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Preparation and Electrophoretic deposition of Zirconium dioxide nano-composite on Ti-6Al-4V for biomedical applications

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Abstract: The advancement of nano-science and nano-technology produces intriguing changes for the existing materials applications. In biomaterial science, especially inorganic materials such as silica, zinc oxide, zirconium dioxide, and titanium dioxide have been prepared by various methods including sol-gel synthesis. In sol-gel synthesis, nano-particles are produced and have been used for various applications and applied in surface modification of implantable biomaterials like metals. Ceramic materials are having more biocompatibility, bio-inert, less corrosion resistant properties when implanted into the physiological system. Various coating methods have been proposed of which, Electrophoretic technique (EPD) is an old and convenient method and can be applied in complex shaped structures. In this paper, the sol-gel prepared zirconium dioxide, zinc oxide nano-particles were mixed to attain better hard coatings with antibacterial properties to avoid bacterial contamination during implantation and removal surgery with less interfacial bonding between substrate and tissue when removable implants employed such as bone plates and bone screws. The prepared materials and its composite were characterized by FT-IR, XRD. The corrosion resistant property of the EPD coated Ti-6Al-4V was studied by electrochemical techniques such as polarization (Tafel) and EIS analysis. The results of study was clearly demonstrates a uniform homogeneous hard coating with increased corrosion resistant values comparing to the blank Ti-6Al-4V.
Keywords: Ti–6Al–4V implant, Sol-gel, Electrophoretic coating, Impedance, Tafel.

Introduction

Bio-medical devices and its components such as orthopedic, dental, cardiac, senses, organs, bone plates and screws are used as implantable materials for aiding, healing or correcting abnormalities of the systems of affected one due to its unique mechanical and biological properties. An implantable device is generally derived from metallic, ceramic and polymeric biomaterials and has been used for structural and functional characteristics depend on its nature of applications. Metallic biomaterials such as stainless steel, Co-Cr based alloys, titanium and its alloys have recently been found widespread use in orthopedic surgery and dental applications in that Ti-6Al-4V has typically been used as bone plates and screws of easily removable implants after treatment based on specific requirement[1].

Metals are very sensitive to its surrounding environments where it has been used due to its inherent properties. However titanium and its alloys are preferably selected and used in orthopedics and dental applications due to its intriguing properties such as biocompatibility, low density and high tensile strength, corrosion resistant and bio-inert properties. Implantable materials always must be a bioactive, highly corrosion resistant with low wear resistant and required toughness to match with bone. The metallic materials high toughness means of less brittleness and ceramic materials corrosion resistant, wear and oxidation resistant nature with excellent biocompatibility, bioactive, bio-inert properties which has been combined effectively with metals to produce better implantable devices based on the nature of requirement of its usage of short period or long period of time[2,3]. When bone plates, screws and more others of short duration implants has been used, possibly its surface should be bio-inert with more corrosion resistant to avoid damage of cured bone from re-fracturing during removal surgery[4]. The uniqueness of the sol-gel method and nano-zirconium dioxide's interesting chemical and biological activities such as high biocompatibility, corrosion resistant, wear resistant, high toughness with increased strength, bio-inert has been utilized to make composite[5]. The zinc oxide's characteristic antibacterial, low thermal expansion coefficient with better lubricity properties has been utilized for better, crack free, well adhered, hard deposition of nano-ZrO_2 on Ti-6Al-4V with avoidance of bacterial contamination of implantable materials during the time of implantation and removal surgery of temporary implants such as screws, plates etc.[6,7].

Surface modification techniques such as sol-gel, chemical vapour deposition, micro-arc oxidation, plasma spraying, dip coating and biochemical modification were developed and have been in a crucial concern of the implants improved surface for its biocompatibility, bioactive and bio-inert properties. Moreover the above described methods of each have its own merits and demerits. Electrophoretic deposition method has been selected due to its typical uniqueness for producing few tens of microns to millimeter thickness of layer comparing to other systems with low cost, short time interval and simple set up in aqueous and non-aqueous media with controlled sintering temperature in the oven, furnace for dehydration and densification of coating. In addition, the coating has been produced by fine particles and capacity to coat complex geometries and patterns of substrate. The successful application of EPD depends upon ceramic material's electrical charge and dispersion capacity in liquid medium[8].

