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Fabrication and characterization of nano prism-like hydroxyapatite coating on porous titanium substrate by combined biomimetic-hydrothermal method

Guifan Feng, Xiaoling Cheng*, Dehui Xie, Kelai Wang, Bentian Zhang

School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

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ABSTRACT

Crystalline hydroxyapatite (HAP) was successfully coated on titanium substrate via a combined biomimetic-hydrothermal method, throughout all synthesis processes were simply chemical-treated under a moderate condition while the highest temperature would not exceed 180 °C. Biomimetic mineralization was applied to provide the seeded layer, which was prerequisite and facilitated the subsequent hydrothermal growth, while hydrothermal process promoted the nucleation and crystal growth, finally the phase-pure and high crystalline nano prism-like HAP was achieved well-arrayed onto titanium surface with a multi-level structure. Furthermore, this way combined biomimetic-hydrothermal method could be easily extended as a universal technique for surface modification and coating fabrication of versatile materials.

1. Introduction

Titanium (Ti) has been extensively applied to orthopedic and dental implants due to its excellent physical and mechanical properties, however, the bioinert nature restrain its further uses, surface modification should be implemented to enhance its osteogenic activity; hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) regards as a calcium phosphate based biological ceramic, exhibiting high performance of bioactivity and biocompatibility, with the composition and structure both are similar to the natural bone, which is recognized as the most eligible material could be potentially integrated with the advantages of titanium to form a composite coating for versatile usages such as medical implant, drug delivery and so on [1–3].

Briefly, varied techniques have been developed to fabricate as-discussed composite coating. Plasma spraying [4], sputter coating [5] and electrochemical deposition [6], which are even commercially applied but the operation is complex and high-cost, either, phase-pure and crystalline coatings were seldom obtained through these methods; hydrothermal process [7–9] is one excellent method for synthesizing crystalline coatings onto different substrates, however, single step hydrothermal requires high roughness of the substrate surface so that a high temperature is always used to annealing-treat the metal substrate could possibly damage the original phase and cause undesired by-products.

A combined method is also be exerted to maximize the advantages and eliminate the defects of each technique, while the typical one is electrochemical-hydrothermal deposition [10,11]. Recently, with the development of biomimetic technique due to the excellent natural adhesive effect of polydopamine was inspired by mussels [12], herein we attempt to construct the seeded HAP [11] layer by biomimetic mineralization close to the natural environment and introduce a novel combined biomimetic-hydrothermal method in order to simplify the reaction conditions and achieve the anticipated productions.

2. Material and methods

Analytical grade reagents were received from Guangzhou Chemical Reagent Factory (China); 3, 4-Dihydroxy-L-phenylalanine (L-Dopa) was obtained from Aladdin Industrial Inc. (China); deionized water was used throughout all the experiments; titanium specimen (Commercial pure, 10x10 × 1 mm^3) was polished by emery paper (600-2000#), ultrasonically cleaned with acetone/ethanol and deionized water respectively and marked as 1-Ti.

Before biomimetic mineralization, piranha solution (H_2SO_4:H_2O_2=7:3, Volume ratio) was used for ultrasonically etching the 1-Ti at 60 °C for 30 min; and the specimen was immersed into a fresh solution consist of 2 mg/ml L-dopa dissolved in 10 mM Tris–HCl buffer (pH=8.5) at room temperature till the color of the solution change to dark brown; then the specimen was

* Corresponding author.
E-mail address: ggcxl@163.com (X. Cheng).

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incubated in the simulated body fluid [12] (1.5 SBF) at 37 °C for 2 days and marked as 2-Ti.

Using typical hydrothermal synthesis, the 2-Ti was fixed vertically in the middle of a Teflon-lined reaction vessel. $Ca(NO_3)_2 \cdot 4H_2O$ (0.20 M) and chelating reagent $Na_2EDTA \cdot 2H_2O$ (0.20 M) were prepared in 25 mL deionized water, while $(NH_4)_2HPO_4$ (0.12 M) was prepared in 25 mL deionized water separately. The two source solutions were mixed together after pH of each one was raised to 9.5 with ammonium hydroxide and transferred to the reaction vessel sealed in a stainless steel autoclave. The hydrothermal process was conducted at 180 °C for 24 h, after cooling down, the specimen was rinsed, dried in a 60 °C oven and marked as 3-Ti.

Thin film X-ray diffraction (TF-XRD, X'Pert Pro MPD, PANalytical, Netherlands) was used to identify the phase formation under the following conditions: 40 KV, 40 mA, CuKα radiation (λ=1.5406 Å), a 0.5° grazing incident angle, and scan rate at 0.02°/s from 10°–70°; the particle morphology was examined by the field emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan) after Au/Pd sputter coating (E1010, Hitachi, Japan); besides, elemental analysis was investigated by the energy dispersive X-ray spectrometer (EDS, EX-250, Horiba, Japan).

3. Results and discussion

The strategy of the synthesis route was shown in Scheme 1. Piranha solution was used to etch and activate the Ti surface to construct a rough and porous structure, and with the joint effect of the polydopamine attached to the Ti surface doubly induced the formation of the HAP seeded layer, which further facilitated the hydrothermal growth process.

