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Reactivity of porous titanium oxide film and chitosan layer electrochemically formed on Ti-6Al-4V alloy in biological solution

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A B S T R A C T

Uniform porous TiO_2 film on Ti-6Al-4V alloy was obtained by hard anodic oxidation and successfully the chitosan layer was electrodeposited. Surface morphology, compositional properties and diffraction patterns were analyzed by scanning electron microscopy with energy dispersive X-ray analysis system and X-ray diffraction. The reactivity of anodic porous TiO_2 film in the presence or absence of chitosan layer was investigated by electrochemical methods in biological solution and compared with the reactivity with the unmodified Ti-6Al-4V alloy surface. The electrochemical impedance spectroscopy method was used to compare the response reactivity of the three surfaces. The combination of the high biocompatibility of chitosan and good mechanical characteristics of Ti-6Al-4V alloy make the obtained porous TiO_2 film combined with chitosan a promising method to improve the reactivity of medical implants in biological solution.

1. Introduction

Materials for biomedical applications are artificial or natural materials, used for making structures or implants, to replace the lost or diseased biological structures and to restore forms and functions. Thus biomaterial helps in improving the quality of life and longevity of human beings and the fields of biomaterials and surface modifications techniques have shown rapid growth during the last decades to keep close with the demands of many biomedical applications [1,2].

Titanium and titanium alloys, such as Ti-6Al-4V are nowadays the most attractive metallic biomaterials for replacing failed tissue in orthopedic and dental fields due to excellent corrosion resistance, good biocompatibility and low Young's modulus compared to other metallic biomaterials [3,4]. Even if titanium and its alloy are the most used metallic biomaterials, it is well known that the titanium has no complete bone integration and reactive bioactivity properties [4]. Different surface modification techniques have been investigated to improve the physical and bone integration properties of the titanium alloys while maintaining their biocompatibility. Anodic oxidation and thermal oxidation treatment [5] are the most used techniques for surface treatment of titanium and its alloys. The surface modified methods can improve the physical properties by obtaining nanotube or nanopore structures [6]. Besides the anodic oxidation modification method, different organic layers such as chitosan (CS) [7], etc. or inorganic layers like hydroxyapatite (HA) [8,9], etc. were electrodeposited on the titanium and its alloys surfaces.

Chitosan is a cationic polysaccharide derived by a deacetylation of chitin and one of the most promising natural biopolymers for tissue engineering. Due to its unique properties such as biocompatibility, biodegradability, anti–bacterial, wound–healing activity and non–-toxicity, chitosan has attracted much attention of researchers for a wide variety of bio–engineering applications ranging from tissues and skin to bones or cartilages [7,10,11]. Previous studies have demonstrated that the chitosan is active against such *Escherichia coli*, *Streptococcus mutans*, *Staphylococcus aureus*, *Bacillus subtilis*, *Actinomyces naeslundii* [10,12,13]. Chitosan coatings could be used in a wide range of applications, including dental/orthopedic implants. Chitosan coated–implants present a good biocompatibility with respect to fibroblast cell [11] and alloy cell proliferation on implant surface. In addition, the presence of porous surfaces increases the surface roughness and cause microscopic tissue-cell ingrowths, thereby improving implant fixation [14–16].

Even if in the literature there are many papers approaching the electrodeposition of chitosan or hard anodization of titanium and its alloys, the combination of anodic oxidation to form a porous TiO_2 film with chitosan electrodeposition to obtain over a chitosan layer

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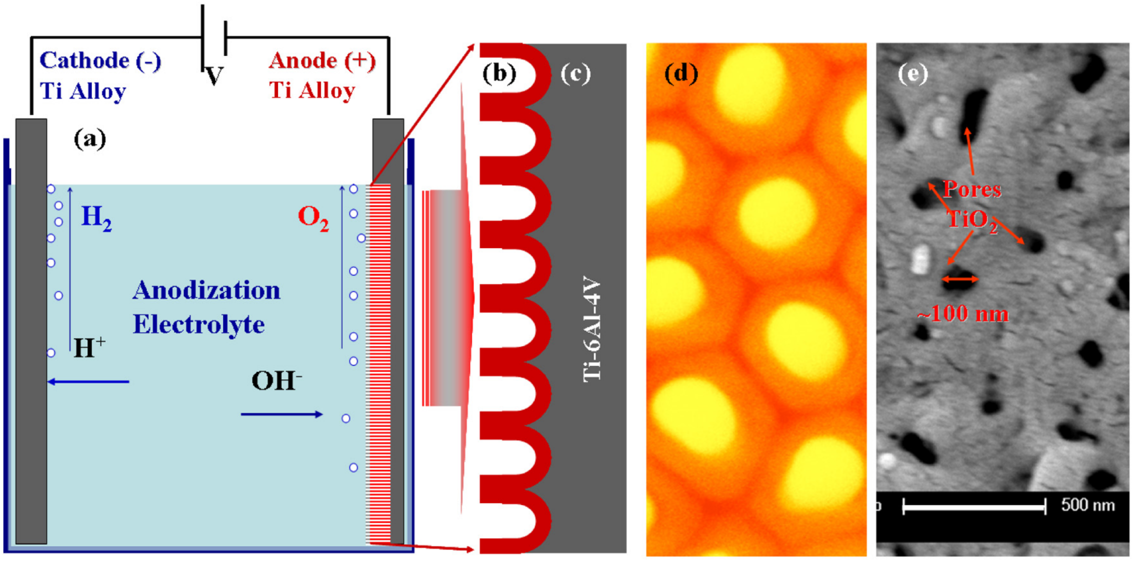