In this study, pure characteristic nano-ZrO_2, nano-ZnO has been synthesized by sol-gel method. The prepared nano-particles have been used in the concentration of 70% of nano-ZrO_2, 30% nano-ZnO respectively to produce composite. This composite has been used for studying electrophoretic deposition (EPD) on Ti-6Al-4V, as well as characterization by FT-IR, Powder XRD. In addition this, an *In-vitro* electrochemical studies such as OCP vs.time, potentiodynamic polarization (Tafel) and EIS analyses were used to understand the nature of corrosion resistant of the prepared composite coating.

Experimental

Preparation of nano-ZrO_2 powder

Pure nano-sized zirconium dioxide was prepared by using zirconium acetyl acetonate as precursor. This precursor material was dissolved in acetone and double distilled with continuous stirring. The prepared solution was transferred to round bottom flask fitted with reflux condenser and pH was adjusted with 1M nitric acid solution to attain the required pH. After that the solution was aged in oil bath at 90^{o}C for 3hrs with stirring and evaporated in water bath at 70^{o}C for 3hrs to get solid precipitate. The obtained precipitate was sintered at 900^{0}C for 2hrs and characterized for its phase formation and its functional groups.

Preparation of nano-ZnO powder

Pure nano-sized zinc Oxide particles were prepared by precise, simple sol-gel process. In that double distilled water, triethanolamine and ethanol were mixed initially before the process to be started in order to get homogeneous mixture. This mixture was transferred to another vessel having 0.5M zinc nitrate hexahydrate with continuous stirring to get clear solution. After transferring, ammonium hydroxide solution was added slowly to maintain the solution pH and allowed to stand for 30minwith continuous stirring for the formation of white precipitate. The precipitate formed was then washed 3-4 times with double distilled water to remove impurities, and then filtered by using Whatmann filter paper. The obtained residue was dried in an oven at a temperature of about 100^{0}C for 24hrs and sintered at 900^{0}C for 2hrs and characterized for phase formation and its functional groups.

Electrophoretic Deposition

The substrate Ti-6Al-4V were polished using 220,400, 600,800,1000 and 1200 grits silicon carbide emery papers, to get a fine polishing followed by the use of 0.3µ diamond paste for mirror finish then thoroughly washed with distilled water, followed by ultrasonically cleaned in acetone for 20 min and dried in over for 10 min and then stored properly in desiccators.

Suspension for coating was prepared by weighing 1.5 gram of composite having 70% nano-ZrO_2 with 30% nano-ZnO into 40 ml Isopropyl alcohol with stirring and allowed to standing overnight. Then 100mg of Povidone K-30 and 10mg of iodine added as additives for better deposition and surface charge for composite. Titanium substrate (anode) and stainless steel (cathode) electrode were fixed 1 cm apart and were used as working and counter electrodes respectively. The coatings were deposited on the implant surface at constant voltage 80V with various time period of 1minto 10min for optimization of deposition. The samples were dried at room temperature to prevent them from cracking and then sintered at 300°C for 30min for the purpose densification and removal of additives. The deposited film was characterized for electrochemical corrosion resistant properties.

Characterization

FT-IR spectra analysis

The obvious functional groups of prepared ofnano-ZrO_2 and nano-ZnO were analyzed by Fourier transform infra red spectroscopy (FT-IR) in the range of 400–4000 cm^{-1} using a SHIMADZU model 8300 spectrophotometer (Shimadzu-Japan) by using KBr pellet technique.

XRD analysis

The XRD patterns were recorded to determine the microstructural characterization in terms of the phases formed by X-ray diffractometer (D8 model, BRUKER, Germany) with a step size of 0.02° and a scan rate of 1°/min with Cu Kα radiation (□= 1.54056Å).

