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Spin-coating synthesis and characterization of Zn-doped hydroxyapatite/polylactic acid composite coatings

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ABSTRACT

Zn-doped hydroxyapatite/polylactic acid (HA/PLA) composite coatings fabricated by spin-coating technique have rarely been studied by other researchers in recent years. In this study, Zn-doped hydroxyapatite (Zn-doped HA) powder were synthesized by chemical precipitation method, and then Zn-doped hydroxyapatite/polylactic acid (Zn-doped HA/PLA) composite coatings were coated on stainless steel substrates using a spin-coating technique for the first time. The effects of heat treatment in air at 600 °C on the composition and morphology of Zn-doped HA/PLA composite coatings with a series of molar ratios of zinc (0 mol%, 5 mol%, 10 mol%, 15 mol% and 20 mol%) were studied. The obtained samples were characterized by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The results showed that Zn^{2+} ions had replaced the partial Ca^{2+} ions and were doped into hydroxyapatite lattice successfully. The synthetic hydroxyapatite nanoparticles showed rod-like morphology, whereas the substitution of the Zn ions restrained the growth of Zn-doped HA crystal and decreased its size. The surface morphology of Zn-doped HA/PLA composite coatings after sintering at 600 °C for 1 h exhibited a uniform, porous structure with a thickness of 60 μm or so. The introduction of PLA in composite coatings could keep metal substrates from catalyzing the decomposition of HA caused by high temperature heat treatment.

1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), a man-made biomaterial analogous to calcium phosphate found in bone, is widely applied as bioactive coating material for orthopedic applications due to its high biocompatibility and bioactivity, as well as its excellent osteoconductivity and affinity to polymers. Most of the biological apatites are non-stoichiometric since the presence of trace amounts of substituting ions such as cations (Mn^{2+}, Ce^{3+}, Mg^{2+}, Zn^{2+}, Ag^{+}, Sr^{2+}) or anions (HPO_4^{2-}, CO_3^{2-}, F^{-}, Cl^{-}), which would affect its physicochemical and biological properties [1–3]. Hence, in order to meet the requirements of practical clinical application, it is necessary to add trace ions, like Zn^{2+}, into HA to improve its performance. It is reported that Zn^{2+} ions can replace Ca^{2+} ions in HA by the sorption mechanism to form Zn-doped HA [4–6]. Zn, an essential trace element for human body, can stimulate the growth of bone tissues [7] and play an important role in normal bone growth, metabolism and functions [8]. It has been well documented that zinc ions in the implant coatings exert great effects in preventing or minimizing initial bacterial adhesion [9]. With the slow release and uptake of Zn^{2+}, HA has great potential in the repair and reconstruction of bone tissue. However, HA as a ceramic material also has some flaws: weak mechanical properties, brittleness and low bending strength, which limits its utilization.

Polylactic acid (PLA), with biocompatibility, biodegradability and no toxicity or stimulation to humans, is widely used as the matrix of biodegradable material in bone fixation devices. The introduction of PLA into the HA matrix, which means to combine their own advantages and overcome their shortcomings, is expected to form bone tissue engineering scaffolds with comprehensive service performance. In addition, PLA can enhance the adhesion and ductility of the composite coatings. With degradation of PLA in the body, HA is gradually transformed into natural bone tissues which may improve the osseointegration ability of composites [10]. And sustained release of Zn^{2+} incorporated into an implant material could promote bone formation surrounding the implant and accelerate healing of the patients. Thus, Zn-doped HA/PLA composites are expected to become a new generation of bone tissue engineering materials with comprehensive performance.

The implant surface represents the site of interaction with the surrounding living tissues and is therefore essential to surface modification to enhance the biological performance of implants [11]. Coating a biocompatible material with a thin layer of calcium phosphate, including HA coatings, on the implant surfaces has proved to be a valid process to bridge the growth between implants and human tissues [11,12]. Various techniques have been used to coat HA on metallic implants such as thermal spraying [13], plasma spraying [14], magnetron sputtering [15],

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pulsed laser ablation [16], ion-beam-assisted-deposition [17], spin-coating [18], sol–gel technique [19] etc. Among these techniques listed, spin coating of composite materials blended in volatile solvents, like dichloromethane, is one of the most widespread techniques used in the coating industry to produce uniformly thin surfaces [20]. Furthermore, spin coating, a facile technique, can coat complex implant surfaces at low temperature [21].To the best of our knowledge, only a few publications on spin-coating of calcium orthophosphates were published, while incorporating Zn ions into HA/PLA composite coatings on stainless steel substrates fabricated by spin coating technique was rarely reported. In this paper, different Zn molar fractions of Zn-doped hydroxyapatite powder were synthesized via wet chemical method and Zn-doped HA/PLA composite coatings were prepared by spin-coating technique for the first time. The effects of heat treatment under air atmosphere at 600 °C on the composition and morphology of Zn-doped HA/PLA composite coatings on metal substrate were studied.

2. Materials and methods

2.1. Chemicals and reagents

$Ca(NO_3)_2{\cdot}4H_2O$, $(NH_4)_2HPO_4$ and $Zn(NO_3)_2{\cdot}6H_2O$ were obtained from Aladdin Industrial Corporation (Shanghai, China). PLA with an average molecular weight of 300,000 g/mol was purchased from Dikang Biomedical Co., Ltd. Ammonia solution was purchased from Xilong Chemical Co., Ltd. Dichloromethane was supplied by Tianjin Baishi Chemical Co., Ltd. Ethanol and acetone were obtained from Guangzhou Donghong Chemical Factory. All the received chemicals were of analytical grade and were utilized without further purification. Deionized water was used throughout the synthetic process as a solvent to mix the salts as described in stoichiometric quantities.

