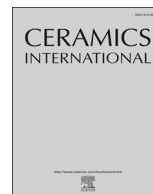




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Composite coatings of lanthanum-doped fluor-hydroxyapatite and a layer of strontium titanate nanotubes: fabrication, bio-corrosion resistance, cytocompatibility and osteogenic differentiation

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ABSTRACT

Poor bio-corrosion resistance and undesirable incomplete osseointegration restrict the application of hydroxyapatite (HA) as an implant coating material. In this study, a novel F-and-La co-substituted hydroxyapatite (FLaHA) coating, which was reinforced with strontium titanate nanotubes (STNTs), was applied on Ti substrates using a combination method of anodization, electrochemical deposition and hydrothermal treatment. To the best of our knowledge, this is the first report on the development of FLaHA/STNT coatings for improving the chemical stability and the mechanical and biological properties of Ti substrates. The STNT exhibits an evenly-distributed porous and latticed structure on Ti substrates that favours the infiltration of FLaHA crystals. Different characterisation techniques, such as x-ray photoemission spectroscopy, x-ray diffraction, field-emission scanning electron microscopy and energy-dispersive spectroscopy, have clearly confirmed the successful synthesis of STNT-FLaHA coatings that constitute oriented nanorod arrays. Isolated hexagonal nanorod grains, with diameters of 200–300 nm, that stand on a substrate provide a uniform morphology to the surface of electro-deposited thin films at micro-scales. The survival of the coatings was prolonged because of their good degradation resistance. Owing to the anchoring effect of the STNT layer, the adhesion strength of the FLaHA/STNT coating was 15.9 ± 5.4 MPa, which was two times higher than that of STNT-free HA coatings. The potentiodynamic polarisation curves and the Nyquist plot confirmed that the conversion coating significantly improved the bio-corrosion resistance of the Ti substrates in the SBF solution. Roughness and hydrophilicity of the control HA layer were even greater than those of the FLaHA/STNT coating. However, it provided better cell adhesion, spreading, proliferation and osteogenic differentiation for mouse pre-osteoblasts cells. That is, the FLaHA/STNT coating could enhance osteoconductivity by improving the cell-adhesion, proliferation and differentiation of osteoblast. Therefore, FLaHA/STNT nanocomposite coatings can be used as implant materials with multi-functional properties, such as good biocompatibility and high mechanical and corrosion-inhibiting properties.

1. Introduction

The promotion of biomineralization by implant surfaces that can make contact with the host tissue to correct skeletal and craniofacial fractures has not been realised yet [1,2]. Titanium (Ti) is the most widely used material for correcting bone fractures because of its

physical–chemical characteristics [3], though its chemical inertness can reduce osseointegration [4,5]. When exposed to the air, the Ti surface is covered by a spontaneously-formed few-nanometre thick titania (TiO₂) film that protects the Ti surface against corrosion [1]. However, this layer of titania can be damaged by mechanical stresses, leading to accelerated corrosion [4]. Moreover, the bond that Ti makes with the

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surrounding tissues is weak [6,7]. These weaknesses of the bare Ti surface can be overcome by introducing a thicker intermediate layer of TiO₂ [7,8] and applying calcium-phosphate-based coatings, such as hydroxyapatite (HA) [1–4]. The TiO₂ layer improves the corrosion resistance of the Ti substrate and its adhesion to the coating [1,7,9]. Moreover, the chemical and biological similarity of HA to the mineral components of natural bone can minimise the healing time by improving the direct bone–implant contacts [1,10,11].

Nevertheless, the easy decomposition of HA coatings can weaken the bonding between implants and bone tissues, thereby increasing the dissolution rate in biological environments [2,12]. Moreover, traditional HA biomaterials do not usually possess excellent osteoinductive ability for facilitating the differentiation of osteoblasts and mesenchymal stem cells for the fast formation of new bone tissues; this leads to the failure of the regeneration of large bone defects [13,14]. The mechanical and biological properties of HA biomaterials can be improved by using modified composite materials [13,15]. For instance, the doping of HA with the ions that are usually present in the natural apatites of vertebrate skeletal systems can improve its tensile strength and chemical stability [15,16]. Moreover, the incorporation of trace elements into HA enhances its bioactivity and bone growth [13]—the trace elements can constantly supply ions that are vital for bone reconstruction [13–15].

Recently, the synthesis of HA composites doped with multiple metal ions, such as strontium (Sr²⁺), magnesium (Mg²⁺), manganese (Mn²⁺), zinc (Zn²⁺), cerium (Ce³⁺) and lanthanum (La³⁺), has received considerable attention [11,15,17]. As a “bone-seeking” element that is comparable in size to Ca [19], La is an important trace element that has been widely used in biomedical applications [18]. The incorporation of La into HA results in high flexural strength, low dissolution rate and great alkaline phosphatase activity [20]. The resistance of hard tissues to acid dissolution increases with the substitution of La for Ca in apatite [16]. La-containing HA can be potentially used for developing a new type of bioactive coating for dental implants [19,21] and for improving the performance of dental implants in osteoporotic cases [22]. The introduction of fluorine (F), another trace element in bone tissues [23], into HA increases its stability [24], reduces its dissolution rate [24] and enhances the proliferation and differentiation of osteoblastic cells and the regeneration of bone tissues [13,21]. Therefore, F-and-La co-substituted HA (FLaHA) may have better chemical stability, corrosion resistance and biological properties than pure HA.

