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The composite films of gradient TiO_2-based/nano-scale hydrophilic sodium titanate: Biomimetic apatite induction and cell response

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ABSTRACT

Chemical treatment was performed to modify the surfaces of the TiO_2-based (TOB) film containing P for improving its bioactivity. The apatite-forming ability of the chemically treated TOB (C-TOB) film was enhanced due to the formation of hydroxyl-functionalized surface during the SBF immersion process. However, further heat treatment of the C-TOB films formed crystalline sodium titanate, showing poor ability to release Na^+ ions, which does not facilitate the formation of hydroxyl-functionalized surface, thus lowering the apatite-forming ability. Firstly, amorphous Ca- and P-containing precipitates formed during the SBF immersion process, eventually transformed to crystalline biomimetic apatite, exhibiting a porous structure on two-scales of micron and nanometer levels. The preliminary cell experiment showed that the C-TOB film has good biocompatibility.

1. Introduction

Titanium and its alloys are used extensively in biomaterials region [1]. However, when a strong interface bonding between implants and living bone is desired, a bioinert feature of titanium and its alloys is required to be modified towards bioactivity. One approach to overcoming the disadvantage of titanium and its alloys is to produce bioactive films on their surfaces [2–4]. Many surface modifying techniques such as plasma spraying [5,6], electrochemical deposition [7,8] and sol–gel method [9,10] have been developed to prepare bioactive coatings on titanium and its alloys. In recent years, biomimetic technique has been developed because it possesses some advantages such as low working temperature, accessibility of pore networks on the nanometer scale and suitability for complex shapes of substrates [11].

To obtain biomimetic apatite, layers that are capable of inducing apatite deposition should be formed on titanium alloy substrate. The previous researches indicated that microarc oxidized (MAO) TiO_2-based (TOB) film on titanium alloy after chemical treatment has high apatite formation ability [12]. Further investigation demonstrated that nano-scale amorphous sodium titanate was formed on the surface of the chemically treated TOB (C-TOB) film, and crystalline sodium titanate was obtained after heat treatment of the C-TOB film [13]. The phase compositions and surface morphology of the heat-treated C-TOB film are highly dependent on the heat treatment temperature [13]. However, the in vitro bioactivity such as biomimetic apatite induction and cell response of the nano-scale hydrophilic sodium titanate on the surface of the C-TOB film are not fully understood. In this work, biomimetic apatite induction and preliminary cell proliferation behavior of the composite film of gradient TiO_2-based/nano-scale hydrophilic sodium titanate were investigated.

2. Materials and methods

2.1. Preparation of the TOB and modified TOB film

MAO technique was used to prepare the TOB film on the surface of titanium alloy. In the MAO process, Ti6Al4V plates ($10\times10\times1.5$ mm^3) were used as anodes, and stainless steel plates were used as cathodes in an electrolytic bath. The Ti6Al4V plates were ground with abrasive papers, ultrasonically washed with acetone and distilled water, and dried at 40 °C. The applied voltage, frequency, duty cycle and oxidizing time were 300 V, 600 Hz, 8.0% and 5 min, respectively. The temperature of the electrolyte was kept at 40 °C by a cooling system. An electrolyte was prepared by dissolving reagent-grade chemicals of $(NaPO_3)_6$ (20 g/l) and NaOH (10 g/l) into deionized water. The TOB film was treated in 5 mol/L NaOH solution at 60 °C for 24 h, and then gently washed with deionized water and dried at 25 °C. The C-TOB film

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Table 1
The sample labels of the TOB film before and after modification.

Sample	Microarc oxidation	Chemical treatment	Heat treatment
TOB	√	–	–
C-TOB	√	√	–
C6-TOB	√	√	600 °C
C7-TOB	√	√	700 °C

"√": With treatment; "–": Without treatment.

Table 2
Ion concentrations of SBF and human blood plasma.

Ion	Concentrations (mmol/L)	
	SBF	Blood plasma
Na^{+}	142.0	142.0
K^{+}	5.0	5.0
Mg^{2+}	1.5	1.5
Ca^{2+}	2.5	2.5
Cl^{-}	147.8	103.8
HCO_3^{2-}	4.2	27
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5

was heat-treated at 600 and 700 °C for 1 h in air, with a heating rate of 10 °C/min and furnace cooling. The sample labels and the parameters for the treatment conditions are shown in Table 1.

