Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 5454–5463

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Influence of ionic substitution in improving the biological property of carbon nanotubes reinforced hydroxyapatite composite coating on titanium for orthopedic applications

D. Gopi[a,b,*], E. Shinyjoy[a], L. Kavitha[c]

[a]Department of Chemistry, Periyar University, Salem 636011, Tamilnadu, India
[b]Centre for Nanoscience and Nanotechnology, Periyar University, Salem 636011, Tamilnadu, India
[c]Department of Physics, School of Basic and Applied Sciences, Central University of Tamilnadu, Thiruvarur 610101, TamilNadu, India

Received 10 November 2014; received in revised form 19 December 2014; accepted 19 December 2014
Available online 31 December 2014

Abstract

The present work is aimed for the development of carbon nanotubes (CNTs) reinforced single mineral (Sr, Mg, Zn) as well as multi minerals (Sr+Mg+Zn) substituted hydroxyapatite composite (M-HAP) coatings on titanium (Ti). The effect of different mineral ions substitution and CNTs reinforcement in HAP composite coating is discussed in detail. Fourier Transform Infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (EDX), and high resolution transmission electron microscopy (HRTEM) were used to characterize the structural and morphological behavior of the composite coatings. The corrosion resistance of the composite coatings in simulated body fluid (SBF) solution was evaluated by the potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) studies. In addition, the biocompatibility of the composite coatings was evaluated by in vitro culture of human osteoblast MG63 cells on the composite coated Ti. All these results essentially suggest that CNTs/M-HAP composite coated Ti can be a potential candidate for orthopedic applications.

Keywords: B: Composites; B: Spectroscopy; D: Carbon; E: Biomedical applications

1. Introduction

Biomedical implants have received considerable interest and intensive research during last few decades as they are used as replacement material of various body parts or organs [1]. Titanium based materials are the best metallic materials for extensive biomedical applications due to their corrosion resistance and biocompatible properties [2]. Despite their successful use, there is still scope for the improvement of few properties like faster bone healing, bone implant contact, etc. In order to ensure their long term clinical application and to enhance the bioactivity of Ti implants, a bioceramic material with osteoconductive property is often coated onto it [3]. Among the various materials used for coating, hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is known to be the best biocompatible and bioactive material that acts as a bridge between the implant and human tissue thereby improving the osseointegration. Hydroxyapatite in bone is a multi-mineral substituted calcium phosphate with the traces of Mg^{2+}, Sr^{2+}, Si^{4+}, CO_3^{2-}, Ba^{2+}, Zn^{2+} and F^- etc [4,5]. Under this perspective, substitution of trace elements into the apatite structure has been the subject of widespread investigation nowadays because of their impending role in the biological process during implantation studies. To date, a number of studies have been devoted to different element substitutions such as Sr^{2+}, F^-, Zn^{2+}, Ce^{3+}, and Ag^+ on the apatite structure [6–8]. Concerning the biological properties of the composite coatings we tried to combine together the bioactive elements such as Sr, Mg and Zn into the coatings to induce favorable biological effects. Each of these mentioned elements plays an ess-

*Corresponding author at: Department of Chemistry, Periyar University, Salem 636011, Tamilnadu, India. Tel.: +91 427 234 5766; fax: +91 427 234 5124.
E-mail address: dhanaraj_gopi@yahoo.com (D. Gopi).

http://dx.doi.org/10.1016/j.ceramint.2014.12.114
0272-8842/

ential part in the biological action course. Among the various substituting ions, Sr is one of the most abundant and nutritionally essential trace elements in the human body and low dose of Sr diminishes the risk fractures in postmenopausal osteoporotic patients [9,10].

Magnesium undoubtedly, is one of the most important bivalent ions associated with the biological apatite. The addition of Mg (the fourth highest concentrated cation in the human body after Ca, K and Na) in apatite is paid attention because of the beneficial effects on the physicochemical properties and bone metabolism [11,12]. Similarly, zinc substitution in HAP supports bone growth [13], inhibits bone resorption [14], enhances antimicrobial resistance [15], and supreme potential for imparting multifunctionality in bone implants [16,17]. Since bioactive elements like Sr, Mg, and Zn have been found to play important roles in regulating the biological responses, it is of great interest to incorporate bioactive elements for developing bioactive composite coatings on Ti orthopedic implants.

