



Electrophoretic deposition of zinc-substituted hydroxyapatite coatings

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ARTICLE INFO

Article history:

Received 15 June 2013

Received in revised form 13 January 2014

Accepted 17 February 2014

Available online 23 February 2014

Keywords:

Zinc substitution

Hydroxyapatite

Electrophoretic deposition

n-Butanol

Triethanolamine

Coatings

ABSTRACT

Zinc-substituted hydroxyapatite nanoparticles synthesized by the co-precipitation method were used to coat stainless steel plates by electrophoretic deposition in n-butanol with triethanolamine as a dispersant. The effect of zinc concentration in the synthesis on the morphology and microstructure of coatings was investigated. It is found that the deposition current densities significantly increase with the increasing zinc concentration. The zinc-substituted hydroxyapatite coatings were analyzed by X-ray diffraction, scanning electron microscopy and Fourier transform infrared spectroscopy. It is inferred that hydroxyapatite and triethanolamine predominate in the chemical composition of coatings. With the increasing Zn/Ca ratios, the contents of triethanolamine decrease in the final products. The triethanolamine can be burnt out by heat treatment. The tests of adhesive strength have confirmed good adhesion between the coatings and substrates. The formation of new apatite layer on the coatings has been observed after 7 days of immersion in a simulated body fluid. In summary, the results show that dense, uniform zinc-substituted hydroxyapatite coatings are obtained by electrophoretic deposition when the Zn/Ca ratio reaches 5%.

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1. Introduction

Due to good biocompatibility and osteoconductivity, hydroxyapatite (HAP) and calcium phosphate coatings on metallic biomedical implants are widely employed in orthopedic and dental applications, which can significantly improve bone integration and accelerate the formation of biological bonds between bones and metallic implants [1–6]. Among various coating techniques, electrophoretic deposition (EPD) of HAP has attracted lots of interest over the past decade [3,7,8]. Many conductive substrates can be modified by EPD of nanosized HAP, such as carbon rod [9], stainless steel [10,11], titanium [1,12,13] and magnesium alloy [5]. As a starting material, natural HAP extracted from bovine cortical bones has been used to coat stainless steel by EPD, and the resulting coatings are continuous and crack-free [10]. Nowadays, nanosized HAP particles can be facilely fabricated by the wet-chemical methods. The main advantage of using HAP nanoparticles during the EPD process is that the obtained coatings possess dense particle packing and homogeneous structures [3]. The *in vivo* experiments have demonstrated that little inflammatory reaction has occurred after implanting the HAP-coated titanium, which indicates better compatibility than bare titanium implants [14]. The shape and structure of metallic substrates can be processed before deposition in accordance with the designed requirements. With the aid of perfusion, EPD techniques can also be

used to deposit calcium phosphate onto porous titanium scaffolds [15]. The porous titanium scaffolds modified by calcium phosphate coatings show high tensile strength and can support the growth of mesenchymal stem cells [2]. EPD techniques can be employed to modify the electrodes with surface patterns and only conductive areas are selectively coated by HAP nanoparticles [16]. Many parameters during EPD play important roles in the final properties of HAP coatings, such as dispersion medium, dispersant in the suspension [17,18] and applied electric field [13,19]. For instance, by varying the applied voltages, EPD can produce HAP coatings with different morphologies [13]. The crystal orientation of (002) plane is predominant on the HAP-coated titanium sheets, and (211) on the HAP-coated titanium rod samples [20]. Some nanoparticles can be inserted or embedded into the HAP coatings, such as carbon nanotubes [21] and Y₂O₃ nanoparticles [22], and therefore the reinforcement of the coatings is achieved.

Electrodeposition is another method for HAP coatings, which is similar to EPD [2,14,23–26]. Electrochemical reactions occur during the electrodeposition process. The starting materials such as phosphate salts and calcium salts are dissolved and the supersaturated solution of calcium phosphate is used to deposit HAP [6]. Because of the mild conditions, some bioactive molecules are able to be embedded in the final coatings during electrodeposition. Via this method, the composite films containing heparin and HAP in the polypyrrole matrix have been fabricated [27]. However, due to the low stability of the supersaturated calcium phosphate solution, the electrodeposition method has its limitations. EPD is more suitable for deposition of biomaterials because EPD is mainly a physical process and is easy to be controlled during the coating process [3].

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It is well-known that natural HAP contains lots of trace elements which play very important roles in the biological process [28–31]. Functional element-substitutions in HAP can be easily fabricated by adding the related ions into the reactions, such as zinc [32], silicon [8] and strontium [4]. Using these element-substituted HAP nanoparticles, special functional HAP coatings can be obtained via the EPD method. The strontium-substituted hydroxyapatite coatings have been found to improve the cell adhesion and proliferation of osteoblast cells and the strontium incorporation greatly inhibits the osteoclast differentiation [4]. The composite coatings containing silicon substituted HAP and poly-(ϵ -caprolactone) have improved bonding strength and also have the ability to induce new bone formation [8].

Zinc plays very important roles in the bone formation and immune regulations [32,33]. Zinc substituted HAP (ZnHAP) nanoparticles containing 1.6 wt.% Zn have been found to enhance bioactivity to human adipose-derived mesenchymal stem cells and antimicrobial capability [34]. Another research also suggests that ZnHAP nanoparticles have antibacterial activity and are non-toxic to osteoprogenitor cells [35]. The aim of this study is to deposit ZnHAP nanoparticles onto stainless steel substrates by EPD. Microstructure, crystallinity and functional groups of ZnHAP coatings have been characterized. The effects of different concentrations of zinc used in the synthesis have been evaluated and discussed.

