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Stacked Bioglass/TiO_2 nanocoatings on titanium substrate for enhanced osseointegration and its electrochemical corrosion studies

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ABSTRACT

We demonstrate an approach for Bioglass/TiO_2 nanocomposites coatings onto the TiO_2 nano-surfaces formed by etching of CP-Ti. The coated surface is further covered with Bioglass fibres to enhance the rate of apatite formation. Different concentrations of Bioglass/TiO_2 composites are prepared by changing the TiO_2 concentration. The coating is performed by electrophoretic deposition technique, and it shows less concentration of TiO_2 gives higher adhesion to the substrates. The *in vitro* electrochemical corrosion and immersion studies confirm that the lower concentrations of TiO_2 containing Bioglass/TiO_2 composites coated sample possesses higher corrosion resistance and bio-mineralization that is highly suitable for bone osseointegration applications.

1. Introduction

Titanium and its alloys have wide applications as artificial implants in the field of dentistry and orthopaedic applications [1,2]. Since 1970s the application of Commercially pure Ti (CP-Ti) and its alloys have become more widespread as they possess high strength, low modulus, lower density, and a good combination of mechanical and outstanding corrosion resistance [2,3]. The inability of these implant surface to integrate with adjacent bone and tissues, results in implant loosening, which subsequently leads to implant failure and causes revision surgery is required [4,5]. The major reasons for revision surgery are loosening, infection and dislocation [6]. In most of the cases the revision surgery are not successful as primary surgery, which leads to various health complication. To overcome these issues, recently a bone mimetic and biocompatible coating are being carried out to enhance osseointegration of the implant [7].

Bioactive materials including hydroxyapatite (HA) [$Ca_3(PO_4)_3OH$] have been preferred as coating material on the implant surface due to their chemical, structural and biological similarity with human bone and also due to their enhanced osseointegration [8]. However, biodegradation of HA in the body is a serious limitation. Biodegradation is a highly undesirable feature for tissue engineering and also for any implant applications [9]. Bioactive glasses and related bioactive composite materials represent promising scaffolding materials, which are proven to be the best alternatives to HA coatings [9]. Also, nano bioactive glasses are expected to enhance the performance of the materials compared to their micro sized material available in the market [10]. A common characteristic of bioactive glasses is the time-dependent kinetic modification of the surface that occurs upon implantation. During *in vivo*, the surface forms a biologically active hydroxycarbonate apatite (HCA) layer that facilitates the bonding interface with the tissues. The HCA phase that forms on bioactive implants have equivalent chemical and structural nature similar to the mineral phase in bone [11]. In the present study Bioglass 45S5 system is chosen to improve the osseointegration of the implant material, as this material possesses both osteoconductivity and osteoinductivity properties [12–14]. Even though Bioglass 45S5 has superior biocompatible properties it has poor mechanical properties and hence it could not be used for high stress applications like hip and knee joint prostheses. To overcome such drawbacks of Bioglass, bioceramics/metal oxide or bioceramics/metal combinations are preferred [15,16]. Such composites are expected to have improved mechanical and chemical properties compared to pure bioceramics. Titanium dioxide (TiO_2) is one of the bioactive metal oxides constituents which helps to enhance the mechanical and chemical property of the HA [17]. When both TiO_2 and Bioglass are present in the nano level, it gives an added advantage to enhance the material properties. Nanostructured materials with particle size/grain size

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less than 100 nm can significantly improve the bioactivity of the implant and enhance the osteoblasts adhesion. This is because of the collagen matrix, which is the building block of the bone in the nano regime [18].

Electrophoretic Deposition (EPD) coating is an effective method to fabricate ceramic coatings and also one of the attractive techniques for nanostructural depositions from colloidal solutions because of its high homogeneity. The greatest advantages for EPD are less process time, perfect coating, inexpensive and also the possibility to obtain complex shapes [19]. Usually a trial and error approach is done elsewhere for obtaining the coating, but it is very tedious and less repeatability [16]. In our present work, we focused on "Design of Experiments (DOE)" for obtaining the optimization conditions for Bioglass/TiO_2 nanocomposites coatings obtained using the EPD technique [20]. In order to enhance the adhesion and biocompatibility of the coating, pre-deposition surface treatment is carried out. This treatment compresses the TiO_2 formation on the surface of CP-Ti by HF etching, followed by Bioglass/TiO_2 coating and thereafter over coating of the Bioglass fibres. The TiO_2 surface formed over CP-Ti enhances the surface roughness and improves bonding with TiO_2/Bioglass coatings. The Bioglass fibres coated on the composite coatings improve the rate of formation of HCA and bone bonding nature of the coating.

2. Experimental techniques

2.1. Synthesis of Bioglass, TiO_2 and composites

Calcium nitrate tetrahydrate, sodium hydroxide, tetra ethyl ortho silicate (TEOS), orthophosphoric acid were procured from Alfa Aesar, India and used as precursors for the synthesis of Bioglass 45S5. The Bioglass having weight percent composition (45% SiO_2–24.5% Na_2O–24.5% CaO–6% P_2O_5) was prepared by conventional sol–gel process. The procedure involves mixing of tetra ethyl ortho silicate (TEOS) and nitric acid (HNO_3), followed by ethanol for hydrolysis and stirred for 30 min to obtain the gel. The ratio of TEOS:HNO_3:ethanol:water is 1:0.5:0.25:4. After complete gelation, the following reagents were added in the interval of 30 min in the order of sodium hydroxide, calcium nitrate and orthophosphoric acid. The solution was stirred for 4 h to get a homogenous gel. The sol was aged at a temperature of 70 °C for 24 h, and then sintered at 600 °C for 2 h.