2.2. Synthesis of pure and zinc doped HA

Pure and Zn-doped HA powder were synthesized under atmospheric conditions by a wet chemistry method. 0.1 mol $Ca(NO_3)_2{\cdot}4H_2O$ and 0.06 mol $(NH_4)_2HPO_4$ were dissolved into 50 mL deionized water respectively. The phosphate solution was added dropwise to the calcium solution by a constant-current pump at a rate of 2 mL/min with vigorous stirring. All reactions were kept in 80 °C water bath for 5 h and the pH was maintained between 9.5 and 10 using ammonia solution during the experiments. After aging for 12 h, the precipitates were filtered and washed three times by deionized water. Then the precipitates were dried in an oven at 90 °C for 10 h. Synthesis of Zn-doped HA powder was similar to the above procedure, an appropriate amount of $Zn(NO_3)_2{\cdot}6H_2O$ was added to calcium solution before the titration. The (Ca + Zn)/P molar ratio was kept constant at 1.67 throughout the experiments. The Zinc fraction for each composition was represented as [Zn]/[Ca + Zn] × 100(mol%). The amount of zinc was chosen to be 5, 10, 15 and 20 mol% and the samples were referred to as 5ZnHA, 10ZnHA, 15ZnHA and 20ZnHA, respectively. Finally the dried precipitates were ground into powder and sintered in a muffle furnace at 700 °C for 2 h.

2.3. Steel plate pretreatment

Type 304 Stainless Steel (304 SS) plates were cut into 10 mm × 10 mm × 1 mm sheets and polished using Silicon carbide (SiC) paper of different grit sizes ranging from 220, 600, 2000 and 5000. The polished plates were sequentially cleaned with acetone, ethanol and deionized water for 10 min using ultrasonication, respectively. After the cleaning process, the plates were dried at 60 °C for 2 h in vacuum oven.

2.4. Preparation of Zn-doped HA/PLA coatings

The PLA was dissolved in methylene chloride solution at room temperature, and stirred for 2 h until the PLA was completely dissolved. Zn-doped HA powder passed by a 200 mesh sieve was then mixed with PLA solution while the ratio of weight between PLA and Zn-doped HA was kept at 1/10. The suspension was stirred for 12 h until the solution dispersed homogeneously. Zn-doped HA/PLA coatings on stainless steel substrates was prepared by spin-coating technique. A few drops of the prepared solution were dropped on the stainless steel specimens which was sticky to the spin coater (Type SC-1B). The spin-coating process was performed for 30 s using a speed of 3000 rpm. The substrate covered with polymer solution was rotated rapidly. The solution spreads due to the centrifugal force and the coating with appropriate thickness was obtained once the solvent has evaporated. The coatings were then sintered in air for 1 h at 600 °C.

2.5. Characterization

The crystal structure of the product was analyzed by X-ray diffractrometry (Bruker AXS-D-8 ADVANCE, Germany), which used a tube voltage of 40 kV and current of 40 mA in the 2θ ranging from 10° to 60° with Cu-Kα radiation of 1.5406 Å. The functional groups and composition of the pure and Zn-doped HA samples were identified using a Fourier transform infrared spectroscopy (FTIR, Shimadzu IRAffinity), over the region 400–4000 cm^{-1} using the KBr pellet technique. The particle size and morphology were examined by transmission electron microscopy (TEM, FEI Tecnai G2 F30). The powder sample was dispersed in ethanol to form dilute suspension which was treated by sonication, and a few drops of this suspension were applied onto a carbon film supported by copper grid. Morphology and chemical composition of the composite coatings were evaluated using scanning electron microscopy (SEM, S-3400 N Type II) and energy dispersive X-ray (EDX, TEAM Octane Plus) analyzer. The elements and chemical state of the coating was tested using X-ray photoelectron spectroscopy (XPS, MICROLAB-350) with an Al-Kα (h•v = 1486.6 eV) as excitation source. The measured binding energies were calibrated by referring the binding energy of C(1 s) at the binding energy of 284.6 eV. The adhesion strength of the samples was tested using a universal material testing machine (CMT4204, Sans Material Test Instruments Co., Ltd.) with a crosshead speed of 2 mm/min. When the coating was peeled from the substrate, record the maximum load. The adhesion strength

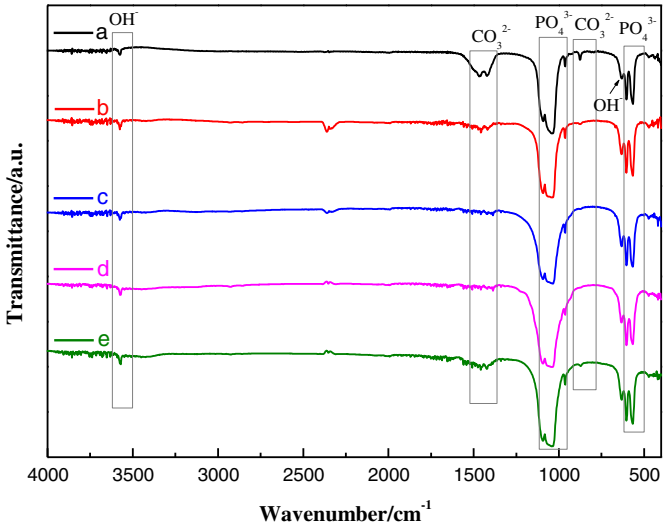

Fig. 1. FTIR spectra of pure and Zn-doped HA powders with varied molar fractions of zinc (sintered at 700 °C for 2 h): (a) pure HA, (b) 5ZnHA, (c) 10ZnHA, (d) 15ZnHA, and (e) 20ZnHA.