However, these bioceramic coatings could not maintain long-term stability, and may delaminate from the surface of the implants in certain situations due to the lack of bonding strength, which in turn may lead to clinical complications and implant failure [12,18]. Hence, it is necessary to improve the mechanical properties of the pure and substituted HAP coatings without compromising its biocompatibility. CNTs have been suggested as the best material for improving the mechanical property of inorganic bioactive coatings (i.e., HAP), without offsetting its bioactivity [19]. To facilitate its applications in biomedical field, chemical oxidation of CNTs is performed for good dispersion in the solvent which helps them to easily integrate with inorganic, organic and biological systems [20,21]. Many methods are in practice for the development of bioceramic composite coatings onto the implant surfaces [22,23]. Among them, electrolytic deposition is a simple technique for the fabrication of coatings of varied materials on metal surfaces [24,25]. This method involves low temperature, has good control over the deposition thickness and quality, low energy consumption and also it is an environmental friendly process. To the best of authors' knowledge, there are no reports on the CNTs reinforced multi minerals substituted HAP composite coating on Ti implant for improved biological properties by the electrodeposition process. Hence, the present work deals with the development of CNTs reinforced: Sr-HAP, Mg-HAP, Zn-HAP and M-HAP composite coating on Ti with enhanced corrosion resistance and biocompatibility for promising biomedical applications.

2. Materials and methods

2.1. Specimen preparation

The pure Ti specimens (99.99%) of size $10 \times 10 \times 3$ mm^3 embedded in epoxy resin leaving area of 1 cm^2 were designed as the substrates for electrodeposition. Prior to deposition, the surfaces of the substrates were mechanically polished with 400, 600, 800, 1200 and 1500 grades of abrasive silicon carbide paper and then ultrasonically cleaned in acetone, ethyl alcohol and deionized (DI) water, respectively for 15 min, and then dried at room temperature.

2.2. Electrodeposition of CNTs/Sr-HAP, CNTs/Mg-HAP, CNTs/Zn-HAP and CNTs/M-HAP on Ti

The electrodeposition of CNTs/Sr-HAP, CNTs/Mg-HAP, CNTs/Zn-HAP and CNTs/M-HAP on Ti was performed in a conventional three electrode cell configuration using a CHI 760C electrochemical workstation (USA). Four series of electrolytes utilized for the electrodeposition, are given in Table 1. For comparison purpose CNTs/HAP composite coating was performed by adopting procedure as discussed in our previous work [26]. The electrodeposition process was carried out in potentiostatic mode by applying a potential of -1.4 V vs. SCE using the electrochemical workstation CHI 760C (CH instruments, USA). After the deposition, the coated substrates were gently rinsed with deionised water and then dried at room temperature for 24 h.

2.3. Phase composition, structure, and morphological characterization of the coatings

Fourier transform-infrared spectroscopy (Impact 400 D Nicholet Spectrometer) was utilized to identify and confirm the functional groups of the composite coatings in 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 compositions of the composite coatings were analyzed by X-ray diffraction (Seifert, X-ray diffractometer Siemens D500 Spectrometer). The morphological features of the as-deposited coatings were observed using a high resolution scanning electron microscopy (JEOL JSM-6400, Japan) and the elemental composition was analyzed by using an energy dispersive X-ray spectroscopy. The microstructure of the composite coatings was characterized using high resolution transmission electron microscopy (JEOL JEM 2100 Co., Tokyo, Japan).

Table 1
Chemical composition of electrolytes used in the deposition of different composites on Ti.

S. no.	Composites	Concentration of ions used in the electrolytes						(Ca+X)/P
		Ca^{2+} (M)	Sr^{2+}	Mg^{2+}	Zn^{2+}	PO_4^{3-} (M)	CNTs (wt%)	
1.	CNTs/Sr-HAP	0.30	0.2 M	–	–	0.3	1	1.67
2.	CNTs/Mg-HAP	0.45	–	0.05 M	–	0.3	1	1.67
3.	CNTs/Zn-HAP	0.45	–	–	0.05 M	0.3	1	1.67
4.	CNTs/M-HAP	0.20	0.2 M	0.05 M	0.05 M	0.3	1	1.67