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Synthesis and characterization of Cerium-doped hydroxyapatite/polylactic acid composite coatings on metal substrates

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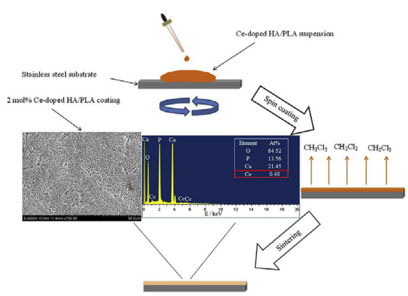
HIGHLIGHTS

- Ce-doped HA composite coatings were synthesized by spin-coating technique for the first time.
- Ce ions were demonstrated to dope into HA crystal lattice successfully.
- The addition of PLA could keep metal substrates from catalyzing the decomposition of HA.
- XPS results showed that Ce ions doped in HA have mixed valences of Ce^{3+} and Ce^{4+}.

GRAPHICAL ABSTRACT



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ABSTRACT

Ce-doped hydroxyapatite/polylactic acid (HA/PLA) composites serving as implant coatings have rarely been studied by other researchers in recent years. This paper was focused to study the existence of Ce ions in structure, chemical composition and surface morphology of HA and its composite coatings. Ce-doped HA powders were synthesized by chemical precipitation method with different Ce molar fractions (0(pure HA), 0.5 mol%, 1 mol% and 2 mol%). And Ce-doped HA/PLA composite coatings were fabricated for the first time on stainless steel substrates by spin coating technique. The obtained samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) coupled with energy dispersive X-ray detector (EDX), thermo gravimetric-differential thermal analysis (TG-DTA) and X-ray photoelectron spectroscopy (XPS). The results showed that Ce ions were doped into the crystal lattice of apatite successfully. The (Ce + Ca)/P atomic ratios in the doped HA/PLA samples ranged from 1.614 to 1.673, which were very close to the theoretical value of 1.67 for the stoichiometric HA. The addition of PLA could keep metal substrates from catalyzing the decomposition of HA. TG-DTA analysis indicated that Ce-doped HA powder had high thermal stability, and the SEM micrographs revealed that the surface topography of Ce-doped HA/PLA composite coatings was uniform and dense when the Ce molar fraction was 2 mol%. XPS results indicated that the Ce ions doped in HA showed mixed valences of Ce^{3+} and Ce^{4+}.

1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) is widely applied in clinical research as it has the similar component of the mineral

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formed human skeleton [1,2]. Owing to its excellent biocompatibility and osteoconductivity [3,4] as well as great bioactivity and chemical stability [5,6], HA is extensively used as bioactive coatings on metal implants to assist the osseointegration of these implants with surrounding tissues without causing any reject reaction. HA has been the focus and hotspot as a good support material in tissue engineering, but the application of HA in clinical research is limited as its brittle and weak in intensity and adhesion [7,8]. Polylactic acid (PLA) is biodegradable material which is widely applied as material for bone reconstruction for its great biocompatibility [9,10]. Producing organic/inorganic composite coatings by composing HA with PLA can improve the adhesion and ductility of the composite materials, forming tissue engineering scaffolds with comprehensive service performance. In fact, most natural apatite is non-stoichiometric because of containing multiple trace elements such as Na, Mg, Mn, Si, Ce, Sr etc. Hence it's useful to incorporate these kinds of elements into HA lattice to improve the property of the composites and to meet the demand of clinical application. Ce-doped HA is one of these kinds of modified materials. The radii of Ce^{3+} and Ce^{4+} are 0.107 nm and 0.087 nm respectively [11] which are both close to the radius of Ca^{2+} (0.100 nm). So cerium ions in organism can take place of calcium ions in the HA lattice. The small amount Ce ions in human bones can speed up organisms metabolism [12,13] and are also used in antibacterial agents due to its excellent antibacterial property [14–16]. It is reported that doping Ag^{+} and Ce^{3+} into HA can change the structure, morphology and cell parameters of HA and improve the antibacterial property of HA [17,18]. In order to ameliorate the clinical and biomedical application of HA, it's crucial to study cerium doped hydroxyapatite.

In the orthopaedic fields, metallic materials are widely used as various implants because of their high fracture toughness and good biocompatibility [19,20]. However, they do not typically bond to living bones. Therefore, some orthopaedic implants have been subjected to surface modification by different physical and chemical methods, including grit blasting [21], acid etching [22] and plasma functionalization [23]. When a rough texture is produced on its surface by these modifications, orthopaedic implants can form a direct contact with living bones to enhance bone bonding and osteoconductive ability. HA can be coated onto their surfaces as a biocompatible coating to bridge the growth between implants and human tissues. 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 [24].

