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Titania nanotube/nano-brushite composited bioactive coating with micro/nanotopography on titanium formed by anodic oxidation and hydrothermal treatment

Daqing Wei*[1], Wei Feng, Qing Du, Rui Zhou, Baoqiang Li, Yaming Wang, Yu Zhou, Dechang Jia

Institute for Advanced Ceramics, Department of Materials Science and Engineering, Harbin Institute of Technology, P.O. Box 3022, Yikuang Street, Harbin 150001, PR China

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Abstract

This work was to improve the bioactivity of biomedical titanium (Ti) through constructing a bioactive surface with micro/nano-topography on Ti. Firstly, Ti plates were sandblasted, acid etched and anodized (SBAO) to obtain the controlled micro/nano-topography. And then, heat treatment was used to change the amorphous phase of Ti oxide nanotubes to anatase on the SBAO sample. The SBAO sample and heat treated SBAO sample (SBAOT) both have super hydrophilicity mainly due to their micro/nano-topography. At last, nano-brushite was deposited on the SBAOT surface by hydrothermal treatment to further improve its bioactivity. The simulated body fluid incubation indicated that this novel coating with nano-brushite has more excellent bioactivity as compared to Ti, and SBAO and SBAOT.

keywords: E. Biomedical application; Anodic oxidation; Hydrothermal treatment; Micro/nano-topograghy; Titanium

1. Introduction

Ti and its alloys as hard tissue replaced implants still have drawbacks such as its poor bioactivity and osseointegration [1]. The interface bonding between Ti implant and tissue inclines to loose due to the poor osseointegration and the stress shielding caused by the mismatch of Young's modulus [2]. Various kinds of surface modification methods have been developed to enhance the bioactivity and osseointegration of Ti implants. Some of these treatments focus on changing the morphology of implant, such as acid etched [3] which fabricates surface roughness on Ti. Some of them concentrate on adding bioactive radical group [4–6] or bioactive phase such as hydroxyapatite [7–9] to the surface of Ti implant.

Previous studies have demonstrated that the morphology of implants have a direct influence on osseointegration. Primarily, micro-scale roughed morphology is beneficial to the mechanical interlocking between implants and newly born bone [10]. Besides, the topography on micro-scale markedly affects protein adsorption and cell proliferation and differentiation thus affecting the integration of implants and surrounding tissue [11–13]. Subsequently, research works show that surface with roughness in nano-scale also plays an important role in osteoblast differentiation and tissue regeneration [14,15]. Now recent research works have concentrated on the combined micro- and nano-scales topography, exploring their regulation on cell proliferation and differentiation as well as effect on esseointegration [16–18]. Therefore, a simple and feasible method to construct nanostructure without dramatically changing the original microstructure and bioactive composition on implant surface, become an important objective of recent

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*Corresponding author.
Tel.: +86 451 8640 2040/8403; fax: +86 451 8641 4291.
E-mail address: daqingwei@hit.edu.cn (D. Wei).

[1] Postal address: Institute for Advanced Ceramics, Science Park, Harbin Institute of Technology, Yikuang Street, P.O. Box 3022#, Harbin, 150080, P. R. China.

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studies. Moreover, Hydrophilicity is an important factor which determines the protein adhesion, cell proliferation and other interactions between implants and tissue [19,20]. Generally, enhancing hydrophilicity of implant surface is beneficial the growth of cells and tissue [21,22].

Sandblast and acid etched (SBA) is a widely applied surface modification treatment on commercial implants, creating micro-topography on the surface of implants [3,23]. It is usually used for dental implants, which loads slightly. Anodic oxidation in the electrolyte containing fluoride, which can fabricate nanotubes on the surface of Ti, has caused great attention in dental and orthopedic applications [24,25]. Experiment in vitro and vivo both reveal that the nanotubular TiO_2 shows brilliant hydrophilicity and cell response [14,26,27]. TiO_2 nanotubes can also be used to induce the formation of other nanostructures such as $CaTiO_3$ nanobricks [28] and nano-scale hydroxyapatite [29].