Electrochemical Characterization

The electrochemical characterization by Potentiodynamic polarization studies were performed by using Potentiostat Biologic VMP3-based instruments SP-150-France with EC-Lab software installation interfaced with computer. The experimental procedure consists of a conventional three-electrode electrochemical glass cell arrangement with the cell volume of 100 ml. The study was carried out by using Ringer's solution with the pH of 7.4 at room temperature. Ti-6Al-4V alloy with surface area of 1 cm^2, Pt and Ag/AgCl with KCl saturated electrodes are employed as working, auxiliary and reference electrodes respectively. The simulated body fluid Ringer's solution was prepared by using 8.6 g/L of NaCl, 0.60 g/L of KCl, and 0.66g/L of $CaCl_2.2H_2O$ respectively with double distilled water.

Open circuit potential (OCP) study

To understand the electrochemical corrosion behavior of the prepared coating and to attain equilibrium with environment open circuit potential study was carried out until the OCP values are stabilized.

Tafel Analysis

From the polarization curve, the corrosion potential (E_{corr}), the corrosion current density (I_{corr}), values of uncoated and composite coated Ti-6Al-4V was determined by Tafel extrapolation analyses

Impedance Analysis

The measurements of the EIS were performed at OCP using a frequency scan from 10, 00, 00 Hz to 0.01 Hz. The Nyquist plots were analyzed by EC-lab software analyzer to determine the parameters such as charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}). By using equivalent circuit, the measured impedance data's are numerically fitted with variety of electrical circuits and studied

Results and Discussion

Characterization of powders

FT-IR spectra analysis

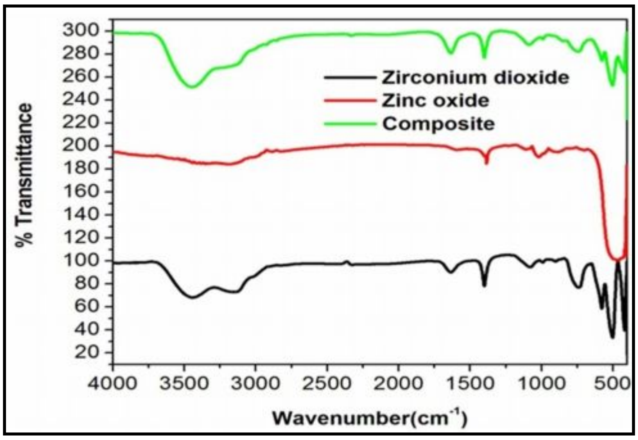

Fig. 1. FT-IR spectrums for sintered nano-ZrO_2, nano- ZnO and its separately mixed composite powder

The purity and evolution of functional groups with characteristic band positions, intensity of peak was clearly studied by FT-IR spectral analysis. Fig.1 shows the spectra of sintered nano-ZrO_2, nano-ZnO and its separately mixed composite powder. The study was clearly exhibiting the typical nature of the prepared nano-particles and its powder composite. In zirconium dioxide after sintering at 900°C for 2 hrs, the band at 3444 cm^{-1},may be due to the stretching vibration of the OH^- group and at 1631 cm^{-1} confirms the absorption peak of adsorbed water, hydroxides respectively; the peak at 1400 cm^{-1} corresponds to bidental ligand of CH_3COO^-,and Zr-O-Zr absorption peaks was seen below at 740cm^{-1}. The distinctive peaks around 437$cm^{-1}$and 501cm^{-1}confirms the Zr-O bond in tetragonal Zirconia; 659 cm^{-1} are corresponds to Zr-O stretching. The narrow peaks at 578 and 744 cm^{-1}clearly shows the formation of pure m-ZrO_2 and the peak at 2366 cm^{-1} confirms the presence of mixture of tetragonal and monoclinic zirconium phases and the results are in evident with previous literature study[9, 10, 11, 12].

