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Construction of micro–nano network structure on titanium surface for improving bioactivity

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ABSTRACT

A novel hierarchical micro–nano structured titania layer was constructed on Ti surface to mimic the multi-level bone structure. The Ti substrate was subjected to a suitable acid etching and subsequent anodization in NaOH electrolyte to form a micro–nano porous titania layer. It was indicated that this microporous/nano-network (micro/nano-network) structured surface presented the enhanced wettability and superhydrophilic property. The polarization curve measurements showed that the as-prepared micro/nano-network structured TiO_2 surface was of better corrosion resistance compared to the blank Ti surface, according to its corrosion current decreased, corrosion potential shifted positively and polarization resistance increased in Hank's solution. Meanwhile, the Mott–Schottky plots revealed that less oxygen vacancies existed in the micro/nano-network structured TiO_2 film in contrast to the natural oxide film on blank Ti surface. Moreover, it was observed that the micro/nano-network structured surface was completely covered by a homogeneous apatite layer when immersed in simulated body fluid (SBF) for 14 days, exhibiting an excellent ability of biomineration. Furthermore, the superior cell adhesion and viability were discerned on such hierarchically structured surface, through a comparison of MG63 cell behaviors on blank Ti surface, nano-network structured surface and micro/nano-network structured surface. All results suggest our construction of micro–nano porous TiO_2 surface is a promising strategy for improving the bioactivity of titanium implants.

1. Introduction

Hard tissues in a human body inevitably suffer damage because of accidents, wars, diseases or other factors. In some severe cases, the hard tissues have to be substituted by artificial materials especially the biomedical metallic materials [1]. Among various biomedical metals, titanium and its alloys are widely applied in hard tissue replacements such as dental implants, bone fracture-fixation and artificial joints, due to their good mechanical properties, favorable biocompatibility and excellent corrosion resistance. The application of titanium and its alloys as clinical substitutes began in 1960s and the relative research activities have been growing since then [2]. Recently, besides unalloyed Ti (cp grades 1–4), Ti6Al4V and TiNi, other titanium-based alloys are being developed for medical applications. It is generally accepted that titanium and its alloys appear to be the most suitable and biocompatible medical replacement compared with stainless steels and Co–Cr alloys. However, the machined titanium metal does not induce bone tissue regeneration and is easily encapsulated by fibrous tissue when implanted in bone tissue, which generally leads to clinical failures [2,3]. Surface modification is an effective pathway to promote the bioactivity and biocompatibility of Ti implants. Hence, several methods have been used to produce a bioactive layer on Ti surface, including sol–gel process [4], alkali-heat treatment [5], sandblasting/acid etching [6] and anodization [7,8].

It has been previously reported that a micro-textured titanium surface favors osteoblast attachment, differentiation, local factor production and wound healing [9,10], and some titanium implants have been treated with a microrough structure to enhance the bioactivity and osseointegration in vivo. However, the effects of micro-scale structure on osteoblast proliferation and bone mass accumulation are far from satisfactory [11]. Recently, nanotechnology is attractively applied in enhancing the bioactivity of titanium metal [12]. Nanostructured surfaces with a nanotube, nanonodule or nanoparticle layer are thought to directly interact with some proteins and cell membrane receptors, effectively promoting cell adhesion, spreading and proliferation [10]. Hence, some studies

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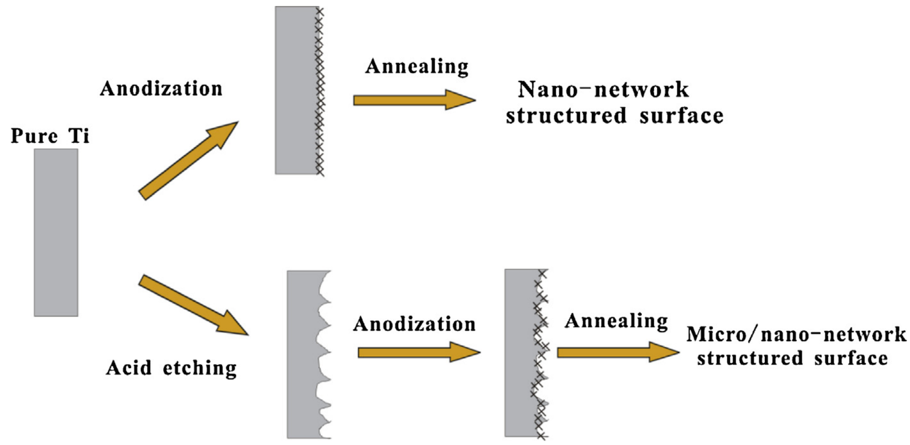

Fig. 1. Scheme of the preparation process of the nano-network and micro/nano-network structured surfaces.

have attempted to combine both micro-scale and nano-scale structures to promote cell activities on titanium surface [13–15]. Despite some promising results have been reported, further studies of precise construction of micro–nano textured structure on titanium surface, surface physicochemical properties, as well as bioactivity and biocompatibility are still needed.

