Corrosion Science 73 (2013) 321–330

Contents lists available at SciVerse ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Development of carbon nanotubes reinforced hydroxyapatite composite coatings on titanium by electrodeposition method

D. Gopi [a,b,*], E. Shinyjoy [a,b], M. Sekar [a,c], M. Surendiran [a], L. Kavitha [b,c,d], T.S. Sampath Kumar [e]

[a] Department of Chemistry, Periyar University, Salem 636 011, Tamil Nadu, India
[b] Centre for Nanoscience and Nanotechnology, Periyar University, Salem 636 011, Tamil Nadu, India
[c] Department of Physics, Periyar University, Salem 636 011, Tamil Nadu, India
[d] The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy
[e] Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Chennai 600 036, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 27 November 2012
Accepted 7 April 2013
Available online 18 April 2013

Keywords:
A. Ceramic
A. Titanium
B. Potentiostatic
B. Polarisation

ABSTRACT

Carbon nanotubes (CNTs) are outstanding reinforcement material for imparting strength and toughness to brittle hydroxyapatite (HAP). This work reports the electrodeposition of CNTs reinforced HAP on titanium substrate at −1.4 V vs. SCE during 30 min with the functionalised CNTs concentration ranging from 0 to 2 wt.%. Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (EDX), high resolution transmission electron microscopy (HRTEM), mechanical and biological studies were used to characterise the coatings. Also, the corrosion resistance of the coatings was evaluated by electrochemical techniques in simulated body fluid (SBF) solution.

1. Introduction

The foremost requirement for any material to be placed in the human body is that it should exhibit good biocompatibility and corrosion resistance in physiological body fluid [1]. The corrosion property of the implant is significant as it can adversely affect the mechanical and biological property [2]. Hence, the metal that is to be used as implant must possess high corrosion resistance and better biocompatibility. Till today titanium is the most commonly used biometal to orthopedic prostheses due to its excellent corrosion resistance and biocompatibility [3]. In order to enhance the cell implant material interaction and to increase the longevity of material, bioactive ceramic based coating have been applied to Ti [4]. HAP is an attractive biomaterial for human hard tissue implants since it contains the similar chemical composition of the natural bones and teeth [5,6]. HAP plays an excellent role in biomedical applications owing to their excellent biocompatible, osteoconductive and bioactive properties, and its close resemblance to mineral component of bone tissue [7–13]. Though HAP can bond directly to natural bones, the brittle nature and poor strength impedes its clinical applications under load-bearing conditions. One of the most common approaches to overcome this weakness and to provide better corrosion resistance, incorporation of reinforcing materials like CNTs, TiO_2, ZrO_2 is followed [14–19].

CNTs are highly versatile materials with an enormous potential for biomedical applications. They are unique, one dimensional macromolecules, whose outstanding properties have sparked an abundance of research since their discovery in 1991 by Iijima [20]. They have excellent mechanical, good corrosion resistance and unique structural properties, with high aspect ratio, good biocompatibility and less toxicity that categorised them as outstanding reinforcement materials in the nanocomposites [21–24]. They also possess large surface area, low density, and high tensile strength. All these properties make CNTs a suitable material for variety of applications like high performance transistors, switches in nanoelectronic devices and incorporation in nanocomposites based on metals, ceramics, and polymers [25]. They may be used in orthopedics as mechanical reinforcement, to tailor surface properties and thus provide a nanostructured surface that promotes bone cell adhesion and function. The advantage of CNTs as a reinforcing material is that, they provide increased toughness and mechanical properties when used in composite [26]. CNTs have recently emerged as materials with exceptional properties exceeding those of any conventional material. These exceptional physical and mechanical properties make CNTs good candidates as reinforcements in composite materials to increase both stiffness and strength. Furthermore, the dispersion and structure of the nanotubes are the dominating factors for the mechanical improvement of CNTs reinforced HAP composites. CNTs as a reinforcing material could impart mechanical integrity to the composite without

* Corresponding author at: Department of Chemistry, Periyar University, Salem 636 011, Tamil Nadu, India. Fax: +91 427 2345124.
E-mail addresses: dhanaraj_gopi@yahoo.com (D. Gopi), louiskavitha@yahoo.co.in (L. Kavitha).

0010-938X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.corsci.2013.04.021

diminishing the bioactivity of HAP [23,27]. Addition of CNTs can strengthen the composite coatings and the CNTs reinforced composite coatings might have excellent properties including high tensile strength and excellent bioactivity for the application in orthopedic implants. It is well known fact that, the nonfunctional CNTs have a systematic tendency to agglomerate and favors the formation of bundles. Further this aggregation tendency of CNTs is physically due to the Van der Waals forces between them and poor interaction with lack of interfacial bonding with HAP matrix due to their smooth surface [28]. Also, the non functionalised CNTs are insoluble in water and organic solvents which leads to an inhomogeneous distribution of pristine CNTs in the HAP matrix. Therefore functionalisation of CNTs is to be invoked to overcome these difficulties and to achieve a good dispersion of CNTs in HAP matrix [26]. Many functionalisation routes have been developed in recent years to solubilize CNTs and improve their biocompatibility [29]. Motivated by this we have performed the covalent functionalisation of CNTs by acid treatment [30] which resulted in an increased water solubility of CNTs in HAP matrix.

