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Synthesis and characterization of sol–gel derived calcium hydroxyapatite thin films spin-coated on silicon substrate

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Abstract

The goal of this study was to demonstrate that sol–gel processing route is suitable for the fabrication of calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, CHA) thin films on Si substrate by spin-coating technique. The substrate was spin-coated by precursor sol solution 1, 5, 15 and 30 times. The samples were annealed after each spin-coating procedure at 1000 °C for 5 h in air. In the sol–gel process ethylendiamintetraacetic acid and 1,2-ethandiol, and triethanolamine and polyvinyl alcohol were used as complexing agents and as gel network forming agents, respectively. The coatings were characterized using X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared (FTIR) and Raman spectroscopies, profilometry and the contact angle measurements (CAM). It was demonstrated, that properties of calcium hydroxyapatite thin films depend on spinning and annealing times.

Keywords: Calcium hydroxyapatite; Thin films; Silicon substrate; Spin-coating; Sol–gel processing

1. Introduction

Calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, CHA) is very important macroporous bone mineral (55–70% interconnected porosity) from the scientific point of view and view of application [1–4]. Synthetic calcium hydroxyapatite is used as bioceramic coating for medical implants due to excellent biocompatibility and osteoconductivity. The coatings of CHA improve fixation of implant to natural bone tissues, interact with proteins and cells, therefore prolonging lifetime of implant [5–7]. Moreover, CHA coatings could be used as intermediate layer due to better mechanical compatibility with bone than pure metal implant. Therefore, these coatings are used for orthopaedic and dental applications due to excellent mechanical properties [8,9]. CHA coatings must have particular physicochemical properties in order to sustain successfully long bioactive life of implant. It is very important to keep ratio of Ca/P=1.67 like in natural bone, because the slight imbalance of this ratio influences appearance of additional phases. For instance, if the ratio of Ca and P is lower than 1.67, the alpha- or beta-tricalcium phosphate may form during processing. If the Ca/P ratio is higher than 1.67, calcium oxide (CaO) is forming along with the CHA phase. These additional phases can influence the biological response to the implant [10,11]. One more very important requirement for CHA coatings is porosity, because bone cells osteoblasts and osteoclasts, also proteins could flow inside pores supporting formation of new bone. The CHA coatings should have a high degree of crystallinity, correct stoichiometry and very good adhesion to the substrate [1,12,13]. Cell colonization and bone growth occur when pores are larger than 50–300 μm [2,11,14–17].

CHA coatings were synthesized using many preparation methods including plasma spray, ion-beam sputtering, laser ablation, electrochemical deposition, pulsed-laser deposition, thermal dissociation under hydrothermal conditions, biomimetic

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processes, liquid immersion techniques, magnetron sputtering and sol–gel techniques [1,5,6,10,18–24]. It is very important to choose a controllable method for the synthesis of CHA to ensure homogeneity, good mechanical properties and adherence of coatings. The coatings of calcium hydroxyapatite were synthesized in a wide range of temperatures (500–1500 °C) [25,26]. The crystalline calcium hydroxyapatite films could be fabricated by sol–gel technique at low temperatures on different substrates with long-term stability [20,27–30]. In vivo response at bone tissue level predicted that chemical and structural properties of sol–gel derived calcium hydroxyapatite coatings are ideal for their application in biological media [6,31]. The most popular substrate used for orthopaedic and dental implants is titanium due to the strength and slow corrosion in human fluids [32–38]. However, the preparation of calcium hydroxyapatite films on Ti is problematic due to oxidation of titanium and formation of TiO_2. To obtain better interactions between osteoblastic cells different titanium surfaces, such as mirror-polished (smooth-Ti), alumina grit-blasted (alumina–Ti) or biphasic calcium phosphate ceramic grit-blasted (BCP–Ti) for the preparation of CHA films were used [39,40]. Moreover, steel, alumina, glass, zirconia, MgO, quartz and calcite were also used as substrates for the preparation of CHA films [18,23,24,28,29,41–49]. Recently, it was demonstrated that silicon- and silver-containing CHA provide enhanced bioactivity and antibacterial properties over pure CHA, respectively [50,51]. Besides, silicon significantly improve osteoblastic response on calcium phosphate bioceramics, probably, since it presents in trace concentrations in natural bone [52]. Therefore, this paper focuses on the synthesis of CHA coatings on silicon substrate by sol–gel processing route using spin-coating technique. The proposed fabrication method has some advantages, such as simplicity, synthesis at low temperatures, effectiveness, suitability for complex-shaped implants and cost efficiency.

