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Full Length Article

In-vitro bioactivity and electrochemical behavior of polyaniline encapsulated titania nanotube arrays for biomedical applications

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ABSTRACT

Titania nanotube arrays (TNTA) have attracted increasing attention due to their outstanding properties and potential applications in biomedical field. Fabrication of titania nanotubes on titanium surface enhances the biocompatibility. Polyaniline (PANI) is one of the best conducting polymers with remarkable corrosion resistance and reasonable biocompatibility. In this work, the corrosion resistance and biocompatibility of polyaniline encapsulated TiO_2 nanotubes for orthopaedic applications were investigated. The vertically oriented, highly ordered TiO_2 nanotubes were fabricated on titanium by electrochemical anodization process using fluoride containing electrolytes. The anodization parameters viz., voltage, pH, time and electrolyte concentration were optimized to get orderly arranged TNTA. Further, the conducting polymer PANI was encapsulated on TNTA by electropolymerization process to enhance the corrosion resistance. The nanostructure of the fabricated TNTA and polyaniline encapsulated titania nanotube arrays (PANI-TNTA) were investigated by HR SEM analysis. The formed phases and functional groups were find using XRD, ATR-FTIR. The hydrophilic surface of TNTA and PANI-TNTA was identified by water contact angle studies. The corrosion behavior of specimens was evaluated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization studies. *In-vitro* immersion studies were carried out in simulated body fluid solution (Hanks' solution) to evaluate the bioactivity of the TNTA and PANI-TNTA. The surface morphological studies revealed the formation of PANI on the TNTA surface. Formation of hydroxyapatite (HAp) on the surfaces of TNTA and PANI-TNTA enhanced the bioactivity and corrosion resistance.

1. Introduction

Metals and their alloys viz., 316L SS, titanium and its alloys, Co-Cr alloys, etc., are being used for orthopaedic and dental applications because of their desirable physical, mechanical and chemical properties such as high strength, corrosion resistance and low elastic modulus [1,2]. Among them, titanium and its alloys have unique properties viz., good biocompatibility, High strength-to-weight ratio and high corrosion resistance due to the formation of TiO_2 oxide layer on the surface. However, titanium and its alloy are bio-inert, they are not able to directly bond with human bone after implantation [3,4]. The surface properties of a biomaterial play an important role in determining cellular response (cell adhesion and proliferation) to the material. In order to improve the osseointegration of the bone-implant interface has the success of the implant. The properties of implant materials surface can be changed using suitable surface modification techniques [5,6].

Numerous surface modification techniques are available which include sol-gel, electrophoretic deposition, physical vapour deposition (PVD), chemical vapour deposition (CVD) and electrochemical anodization [5,7–11]. The growth of TNTA on titanium by electrochemical anodization in fluoride containing electrolytes was first reported by Zwilling et al. [12]. The anodic TiO_2 nanotubes have high surface-to-volume ratio. Electrochemical anodization is periodically used because it is cost effective and helps in the uniform growth of compatible TiO_2 nanotubular layer on the titanium surface [13]. The surface morphology of nanostructures, its geometry and shape determine the accomplishment of an implant [14]. Anodization parameters like applied current, voltage and electrolyte concentration could be easily controlled to obtain TiO_2 nanotubes of desirable properties [15]. Literature survey reveals that TiO_2 nanotubes favour better osteoblast cell adhesion, proliferation and differentiation [4].

Conducting polymers have gained considerable attention as bio-interfaces due to their biocompatibility and cell signal transmitting ability. Conducting polymer based implant materials are able to transmit signals from one cell to another cell thereby,

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inducing better cell growth and differentiation. The conducting polymer composites induce the bone healing ability through its owning electrical stimulation behavior [16]. PANI is one of the best conducting polymers with remarkable corrosion resistance [17] and reasonable biocompatibility [18]. It is also known for its antioxidant property [19]. It has been widely used in cardiovascular [20] and nervous systems [21]. Previous literatures reported that *in-vivo* studies of PANI has enough biocompatibility of use as a biomaterial [16].

In this work polyaniline conducting polymer was encapsulated into TNTA formed on commercially pure (Cp) - titanium by anodic oxidation followed by electropolymerization. The surface features of TNTA and PANI-TNTA was characterized by HR SEM, corrosion resistance and bioactivity analysis were done by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) studies in Hanks' solution.

2. Materials and methods

2.1. Fabrication of titania nanotube arrays

The chemical composition of commercially pure titanium (Cp-Ti) is given in Table 1. Commercially pure Ti (Cp-Ti) specimens were procured from M/s Uniforce Engineers, Chennai, India. Ti samples with the dimensions of 15 mm × 20 mm × 2 mm were ground with different grades of silicon carbide papers up to 1200 grits in order to obtain smooth surface. The samples were ultrasonically cleaned using acetone and double distilled water. The ground samples were chemically etched using Kroll's reagent (6 ml of H_2O + 2.5 ml of conc. HNO_3 + 1.5 ml of HF) for 10 s. After etching, the samples were cleaned and dried in air at room temperature.