2. Materials and methods

2.1. Synthesis of ZnHAP nanoparticles

The ZnHAP nanoparticles with different zinc concentrations were synthesized by co-precipitation [32,36,37]. Briefly, 270 ml of 0.11 M $\text{Ca}(\text{NO}_3)_2$ solution was mixed with 0.01 M $\text{Zn}(\text{NO}_3)_2$ solution. Then, 300 ml of 0.06 M $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ solution was added to the mixture during stirring. The Ca/P ratio was maintained at 1.65 and the Zn/Ca ratio was adjusted from 1% to 10% by adding different volumes of $\text{Zn}(\text{NO}_3)_2$ solution (30 ml, 150 ml and 300 ml). All the reactions were kept at 80 °C and pH was adjusted to about 9–10 using ammonium solution. After 3 h of aging, the obtained precipitates were separated from the solution by filtration and washed using distilled water. The ZnHAP nanoparticles were dried in 80 °C oven overnight.

2.2. Electrophoretic deposition

Herein, 304 stainless steel plates were cut into 20 mm × 20 mm and used as cathode. The carbon rod was used as anode. The steel plates were washed with acetone and ethanol before usage. For EPD, about 0.6 g of ZnHAP powder was dispersed in 60 ml n-butanol containing about 2% triethanolamine (TEA). The suspensions were ultrasonicated for 5 min and aged overnight. The TEA adsorbed onto HAP nanoparticles and made them positively charged [17,18]. Before EPD, 2 drops of HCl were added to the suspension and ultrasonication was applied for 10 min to achieve homogenous dispersion [9]. The stainless steel plate as cathode and the carbon rod as anode were immersed in the ZnHAP suspension. The distance between the two electrodes was 10 mm. The deposition was performed at a constant voltage of 30 V. The currents were recorded during the EPD process. The coatings were gently rinsed with ethanol and dried in 60 °C oven overnight.

2.3. Characterization

2.3.1. X-ray diffraction

The dried ZnHAP powders and coatings were analyzed using X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The phases of the samples were determined using a $\text{Cu-K}\alpha$ radiation (40 kV, 40 mA) over the 2θ range of 10°–70° with a step size of 0.1° at 0.1 s.

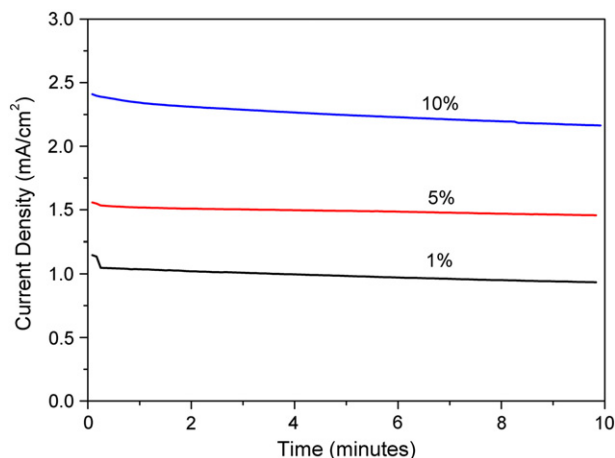


Fig. 1. Current density during the electrophoretic deposition of ZnHAP nanoparticles with different Zn/Ca ratios in the reaction.

2.3.2. Transmission electron microscopy

The dried ZnHAP powders were dispersed in ethanol by sonication for 15 min. A drop of the suspension was applied on the carbon coated copper grids and dried in air. The samples were observed using a transmission electron microscope (TEM, Tecnai G2, FEI, Netherlands). The selected area electron diffraction (SAED) patterns of ZnHAP nanoparticles were studied.

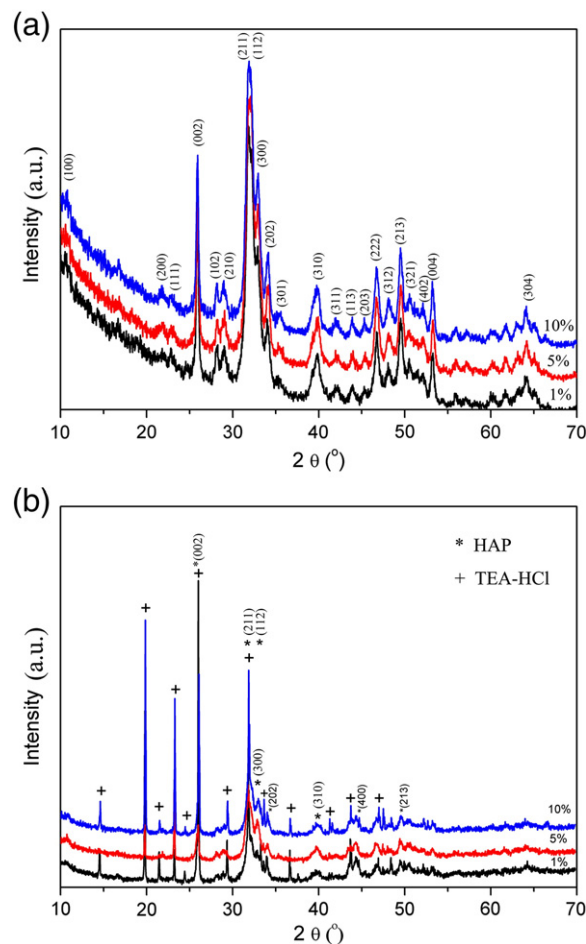


Fig. 2. X-ray diffraction patterns of (a) ZnHAP powders and (b) ZnHAP coatings on stainless steel plates.

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