The XRD patterns were displayed in Fig. 1. Pattern 1-Ti showed the diffraction peaks referred to the pure titanium (JCPDS #44-1294) for contrast; while diffraction peaks occurred in pattern 2-Ti could be probably recognized as deposition of the thin HAP seeded layer; in pattern 3-Ti, besides α-titanium was retained as the pure phase of titanium, the rest of the diffraction peaks were totally in agreement with HAP (JCPDS #74-0566), remarkably no titanium oxide (TiO_X) and other phases of Ca/P such as OCP or TCP were detected. Particularly, peak positions at 2θ of 25.8°, 31.8°, 32.2°, 32.8° were exhibited clearly and well corresponded to the (002), (211), (112), (300) planes of HAP respectively, the intensity ratio of the (002) to the (211) plane shown here was rapidly enhanced in comparison with the standard, which indicated the type of *c*-axis oriented crystallinity also coincided with previous studies [13]. Also, the strong and sharp diffraction peaks reflected the high crystallinity of the coated HAP. Furthermore, select 2θ ranged from 25–35° using Jade 6.0 (MDI, USA) to calculate the lattice parameters and the crystallite size, the average lattice constants were $a=b=9.651$ Å, $c=6.892$ Å ($\alpha=\beta=90°$, $\gamma=120°$, Hexagonal), and the average crystallite size was 28.6 nm respectively. However, using 1-Ti to conduct the hydrothermal process directly without

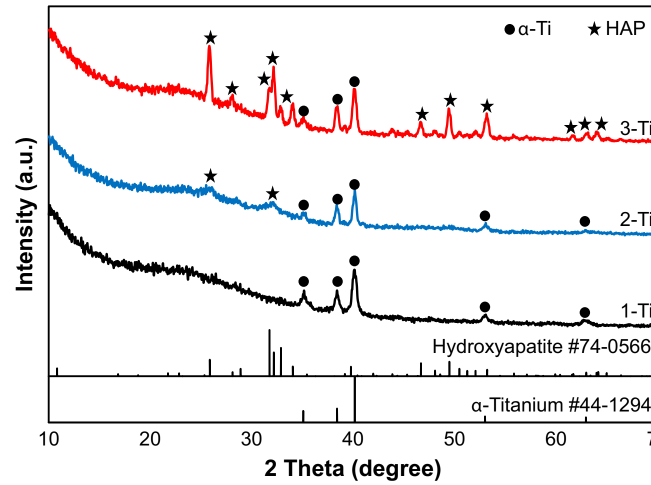
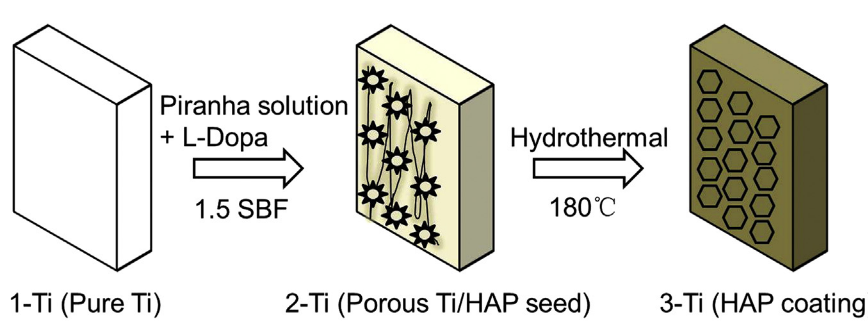


Fig. 1. XRD patterns of as-obtained samples.

the intermediate treatment, the resultant pattern was quite similar to that of 1-Ti, no characteristic diffraction peaks of Ca/P phase could be detected.

The SEM images were shown in Fig. 2. Pic. (a) referred to 1-Ti above, showing the plain and clean surface of titanium for contrast; while 2-Ti surface became relatively rough and porous at a micro/nano scale and nucleation of Ca/P agglomerates could be observed covering mostly upon the Ti surface to form the interactive layer in Pic. (b), which confirmed the seeded HAP as XRD analysis; top-viewed morphology changes of 3-Ti were displayed in Pic. (c–e), showing high crystalline, homogeneous and crack-free HAP coating was achieved, with typical hexagonal prism shape arrayed at average length about 5–10 μm and particle diameter less than 1 μm, which was consistent with recently reports [7–9,11]. Also, the well-defined hexagonal crystal habit and preferably c-axis of HAP crystals orientation normal to the substrate were found here relevant to the XRD illustration, besides, the high density of the coating reflected part of the a-axis orientation [14]. Interestingly, high magnification image found that the formation of hexagonal prism was due to the stack by stack of the small sphere grains, attributing to the seeded effect. However, Pic. (f) showed morphology using 1-Ti to hydrothermal straightly, though small particles existed randomly and irregularly onto the substrate, no characteristic microstructure of HAP could be observed, either XRD failed to find peaks, which further proved that crystalline HAP could not be coated on unseeded Ti this way. Side-view of 2-Ti and 3-Ti were shown in Pic. (g) and (h) respectively, the thickness of HAP seed was less than 5 μm while the HAP coating was sticky to the substrate and adherent with a uniform thickness of about 70 μm as observed.

The EDS spectra were shown in Fig. 3. The essential elements such as Ca, P, and O could be detected in spectrum 2-Ti, which was



Scheme 1. Schematic illustration of biomimetic-hydrothermal synthesis route.