Some contributions can be found in the literature on composite coatings of HA/PLA, while incorporating Ce ions into HA/PLA composite coatings on stainless steel substrates fabricated by spin coating technique was rarely reported. In this paper, we synthesized Ce-doped HA powder with different Ce molar fractions using chemical precipitation method, and prepared Ce-doped HA/PLA composite coatings on metal substrates by spin coating technique for the first time. The obtained samples were examined by a series of means such as XRD, FT-IR, SEM, EDX, TG-DTA, XPS etc. We also discussed the changes of HA crystal structure caused by adding Ce ions and the influences on composite coatings after composing HA with PLA.

2. Materials and methods

2.1. Chemical materials

All chemicals used in our research were of analytical grade and used without further purification. Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), Diammonium hydrogen phosphate ($(NH_3)_2HPO_4$) and Cerium nitrate hexahydrate ($Ce(NO)_3 \cdot 6H_2O$) were all purchased from Aladdin Co Ltd (Shanghai). Polylactic acid (PLA) with molecular weight of 30000 was obtained from DikangZhongke biomedical material Co Ltd (Chengdu). Sodium hydroxide (NaOH) and dichloromethane (CH_2Cl_2) were bought from Baishi chemical engineering Co Ltd (Tianjin). Ethyl alcohol (CH_3CH_2OH) and acetone ($(CH_3)_2CO$) were supplied by Donghong chemical plant (Guangzhou).

2.2. Pretreatment of metal substrates

Type 304 stainless steel was used as substrates for deposition of Ce-doped HA/PLA composite coatings. The substrates, 10 mm × 10 mm × 1 mm in size, were grinded using SiC water sandpaper with different grit sizes including 220, 600, 2000 and 5000 successively. The substrates were then washed by acetone (10 min), ethyl alcohol (10 min) and rinsed with distilled water (10 min) under ultrasound. Then the substrates were finally dried in the vacuum at 60 °C for 2 h.

2.3. Synthesis of Ce-doped HA powder

We used chemical precipitation method to synthesize Ce-doped HA powder. The molar ratio of [Ce]/[Ce + Ca] × 100(mol%) were 0 mol%, 0.5 mol%, 1 mol% and 2 mol%. The solutions of $Ca(NO_3)_2 \cdot 4H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were mixed in specific molar fractions. The solution of Na_2HPO_4 was then added into the mix solution using constant titration pump at the speed of 2 mL min^{-1} in order to keep the value of n(Ce + Ca)/n(P) as 1.67. The pH of the mix solution was adjusted to 10.5 by NaOH and the mixed solution was stirred in high speed at temperature of 40 °C by water bath. The whole solution was stirred for extra 2 h after the titration and then it was aged at room temperature for 24 h. Samples were then rinsed by distilled water for three times and rinsed by ethyl alcohol once. The samples were dried in vacuum oven at 90 °C for 12 h. At last we sintered the samples in muffle furnace at 700 °C for 2 h to obtain Ce-doped HA powder.

2.4. Preparation of Ce-doped HA/PLA composite coatings formed on metal substrates

Ce-doped HA/PLA composite coatings were produced by spin-coating technique. PLA with molecular weight of 30000 was totally

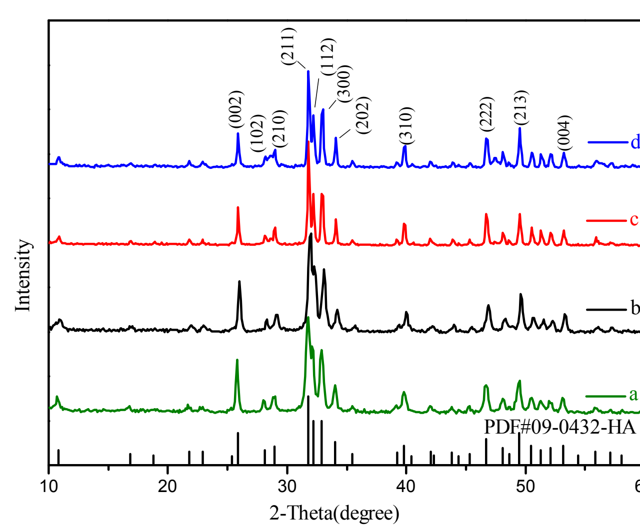

Fig. 1. XRD Patterns of Ce-doped HA powders with varied molar fractions of Cerium (sintered at 700 °C for 2 h): (a) 0 mol% Ce, (b) 0.5 mol% Ce, (c) 1 mol% Ce, (d) 2 mol% Ce.