2. Experimental

Fig. 1 shows procedure of sol–gel preparation of calcium hydroxyapatite thin films on Si substrate. For the preparation of calcium hydroxyapatite, calcium acetate monohydrate ($Ca(CH_3COO)_2 \cdot H_2O$ (99.9%; Fluka)) was dissolved in distilled water and mixed on magnetic stirrer for 30 min at 65 °C. Second, 1,2-ethandiol (99.0%; Alfa Aesar) was added to this solution and stirred for 15 min. Next, ethylenediaminetetraacetic acid (EDTA; 99.0%; Alfa Aesar) and triethanolamine (TEA; 99.0%; Merck) as complexing agents were slowly dripped into the solution. After 10 h of stirring, phosphoric acid (H_3PO_4; 85.0%; Reachem) was added to the above solution. The ratio of Ca/P in the solution was maintained 1.67. Finally, PVA (PVA 7200, 99.5%; Aldrich) solution in distilled water was added. The resulting solution was used for the preparation of CHA coatings on the circle of Si (2 cm diameter) substrate using spin-coating technique. Before coating the substrate was cleaned with piranha solution, and subsequently with acetone, ethanol and distilled water. The spin-coating process was performed during 60 s using a speed of 2000 rpm. After spin-coating the samples were annealed at

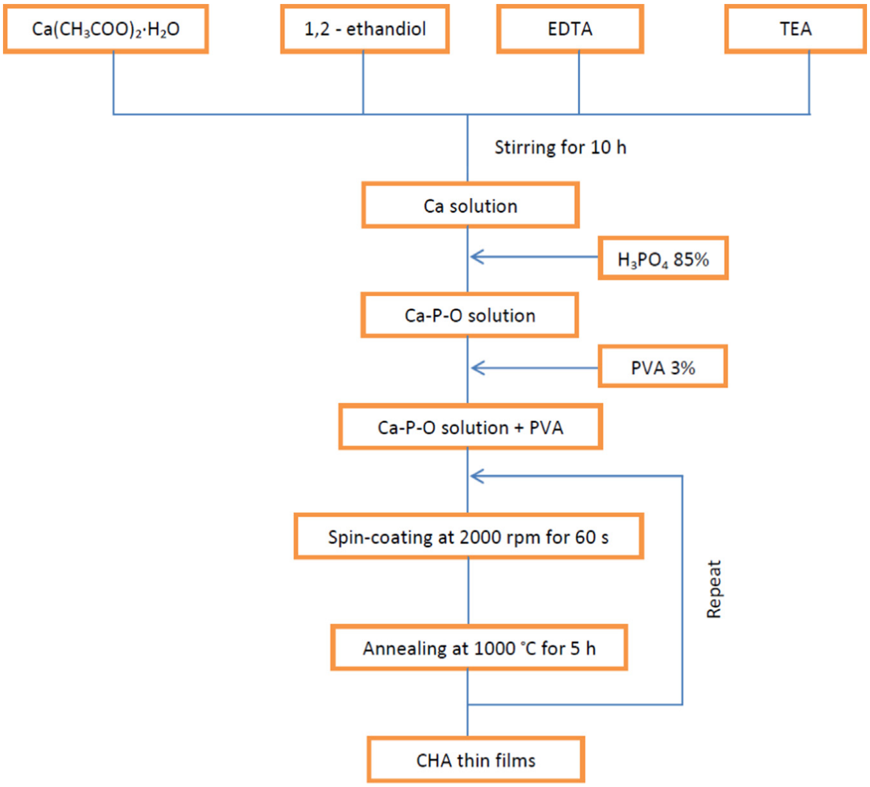

Fig. 1. Flow diagram of preparation of calcium hydroxyapatite thin films.