The FT-IR spectrum of prepared nano-ZnO shows its typical broadpeak at 3300-3600 cm^{-1} which was attributed to OH^- stretching vibrations of adsorbed water. The peaks at 462 cm^{-1}confirms the stretching mode of Zn-O vibration. In addition the increased intensity of this peak compared with the raw ZnO powder (not shown here) confirms the presence of ZnO crystals. The bands at 2946 and 2858 cm^{-1}, 871 cm^{-1} are assigned to the CH_2 groups stretching vibrations and the bands at 1384cm^{-1}, 1066cm^{-1}, 1018cm^{-1} are asymmetric stretching mode of vibration arising from C-N bonds. In composite, all the characteristic peaks of zirconia and zinc oxide with increased intensity are clearly observed.

XRD analysis

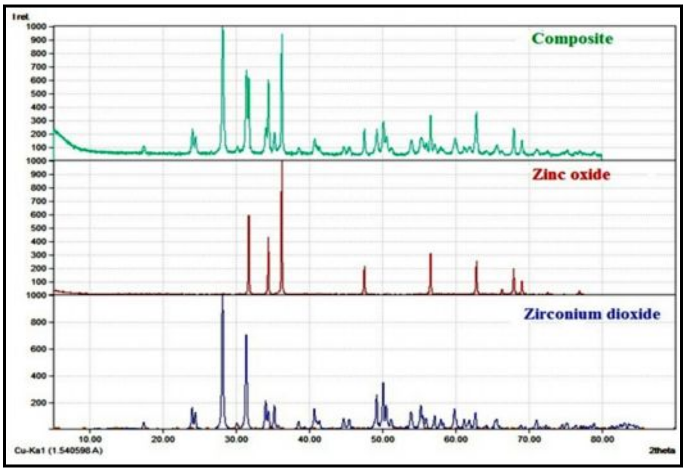

Fig. 2. XRD patterns of sintered nano-ZrO_2, nano- ZnO and its separately mixed composite powder

The structural and phase purity of the sintered nano-ZrO_2, nano-ZnO and its separately mixed composite powder was characterized by XRD analysis and shown in Fig.2. The XRD pattern of sintered ZrO_2 shows characteristic diffraction peaks at 2θ values around 17.4, 28, and 31 which has been specified as t (100), m (111), m (111), respectively as tetragonal, monoclinic phase zirconia[13,14]. In the XRD pattern of ZnO shows a pure wurtzite zinc oxide phase with main characteristic diffraction lines such as (100), (002), (101) with 2θ values around 31,34 and 36 respectively. And, in composite the intensity of peaks was typically in a crucial concern. The increased value for (002) of zinc oxide peak in composite indicated the increase in its crystalline nature. By mixing of both nano-particles does not produce any changes in grain boundaries and crystalline disorder. The crystalline boundaries and crystalline nature has pronounced effect in suspension stability and formation of compact film. The diffraction peaks at 2 θ values 17.4, 28, 31 and 34 confirms the presence of zirconium dioxide and zinc oxide in the prepared composite. [15, 16].

Characterization of Coatings

Open circuit potential (OCP) study

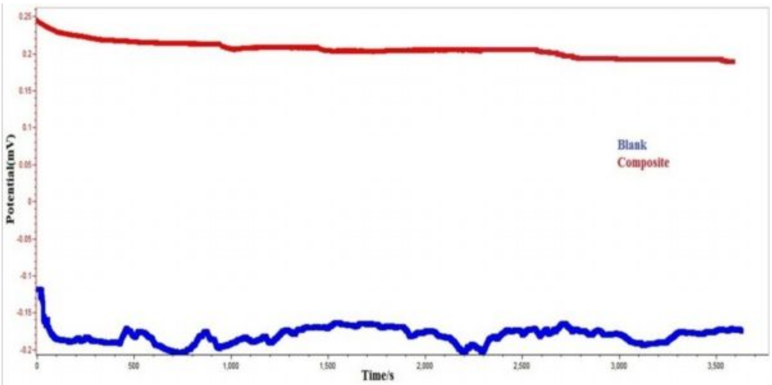

Fig. 3. OCP-time variation measurements for the optimized composite coatings with blank Ti-6Al-4V