Recently many methods have been developed for the coating of the CNTs–HAP composite on the metal substrate. Balani et al. [31] have reported the CNTs reinforced HAP coatings on Ti–6Al–4V alloy by plasma sprayed technique and compared the wear resistance of HAP and the CNTs–HAP composite coatings in SBF solution. But the long term stability of the CNTs–HAP composite coating cannot be achieved by this method because of its high dissolution rate and poor fracture toughness. Aerosol deposition of the CNTs–HAP composite coatings on titanium plate was evaluated by Hahn et al. [32]. From their study, it was observed that nanoindentation tests improved the mechanical properties of CNTs reinforced HAP composite coating. Pei et al. [33] reported the functionally graded CNTs–HAP composite coating by laser cladding method. These methods suffer from complex and time consuming procedures. Although many methods reported for the CNTs–HAP composites coating, invariably each method suffers from one to another. Gopi et al., has reported the coating of HAP on borate passivated 316L SS by dip coating and electrodeposition method and thereby reduced the release of metal ions [34,35]. The authors have also studied the combination of pulsed electrodeposition and addition of H_2O_2 into the electrolyte that promisingly improve the physicochemical properties of HAP [36]. In the recent years, electrodeposition has evolved as a successful technique for the HAP coatings over implantable materials [37,38].

In the present work we have achieved CNTs reinforced HAP composite coatings on titanium substrate using electrodeposition method with the aim of improving the mechanical, corrosion resistive and biological properties of HAP coatings. The mechanical properties of the CNTs–HAP composite coatings were measured by mean of nanoindentation technique as a function of CNTs concentrations (0–2 wt.%). Moreover, the effect of CNTs concentrations on the crystallinity, morphology, adhesion strength, hardness, elastic modulus and in vitro biological affinity of the CNTs–HAP composite coating on titanium for orthopedic applications was also analysed. The corrosion protection performance of the composite coatings on titanium in SBF solution was studied by different electrochemical techniques.

2. Materials and methods

2.1. Materials

Commercially available calcium nitrate ($Ca(NO_3)_2{\cdot}4H_2O$), dipotassium hydrogen phosphate (K_2HPO_4) and single-walled CNTs with a diameter of 1.2–1.5 nm, purchased from Aldrich chemicals (Aldrich, India) were used for fabricating CNTs reinforced HAP composite coatings by electrodeposition method. All the chemicals were of analytical grade and used as received and deionised water was used throughout the experiment.

2.2. Functionalisation of CNTs

The surface treatment of CNTs with acid, oxidising agents and surfactants produces carboxylic, hydroxyl and ketonic groups which alter the properties of CNTs, such as improved dispersion stability and better interactions with HAP matrix [39,40]. The functionalisation of CNTs was carried out in a round-bottomed flask equipped with a reflux condenser and a thermometer. Before oxidation process, 4 g of raw CNTs was taken in the mixture of concentrated HNO_3 and H_2SO_4 (200 ml) with the ratio of 1:3 at room temperature (28 ± 1 °C) and ultrasonicated during 60 min. Then, the mixture was poured into the round-bottomed flask and heated to 110 °C using an oil bath and kept refluxing during 1 h [41] and cooled to room temperature. The acid solution was filtered through a polytetrafluoroethylene membrane filter. The filtered substance was washed repeatedly with deionised water till the filtrate is neutral and finally rinsed with methanol. The final product was dried in a vacuum oven at 60 °C during 48 h.

2.3. Development of CNTs reinforced HAP composite coatings on titanium

2.3.1. Specimen preparation

The pure titanium specimens (99.99%) of the size $10 \times 10 \times 3$ mm were cut and embedded in epoxy resin, leaving area of 1 cm^2 for exposure to the solution. Prior to electrodeposition, the samples were abraded with different grades of SiC emery papers from 400 to 1200 grit and washed with distilled water, degreased with acetone, then dried at room temperature.

2.3.2. Electrodeposition of HAP reinforced with CNTs on titanium

The electrolyte for deposition was prepared by mixing a solution containing 0.042 mol/L of $Ca(NO_3)_2{\cdot}4H_2O$ and 0.025 mol/L of K_2HPO_4 under constant stirring during 2 h. The different concentration (0–2 wt.%) of the functionalised CNTs were gradually added to the above solution and the pH was attuned to 4.7 using NaOH or HCl. Prior to electrodeposition, the electrolyte mixture was subjected to an intense ultrasonic treatment during 30 min to fully disperse the suspended CNTs into the electrolyte. The electrodeposition was performed in an individual cell using a three electrode configuration in which titanium served as cathode and platinum electrode acts as an anode. A saturated calomel electrode (SCE) was used as the reference electrode. The deposition was carried out in potentiostatic mode by applying a potential of −1.4 V vs. SCE during 1 h using an electrochemical system CHI 760C (CH instruments, USA). After the specimen coated with composite coating they were rinsed with deionised water and dried at 40 °C during 5 h.

2.4. Surface characterisation of the composite coatings

The Fourier transform infrared spectroscopy of the samples were recorded using Nicolet 380 FT-IR Spectrometer (Perkin Elmer, USA) over the frequency range from 4000 cm^{-1} to 400 cm^{-1} with a number of 32 scans and spectral resolution of 4 cm^{-1}. The phase composition and the crystallinity of the CNTs–HAP composite coatings were identified by XRD (Bruker D8 advance diffractometer). For the XRD experiments, Cu Kα incident radiation, a tube voltage of 40 kV and a current of 30 mA was used and the scanning angle is ranged from 20° to 60°, with a scan rate (2θ) of 0.02°. The surface morphology and elemental composition of the composite coatings were examined using SEM (JEOL JSM-6400, Japan) equipped with EDX. The microstructure of the composite coating was characterised using high resolution transmission electron microscopy