The failure of substituted HA coatings in *in vivo* stability tests usually occurs at the coating/substrate interface or within the coating [12]. Reinforcing the coating can effectively enhance the bonding at the coating/substrate interface [11,12]. For instance, the use of TiO₂ in the coating structure can improve the interfacial adhesion and the corrosion resistance of the contacting layer [4,7,9]. In some cases, an intermediate layer of TiO₂ is formed between the HA deposit and the substrate [2,4–9]. Moreover, TiO₂ nanotubes can function as a reservoir for drug delivery, particularly for inorganic bioactive elements, such as silver, zinc and strontium [25]. For example, these nanotubes were decorated with strontium titanate (SrTiO₃) to function as a delivery platform in biomedical applications [26,27]. Strontium (Sr), an essential trace element in human body, promotes bone formation and reduces bone resorption [28]. Moreover, HA adhesion can be enhanced by the porosity of SrTiO₃ nanotubes (STNT), resulting in suitable cell anchorage circumstances [5]. Importantly, the interlocking caused by the FLaHA colloidal particles that penetrate the voids of the SrTiO₃ nanotubes can significantly increase the FLaHA/anodized adhesion strength.

The modification of metallic surfaces, particularly for obtaining HA bioactive coatings, can be achieved by techniques, such as plasma spraying, sputtering, pulsed-laser deposition, sol-gel and electrochemical deposition [1,2,4,9,11,12,21,29]. The latter is a suitable technique for growing uniform coatings of tuneable thickness and

chemical composition on the structures of complicate shapes at low temperatures and costs [8,24,29–31]. To the best of our knowledge, the use of electrochemical deposition (ED) for the co-substitution of F and La into the HA coating deposited on SrTiO₃ nanotube arrays has not been reported. Here, we studied the use of ED for fabricating a bilayer nanocomposite coating of FLaHA and SrTiO₃ nanotubes, denoted as FLaHA/STNT, that can integrate the advantages of SrTiO₃ and FLaHA. By conducting electrochemical experiments and bioactivity assays, we evaluated the applicability of the FLaHA/STNT bilayer coating as an implant. Moreover, nanocomposite coatings with hexagonal columnar nanorod crystalline structures were also studied to elucidate the best compromise for the improvement of implant surfaces.

2. Materials and methods

2.1. Preparation of SrTiO₃ nanotubes on Ti substrate

The Ti plates were pre-treated according to our previous works [30,31]. The 10 mm × 10 mm × 0.9 mm Ti plates with a purity of > 99.7% were first polished using SiC sandpapers. Then, they were ultrasonically cleaned with acetone, ethanol and deionised water for 10 min, sequentially. Then, the samples were anodized in an ethylene glycol solution with 0.5 wt% NH₄F and 4 vol% H₂O at 25 V for 1 h. Consequently, TiO₂ nanotubes were formed on the anodized Ti plates. Then, all the samples were annealed in air at 450 °C for 2 h at a heating rate of 20 °C/min. The samples were then cooled in a muffle furnace. The annealed samples were then placed in 25 ml of 0.015 M Sr(OH)₂ solution in a Teflon autoclave that was set at 200 °C for 2 h to obtain strontium titanate nanotube (STNT) arrays. At the end, the residual Sr(OH)₂ solution was removed by washing the samples with 1 M of HCl for 5 min and rinsing them in distilled water. The samples were then dried in air.

2.2. Synthesis of FLaHA/STNT coatings

A standard electrolysis cell was used in the ED where with the Ti sample functioned as a working electrode, the counter electrode was made of platinum and a saturated calomel electrode acted as the reference electrode. The deposition was performed in an electrochemical workstation (CHI 660E, China) at a constant current density of 0.9 mA/cm² for 30 min. The electrolyte contained 0.04 M Ca(NO₃)₂, 0.002 M La(NO₃)₃, 0.025 M NH₄H₂PO₄ and 6 ml/L H₂O₂. The FLaHA coating was directly electrodeposited after NaF (1 mmol/L) was added into the electrolyte. The concentrations of F were according to our previous work [24]. The pH of the electrolytes was adjusted to 4. The temperature and concentration of the electrolyte were fixed at 60 °C by a water bath and a magnetic stirrer. After deposition, the samples were removed from the electrolyte and dried at 70 °C for 2 h. They were heated to 450 °C at 10 °C/min and kept at 450 °C for 2 h. All reagents were at least 98% pure and purchased from Aladdin (China).

2.3. Characterisation of FLaHA/STNT coatings

Field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7500F, Japan) and energy-dispersive spectrometry (EDS) were utilised to study the surface morphology and elemental composition of the fabricated samples. The phase composition and structure of the samples were characterised by X-ray diffraction (XRD, Rigaku D/Max-2500/PC, Japan) using Cu K α radiation with a scanning rate of 0.06°/s from 10° to 70°. Fourier transform infrared spectroscopy (FT-IR, Nicolet 670, USA) was used to evaluate the functional groups and structural changes of the milled samples. The composition and elemental state of the prepared composites were examined with X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI). An atomic force microscope (AFM, Bruker, Dimension Icon, USA) was used to measure the surface roughness of the samples. The adhesion strength of the FLaHA/STNT

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