TiO_2 nanoparticles were synthesized by the sol–gel technique through an alkoxide reaction between titanium tetra isopropoxide (TTIP) and glacial acetic acid in the presence of double distilled water as a solvent. TTIP of 4.6 mL was added to 9.8 mL of glacial acetic acid under vigorous stirring and thereafter 100 mL of water was added drop wise to get a transparent solution. The solution is then continuous stirred for 24 h to form a gel, which is then dried at 60 °C to get the nanoparticles of TiO_2.

Bioglass/TiO_2 composites were prepared by mixing Bioglass and TiO_2 in the ratio of 1:0.25 (BGT1), 1:0.5 (BGT2) and 1:0.75 (BGT3). In order to make the surface more bioactive in the presence of Bioglass, 1:1 ratio was not done in the present work. The weight ratio of the powders were taken in grams and added to 20 mL of water and stirred for 2 h to obtain a homogeneous mixture. The samples were filtered and then dried in hot air oven at 100 °C to obtain dry powder of Bioglass/TiO_2 composites.

2.2. Coating of composites and fibres on CP-Ti substrate

CP-Ti foils of purity 99.9% and thickness of about 0.25 mm Alfa Aesar, India and used as substrate material. This foil was cut into small pieces of dimensions 1 cm × 1 cm and were polished using silicon carbide grits ranging from 600, 800, 1500 to 2000. These samples were cleaned by ultrasonication with double distilled water and acetone. In order to enhance the surface roughness of the substrate, the sample surface were etched in 5% HF placed in a glass petriplate. The etching reaction was allowed to take place for about 10 min. The etched samples were further washed in double distilled water and thereafter dried in ambient temperature. For EPD coating technique, a DC power supply (Keithley 2200-72-1 programmable power supply, USA) is used with the processing condition at 90 V and isopropyl alcohol as electrolyte medium with the composite particle loading of 0.2 gm/10 mL. Polyvinyl alcohol (PVA) was used as binder with the loading weight of 0.05 gm/10 mL [20].

For Bioglass fibres, the precursors of Bioglass were taken in mol% and the solvent contains a mixture of ethanol and water in the ratio of 1:1. 1 M HCl was added as a catalyst. This was considered as a stock solution, from which 5 mL of BG was mixed with 2.5 mL of water and 2.5 mL of ethanol. The solution is loaded into 2.5 mL surgical syringe for electrospinning process. The drum collector setup was used and an aluminium foil is placed onto the drum collector. The coated samples were fixed on the surface of the aluminium foil, facing upwards to receive the fibres. The distance between the syringe and the collector surface was 12 cm. The solution flow rate was optimized as 0.3 mL/h with the DC power supply of 15 kV. In order to achieve densification in the coating, the sintering process was carried out at the heating rate of 5 °C/min up to 600 °C in vacuum condition and maintained at 600 °C for 2 h.

2.3. Characterization techniques

The phase analysis of the sintered samples were investigated by X-ray diffractometer (PANalytic, The Netherlands) using monochromatic Cu Kα (λ = 1.5405 Å) with the 2θ range from 10° to 80° at scanning speed of 0.5°/min. The sample composition was characterized using X-ray photoelectron spectroscopy (XPS) (Omicron Nanotechnology, Germany). The phase analysis of the nanocomposites was analyzed using FTIR analyser using KBr as a standard reference and the spectra were collected in the wave number range 4000–400 cm^{-1}. The surface morphology and elemental analysis were examined by Field emission scanning electron microscopy (FESEM; Hitachi SU6600, Singapore). The samples were coated with gold using ion sputtering techniques at atmospheric pressure of 10 kg/m^3 for 7 s in order to amplify the secondary electron signal.

A three-electrode cell arrangement was used for the electrochemical measurement with a saturated calomel electrode (SCE) as a reference electrode and platinum wire as an auxiliary electrode (ASTM G5-94). Hank's simulating human body fluid (SBF) (ASTM F2129-08) was used as an electrolyte and was prepared using analytical grade chemicals and double distilled water. The pH of the solution was precisely maintained at 7.4. Freshly prepared solution was used for all experiments. Nitrogen gas, with a flow rate of 150 mL/min, was purged through the electrolyte to attain a deaerated atmosphere, and the temperature was maintained at 37 °C (human body temperature). The electrochemical polarization were measured using a potentiostat (Gill AC, ACM Instruments), controlled by the sequencer software. The potentiodynamic polarization was determined in a range of −750 mV to 2500 mV (*vs.* SCE) at a scan rate of 0.166 mV/s. The impedance spectra were measured followsed by polarization experiment with a frequency sweep from 10^4 Hz to 10^{-1} kHz on a logarithmic increment. 100 data points were recorded for each experiment. The best fit circuit was identified based on the subsequent analysis of Nyquist, Bode phase and Bode magnitude plots. Z view (V3.3) software was used for further assistance in circuit fitting.

In order to understand the biocompatibility and biomineralization of the coated substrates, it was immersed in Hank's SBF