The open circuit potential (OCP)-time measurements of the optimized composite coatings on Ti-6Al-4V with blank are shown in Fig.3. The measurements of potential with respect of time for the optimized coatings are used to understand the electrochemical corrosion behavior, stability of the coatings. In addition to that the immersion period maintains equilibrium with environment for stable potential. For the blank Ti-6Al-4V typically the slope of the curve is not gentle and the potential values gradually decreased from higher negative values to lower negative values after stabilization with environment indicates more interaction of the simulated body fluids with substrate and less corrosion resistant nature. The optimized composite coating on Ti-6Al-4V of 80V-7min clearly indicates, almost a high value of positive potential with nobler direction and gentle curve due to the insulation by chemically and thermodynamically stable, less porous thicker better adherent composite coating. Hence the composite coating produces active behavior on the substrate and stabilization of corrosion potential preferably against corrosion with better values.

Potentiodynamic polarization (Tafel analysis)

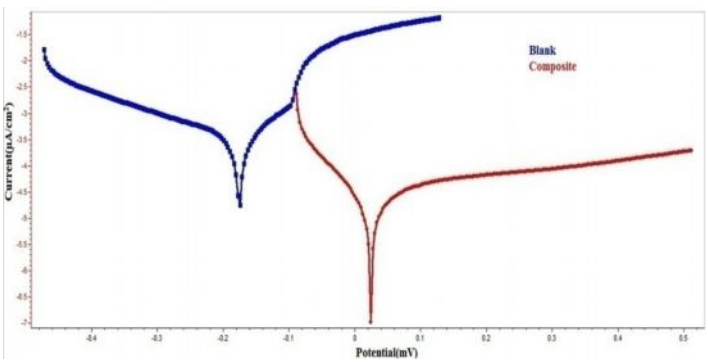

Fig. 4. Potentiodynamic polarization curves of the optimized composite coatings with blank Ti-6Al-4V

The Potentiodynamic polarization study of optimized composite coatings with blank Ti-6Al-4V are shown in Fig.4. This electrochemical technique used as a screening technique for understanding the overall corrosion mechanism. By Tafel extrapolating the polarization curve with anodic and cathodic branches to corrosion potential, the Tafel values are got and are tabulated in table1. The data clearly reveals the nature of study with respect to blank. The corrosion potential (E_{corr}) of the coated samples has nobler values comparing to blank Ti-6Al-4V and the corrosion current density (I_{corr}) of the coated samples shows a very drastic decrease in values compared to blank. This study has been found more consistent with OCP study. According to polarization curve results, the optimized 80V-7min has highest corrosion potential (E_{corr}) of 24.145mV with lowest corrosion current density (I_{corr}) of 0.038mA/cm^2 comparing blank corrosion potential (E_{corr}) of -175.477mV with corrosion current density (I_{corr}) 0.340mA/cm^2 respectively. The study further substantiated by its inhibition efficiency value of optimized composite coating has 88.82% protection capacity against corrosion. The probable hypothesis for better values of the coating is due to the synergistic activity of both zirconium dioxide and zinc oxide composite with well compact strongly adhered less porous coating.

Table 1: Tafel values of blank and optimized composite coating on Ti-6Al-4V

S. No.	Coating	E_{corr} (mV)	I_{corr}(mA/cm^2)	Corrosion Rate(mpy)	IE (%)
1	Blank	-175.477	0.340	0.117635	-
2	80V-7 min	24.145	0.038	0.013147	88.82