2.2. Immersion of the samples in a simulated body fluid

The TOB, C-TOB, C6-TOB and C7-TOB samples were soaked in 15 mL simulated body fluid (SBF) [14] (Table 2), immersing for different time, and the SBF was refreshed every other day to obtain apatite. 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. Characterization

2.3.1. X-ray diffraction (XRD)

A grazing incidence of X-ray diffraction (XRD, Philips X'Pert, Holland) with a Cu Kα radiation was used to analyze the surface phase composition of TOB films before and after treatment. In the XRD experiment, the angle of the incident beam was fixed at 1° against the sample surfaces in order to detect the phase composition of the sample surfaces and the measurements were performed with a continuous scanning mode at a rate of 2°/min.

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

The surface morphologies of the samples were observed by a scanning electron microscopy (SEM, CamScan MX2600, CamScan Co.,

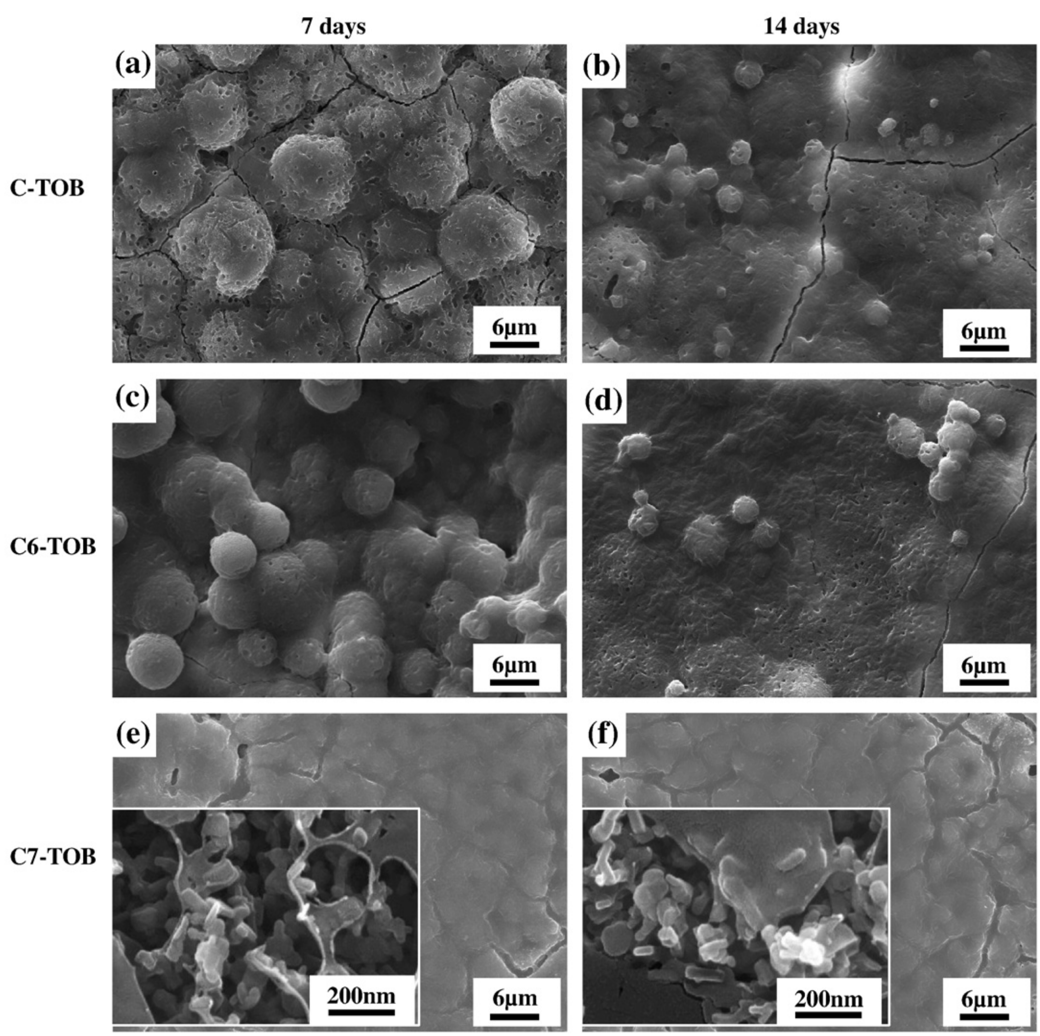

Fig. 1. Surface morphologies of the C-TOB, C6-TOB and C7-TOB films after SBF incubation for 7 and 14 days: (a) and (b) C-TOB, (c) and (d) C6-TOB, (e) and (f) C7-TOB films.