that is, there exists extra $P(M_P)$ groups. As a result of the reaction, extra F is consumed via formation of HF.

At fixed HPF$_6$/Ca ratios and a low Ca/P, the FHA formation process will follow reaction (4), resulting in much loss of fluorine. At high Ca/P ratio, formation of FHA will follow reaction (2) (where $x > 2$), thus extra n-CaF$_2$ is left-over.

5. Conclusion

(1) In the process of formation of fluoridated hydroxyapatite involving HPF$_6$, there exists a direct relationship between the fluorine concentration in the sol and the fluorine content in the coating: when the HPF$_6$/Ca ratio in the dipping sol is below 3:90 (or F/Ca<0.2), the fluorine content in the coating increases almost linearly with the increasing of the F/Ca ratio in the sol.

(2) The F content in the coating increases only to a maximum of F/Ca=0.2 even as the dipping sol contains more F.

(3) The Ca/P ratio in the dipping sol affects the fluorine content in the coating. At given fluorine concentration in the sol, more P-containing groups results in less F/Ca in the coating.

(4) A hypothesis is proposed to explain the consumption of the extra fluorine and the influence of Ca/P ratio at given fluorine concentration. According to this hypothesis, when the sol contains extraneous amount of fluorine in the sol, the formation takes place according to

$$10(3 - x'/6)\{i - Ca_3(PO_4)_2\} + (x'/2)(n - CaF_2) + (x'/3 - 2/3)P(M_P) \rightarrow Ca_{10}(PO_4)_6F_x(OH)_{2-x} +HF \uparrow$$

whereby the extra fluorine forms HF through the reaction between F and the P-groups and escapes from the coating.

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