Electrochemical Impedance Spectroscopy and Nyquist analysis

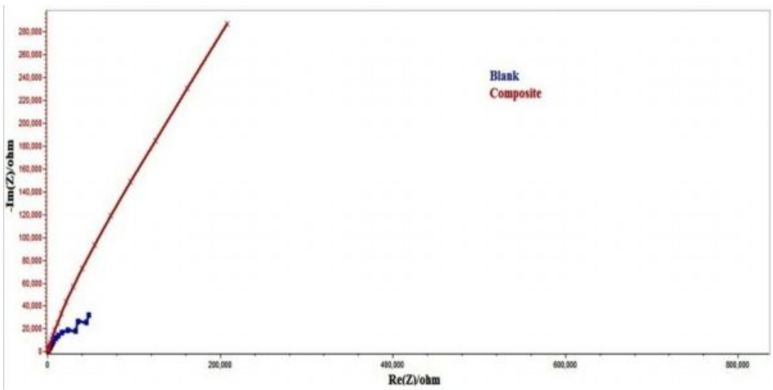

Fig. 5. Nyquist plot for EIS study for the optimized composite coating with blank Ti-6Al-4V

In order to further justification of corrosion resistance of the optimized composite coating on Ti-6Al-4V the electrochemical techniques of EIS was used. This electrochemical technique was obviously a non-destructive in nature and used to understand the protection efficiency of coating in-terms of its impedance values. Fig.5 shows Nyquist plot of EIS data for blank with optimized coating on Ti-6Al-4V samples in the simulated physiological medium of Ringer's solution. The Nyquist plot of the coated samples typically changed with increased in radius of curvature and better values than the blank confirms the coated samples having intriguing capacity to increase corrosion resistance of the Ti-6Al-4V. The simulated values of the study for coating efficiency with proper equivalent circuits are tabulated in table 2. From the values the effectiveness of coating clearly shows that the optimized coating with 80V-7min shows better charge transfer resistance and capacitance values of (R_2) 2.182e^6 Ohms and (Q_2) 16.15e^{-6} Farads respectively comparing to the charge transfer resistance and double layer capacitance values blank (R_2) 60865 Ohms and (Q_2) 57.38e^{-6} Farads respectively indicates a clear trend of resistance of barrier layer by the formation of high magnitude of barrier film-solution interface due to the better surface protected composite coating layer. Additional, the solution resistance of coated sample has increased values indicates the non availability of corroded ions for increasing conductivity of solution. Hence the composite coating should be used for better corrosion resistant of Ti-6Al-4V effectively for biomedical applications.

Table 2: EIS spectra of fitted values of blank and optimized composite coating on Ti-6Al-4V

S. No.	Sample	R_1(Ohms)	R_2 (Ohms)	Q_2 (Farads)
1	Blank	13.58	60865	$57.38e^{-6}$
2	80V- 7 min	20.3	$2.182e^{6}$	$16.15e^{-6}$

Conclusion

1. The nano-ZrO_2 and nano-ZnO particles were successfully synthesized by using sol-gel method and formed functional groups and phases was confirmed by FT-IR and XRD analysis.

2. The composite suspension having 70% of nano-ZrO_2 and 30% of ZnO was prepared having isopropyl alcohol, povidoneK-30 and iodine as additives for homogeneous suspension and successfully deposited on Ti-6Al-4V by EPD method.

3. According to electrochemical corrosion analysis the high OCP values of coated samples with nobler and stable values comparing to blank indicates the coating on substrate capable against corrosion environment.

4. The Tafel polarization and EIS analysis study of optimized composite coating exhibited better passive behavior compared to blank and both analyses were consistent with study. The Tafel analysis clearly shows a characteristic shift of whole polarization curve with lower current density and the high capacitance loop diameter values of the Nyquist plot from EIS study confirms better corrosion resistant of the composite coating

Hence from this study, synthesis of pure nano-ZrO_2, nano-ZnO and its composite are easily possible with efficient surface modification of a Ti-6Al-4V by electrophoretic deposition (EPD). The composite coating has been used in removable implants with better corrosion resistant, possible bio-inert and as well as avoidance of microbial contamination during implantation and revision surgery to remove an implant of temporary usage.The corrosion resistance parameters such as OCP, Tafel and impedance values of composite coating have better values than the blank Ti-6Al-4V values; the composite coating should be a valuable one for further analysis of microstructural, mechanical and *in-vitro* biological study for regular and custom applications.

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