Fig. 1. Schematic experimental set-up for growing the porous TiO_2 film on Ti-6Al-4V alloy surface: (a) anodization cell, (b) schematic cross-section of porous structure oxide film formation on titanium alloy surface, (c) Ti-6Al-4V alloy, (d) schematic typical top-view of porous TiO_2 film and (e) SEM surface morphology of obtained porous TiO_2 film by anodization on Ti-6Al-4V alloy surface.

represents a novel functionalization on titanium alloy surface with improved reactivity and corrosion resistance in biological solutions. The research work performed on surface modification of Ti-6Al-4V alloy by controlled growth of a porous oxide layer and further electrodeposition of chitosan is a really new approach in improving the reactivity and life of titanium alloy implants. Nowhere in the scientific publications was found such an approach.

2. Experimental set-up

2.1. Electrochemical formation of porous TiO_2 film on titanium alloy surface

The porous TiO_2 film was prepared by controlled anodic oxidation method on Ti-6Al-4V alloy surface. Before the anodic oxidation, the samples were mechanical polished to a mirror finish using several grades of SiC grinding paper, diamond paste and a suspension of SiO_2. Polished plates were cleaned in ultrasonic bath for 5 min and dried under air flow. For anodic oxidation process, 1 M H_2SO_4 solution (Sigma Aldrich) was used as electrolyte. The anodic oxidation took place in two-electrode electrochemical cell using two Ti-6Al-4V plates: one as anode electrode (2.5 × 2.5 cm) and the other as cathode electrode (5.7 × 4 cm). The process was carried out using a programmable DC power supply with digital multimeter (Genesys – GEN 300–8) by applying 275 V for 2 min under vigorous stirring. After anodic oxidation treatment the specimens were ultrasonically rinsed using ethanol and distilled water (each for 10 min).

2.2. Electrodeposition of chitosan layer on TiO_2 porous film

Electrodeposition of chitosan layer was conducted at room temperature in an electrolyte containing 28 $g{\cdot}L^{-1}$ acetic acid, 10 $g{\cdot}L^{1}$ chitosan flakes and 8.3 $g{\cdot}L^{-1}$ sodium hydroxide. The solubilization of chitosan flakes was made with acetic acid solution (99.7%) to a pH of 3.4. The pH of solubilized chitosan solution was subsequently adjusted with NaOH to a value of 4.75. The electrodeposition cell set–up was composed by TiO2 film formed on Ti-6Al-4V alloy as working electrode and Pt-Rh grid as counter electrode. For the electrodeposition of the chitosan layer a direct current power source was used by applying a current density of 0.6 $mA\,cm^{-2}$ for 10 min. All used substances were purchased from Sigma-Aldrich.

2.3. Surface characterization of porous TiO_2 film and chitosan layer

The surface morphology of the samples was examined by scanning electron microscopy (SEM - Philips XL 30 FEG). In addition, the elemental compositions of the sample surfaces were detected by an energy dispersive X-ray spectrometer (EDX) equipped on the SEM system. The phase composition of the sample surfaces were analyzed by X-ray diffraction (Seifert 3003 T diffractometer) using a Cu Kα radiation, operated at 40 kV and 40 mA with a step size of 0.02° for 2θ ranging from 10° to 100°.

2.4. In vitro reactivity evaluation of porous TiO_2 film and chitosan layer

The in vitro reactivity tests were carried out electrochemically using a potentiostat/galvanostat controlled by software. The electrochemical impedance spectroscopy (EIS) data were recorded in the frequency range of 100 kHz–10 mHz with 20 points per decade using 10 mV peak to peak sinusoidal potential amplitude. EIS tests were performed in a conventional three-electrode cell consisting of: analyzed samples as working electrode, an Ag/AgCl reference electrode with KCl saturated solution (E = 200 mV vs. standard hydrogen electrode – SHE) and a Pt – Rh grid as counter electrode. EIS measurements were performed at the open-circuit potential by immersing the specimens in the biological Hank's solution. The tested area of the sample surface was 1.94 cm^2. The Hank's solution was prepared by dissolving the following components in deionized water: NaCl – 8.8 $g{\cdot}L^{-1}$, KCl – 0.4 $g{\cdot}L^{-1}$, $CaCl_2$–0.14 $g{\cdot}L^{-1}$, $NaHCO_3$–0.35 $g{\cdot}L^{-1}$, $Na_2HPO_4{\cdot}7H_2O$ – 0.06 $g{\cdot}L^{-1}$, $KH_2PO_4{\cdot}7H_2O$ – 0.1 $g{\cdot}L^{-1}$, $MgSO_4{\cdot}7H_2O$ – 0.2 $g{\cdot}L^{-1}$ and $C_6H_{12}O_6$–1 $g{\cdot}L^{-1}$. The pH of the prepared Hank's solution was 7.4. The EIS data were analyzed using equivalent circuit modeling and curve fitting using ZView software.

3. Results and discussions

3.1. Anodic oxidation treatment to form porous TiO_2 film on titanium alloy surface

Fig. 1 (a–e) is the schematic representation of the experimental set–up used for growing the porous TiO_2 film on Ti-6Al-4V alloy surface. Anodic oxidation treatment of titanium and its alloys is a convenient and reliable surface modification technique that can create