Anodization was carried out using a two electrode electrochemical anodization cell with prepared titanium sample as anode and platinum as cathode. The electrode distance was kept at 2 cm. The electrolyte was prepared by mixing 50 ml of 1.5 M H_2SO_4 and 50 ml of 0.1 M HF. The electrolyte volume was fixed at 100 ml and stirred continuously. A direct power source (DC) was used to maintain the voltages at 10, 20 and 30 V. After anodization, the samples were washed thoroughly with double distilled water and dried at room temperature. The anodised samples were annealed at 450 °C for 3 h in box furnace to transfer the amorphous TiO_2 phase to its crystalline anatase phase.

2.2. Electropolymerization of aniline

Cyclic voltammetry (CV) technique was used to carry out the electropolymerization using PGSTAT Autolab-302N electrochemical workstation. The electrochemical cell containing three electrodes with anodised sample as working electrode (WE), saturated calomel electrode (SCE) as the reference electrode (RE) and platinum foil as counter electrode (CE) was used. The solution contained 0.1 M aniline monomer and 1 M H_2SO_4 as supporting electrolyte. The working electrode potential applied was from −1.0 to 1.2 V at a scan rate of 30 mV s^{-1} for 20 cycles [22]. The samples were washed with distilled water to remove the unreacted monomer molecules and then dried at room temperature.

2.3. Surface characterization

The surface characterization was done using Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectrometer (Bruker–Alpha) in the frequency range from 500 to 4000 cm^{-1}. The phase transitions of the anodized samples were studied by X-ray diffraction (XRD) using Xpert Pan Pro Analytical X-ray diffractometer. Monochromatic Cu kα radiation source (λ = 0.15418 nm) was used and the samples were examined from 20 to 80° at the scanning rate of 0.02° per minute. The surface morphological features of the anodized samples were observed by high resolution scanning electron microscope (HR SEM, Model FEI Quanta FEG 200). The 2D and 3D profile of the HR SEM images were achieved by the scanning probe image processor WSxM 4.0 beta 8.5 software [23]. The wettability of the samples was measured using contact angle analyzer model Phoenix 300 Plus with a drop volume of 8 μl.

2.4. Electrochemical characterization

Electrochemical studies of the test samples were carried out by electrochemical workstation (PGSTAT model 302 N, Metrohm Autolab B.V, Netherlands) controlled by personal computer with NOVA 2.0 software. Three electrode electrochemical glass cell was used, comprising of saturated calomel electrode (SCE) and a platinum foil as reference and counter electrodes respectively and the test sample as working electrode with exposed surface area of 1 cm^2. The corrosion studies were performed in Hanks' solution, which consisting of 0.185 g calcium chloride, 0.4 g potassium chloride, 0.06 g potassium dihydrogen phosphate, 0.1 g magnesium chloride, 0.1 g magnesium sulphate, 8 g sodium chloride, 0.35 g sodium carbonate, 0.48 g disodium hydrogen phosphate and 1 g D-glucose in 1 L of double distilled water. The pH of the solution was maintained at 7.4 [24]. The test sample was immersed in Hanks' solution for 1 h to get the stable open circuit potential (OCP). The electrochemical impedance spectroscopic (EIS) studies were carried out in the frequency range from 0.01 Hz to 100 KHz with applied sinusoidal potential ±10 mV on the OCP. The experimental data were obtained in the form of Nyquist and Bode plots. The impedance data were fitted using ZSimpwin software (Princeton Applied Research, USA) to find the perfect fitting equivalent circuit. The potentiodynamic polarization studies were conducted in the potential range from −1 to 1 V and the potentials were recorded with respect to SCE with the scan rate of 1 mV s^{-1}. The polarization plot is a plot of potential vs. log (i). The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were obtained from this plot. The corrosion current was calculated using Stern–Geary equation [25].

$$R_p = \frac{\beta a \times \beta c}{2.3 i_{corr}(\beta a + \beta c)} \quad (1)$$

where βa and βc were slops of anodic and cathodic parts of the polarization plots. R_p is polarization resistance.

2.5. In-vitro studies

The *in-vitro* bioactivity of the substrate, TNTA and PANI-TNTA were studied by immersing the samples at 37 ± 1 °C in freshly pre-

Table 1
Chemical composition of commercially pure titanium (Cp-Ti).

Elements	C	Fe	H	N	O	Ti
Weight (%)	0.08	0.30	0.015	0.03	0.25	Balance