Now reports on the combined porous structures with micropores and TiO_2 nanotubes are seldom. Though the sandblasted Ti and TiO_2 nanotubes shows osteoinductivity, the effect is limited [26,30]. The reason for this is that no good bioactive materials or structure were formed on their surfaces.

Brushite (dicalcium phosphate dihydrate) material has raised considerable interest recently, because it is metastable under physiological conditions and can be resorbed more quickly than hydroxyapatite cements [31]. Some investigations have suggested that it is a precursor of bone mineralization, including biological apatites [32,33]. The brushite has been widely used in the reconstruction materials, dental cements, as well as in formulation chemistry [34,35]. This study constructed a novel and bioactive composited coating of brushite and titania nanotube with a hierarchical porous structure on pure Ti, through sand blasting, acid etching, anodic oxidation, heat treatment and hydrothermal treatment.

2. Materials and method

2.1. Material preparation

Commercial pure Ti foils ($10 \times 10 \times 0.2\ mm^3$) were polished, and then sand blasted by quartz sand at 0.3 MPa for 30 s. They were ultrasonically cleaned in deionized water to remove the residual sand. After that the samples were immersed in 49 wt% sulfuric acid aqueous solution at 60 °C for 1 h. After being washed with deionized water, the SBA foils were further anodized in glycerol–water based electrolyte (1:1,v:v) containing 10 g/L NH_4F at 20 V for 1 h. The anodic oxidized samples were annealed at 450 °C for 2 h in air with a heating rate of 10 $^\circ C\ min^{-1}$. After heat treatment, the samples were hydrothermal treated in a saturated $Ca(OH)_2$ solution for 2 h at 200 °C. And then, the samples were washed by deionized water for three times and dried at room temperature. And then, these modified samples by $Ca(OH)_2$ solution were further hydrothermal treated in the 0.015 mol/L Na_2HPO_4 solution at pH=8 for 2 h at 200 °C. At last, these samples were washed by deionized water for three times and dried at room temperature. Table 1 shows the sample labels and corresponding modification procedures.

Table 1
Sample labels and modifying procedures.

	SB	SBA	SBAO	SBAOT	SBAOTH
Sand blasted	Yes	Yes	Yes	Yes	Yes
Acid etched	No	Yes	Yes	Yes	Yes
Anodic oxidation	No	No	Yes	Yes	Yes
Heat treatment	No	No	No	Yes	Yes
Hydrothermal treatment	No	No	No	No	Yes

2.2. Simulated body fluid immersion

The samples were soaked in 15 mL simulated body fluid (SBF) [36], immersing for different time, and the SBF was refreshed every other day. The SBF was prepared by dissolving reagent-grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, and Na_2SO_4 into deionized water and buffering at pH 7.40 with tris-hydroxymethylaminomethane ($(CH_2OH)_3CNH_2$) and 1.0 mol/L HCl at 37 °C.

2.3. Surface characterization

2.3.1. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDS)

Scanning electron microscopy (SEM, Helios Nanolab 600i, FEI Co.,USA) was used to observe the surface morphology of the samples. Moreover, the energy dispersive X-ray spectrometer (EDS, Oxford, UK) equipped on the SEM system was used to detect the elemental concentrations of the sample surfaces.

2.3.2. X-ray diffraction (XRD)

The X-ray diffraction (XRD, D/max-γB, Japan) was utilized to investigate the surface phase compositions of the samples before and after SBF immersion using a CuKα radiation with a continuous scanning mode at a rate of 4°/min. The accelerating voltage and current were 40 kV and 50 mA.

2.3.3. Confocal laser scanning microscope (CLSM)

Confocal laser scanning microscope (CLSM, Olympus3000, Japan) provided surface area roughness and 3D topography of the samples at the macro- and nano-scales. The sample was scanned over an area of $256 \times 256\ \mu m^2$.The value of surface area roughness (R_a) and peak-to-valley height (R_z) were calculated.

2.3.4. Contact Angle measurement

Contact angle of every kind of sample was evaluated a goniometer (CAM 100, KSV, Helsinki, Finland) equipped with a digital camera and image analysis software. The wetting liquid was pure water with a drop volume of 2 μL. Four samples of every group were measured three times.