It is well known that bone is of a complex hierarchical hybrid structure, comprising of macro-, micro-, and nano-scale organizations [16]. From the bionic viewpoint, the bone substitute with a multi-level porous structure should be beneficial to bone-implant integration. In this study, a micro–nano structured porous layer was constructed on Ti surface by a combination of dual acid etching and electrochemical anodization. The surface morphology and crystalline composition were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The corrosion resistance, electronic properties and wettability behavior were analyzed, and the biomineration, cell adhesion and viability were investigated to demonstrate the in vitro bioactivity of the prepared samples. The relationship of the surface structure of TiO_2 film and the bioactivity as well as biocompatibility was discussed taking account of the bionic viewpoint.

2. Experimental

2.1. Construction of nano-network and micro/nano-network structured surfaces

Pure titanium plates (10 mm × 10 mm × 2 mm) were polished by SiC papers from No. 400 to No. 1200. The polished titanium plates were ultrasonically cleaned with acetone, anhydrous alcohol, and distilled water for 10 min, respectively. To precisely construct a nano-network structured surface and a micro/nano-network structured surface, the electrochemical anodization as well as the combination of anodization and chemical etching was arranged in this work rather than the traditional sandblasting and acid etching. The polished titanium plates was anodized in 5 M NaOH solution at 15 V for 2 h at room temperature using a platinum plate as a counter electrode to form a nano-network structured surface. For comparison, the polished plates were soaked and etched in a mixed solution of 48% H_2SO_4 and 18% HCl for 1 h at 75 °C, and then subjected to the same electrochemical anodization treatment in order to construct a micro/nano-network structured layer on titanium surface. After anodization, the titanium plates were rinsed with distilled water and annealed at 450 °C for 2 h in a muffle furnace. A schematic diagram of the preparation process is shown in Fig. 1.

2.2. Contact angle measurement

Sessile-drop method, with a water droplet size of 5 μl, was performed to measure contact angle using a contact angle goniometer (Kruss DSA100, Germany) to illustrate the wettability for the different morphologies on titanium by various treatments. Prior to the measurement, the titanium plates were cleaned in distilled water and dried in a desiccator.

2.3. Electrochemical test and Mott–Schottky plots

The measurements of DC polarization and Mott–Schottky plots were carried out in a three-electrode electrochemical cell in Hank's solution at 37 °C using an electrochemical workstation (Autolab PGSTAT 30, Netherlands). The prepared Ti samples with 1 cm^2 exposed area were used as working electrodes. A platinum sheet and a saturated calomel electrode (SCE) were acted as the counter electrode and reference electrode, respectively. The Hank's solution was prepared by dissolving the regents of 8 g/L NaCl, 0.4 g/L KCl, 0.14 g/L $CaCl_2$, 0.35 g/L $NaHCO_3$, 0.06 g/L $Na_2HPO_4{\cdot}2H_2O$, 0.1 g/L $MgCl_2{\cdot}6H_2O$, 0.06 g/L KH_2PO_4, 0.06 g/L $MgSO_4{\cdot}7H_2O$ and 1.0 g/L glucose into ultrapure water and buffering at 7.40 [17]. The polarization curves were recorded in a potential range of ±120 mV with respect to the open circuit potential (OCP) at a scan rate of 0.5 mV/s. The Mott–Schottky plots of capacitance at different potentials in Hank's solution were obtained by a potential sweep towards anodic direction with a sweeping rate of 5 mV/s. The measurement frequency was fixed at 1 kHz and the carrier density of the oxide films was determined by Mott–Schottky analysis.

2.4. SBF immersion test

The effect of surface structure and properties on biomineration ability was evaluated by immersing various titanium samples in SBF solution. The SBF solution, with ion concentrations nearly equal to those in human blood plasma, was prepared according to Kokubo's formulation by sequentially dissolving regent-grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$ and Na_2SO_4 in distilled water and buffered at pH 7.4 with TRIS and 1 M HCl at 36.5 °C [18]. The titanium samples were soaked in SBF solution and kept in a thermostat at 36.5 °C. The SBF solution was refreshed every other day. After immersing for 14 days, the samples were removed from the solution, gently washed with distilled water and dried in a desiccator for further characterization.