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Research Paper

Characterization and nanomechanical properties of novel dental implant coatings containing copper decorated-carbon nanotubes

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ABSTRACT

Fluorapatite–titania coated Ti-based implants are promising for using in dental surgery for restoring teeth. One of the challenges in implantology is to achieve a bioactive coating with appropriate mechanical properties. In this research, simple sol–gel method was developed for synthesis of fluorapatite–titania–carbon nanotube decorated with antibacterial agent. Triethyl phosphate $[PO_4(C_2H_5)_3]$, calcium nitrate $[Ca(NO_3)_2]$ and ammonium fluoride (NH_4F) were used as precursors under an ethanol–water based solution for fluorapatite (FA) production. Titanium isopropoxide and isopropanol were used as starting materials for making TiO_2 sol–gels. Also, Copper acetate $[Cu(C_2H_3O_2)_2 \cdot H_2O]$ was used as precursor for decoration of multi walled carbon nanotubes (MWCNTs) with wet chemical method. The decorated MWCNTs (CNT(Cu)) were evaluated by transmission electron microscopy (TEM). The phase identification of the FA–TiO_2–CNT(Cu) coating was carried out by XRD analysis. Morphology of coated samples was investigated by SEM observations. The surface elastic modulus and hardness of coatings were studied using nanoindentation technique. The results indicate that novel dental implant coating containing FA, TiO_2 and copper decorated MWCNTs have proper morphological features. The results of nanoindentation test show that incorporation of CNT(Cu) in FA–TiO_2 matrix can improve the nanomechanical properties of composite coating.

1. Introduction

Synthetic Hydroxyapatite [HA, $Ca_{10}(PO_4)_6(OH)_2$] shows to possess exceptional biocompatibility and bioactivity properties. It has been widely used clinically in the form of powders, granules, dense and porous blocks, and coating (Cunniffe et al., 2010). Fluorine ion, which exists in human bone and enamel, can be incorporated into HA crystal structure by substitution of fluorine ions with OH^- groups to form Fluorapatite, [FA, $Ca_{10}(PO_4)_6F_2$]. Substitution of F^- in HA structure plays an important role because of its influence on the physical and biological properties of HA (Nikčevic et al.,

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2004). Incorporation of fluorine into HA, or "fluoridation", reduces its solubility (Darroudi et al., 2010), increases chemical stability and promotes bone cell proliferation (Ebrahimi-kahrizsangi et al., 2010) while maintaining a comparable biocompatibility to that of HA (Darroudi et al., 2010). The results of in vitro showed that FA could provide better protein adsorption, comparable or better cell attachment, and significantly improved alkaline phosphates activity (Fathi and Mohammadi Zahrani, 2009).

HA coated implant sometimes failed in long term stability, because the coated film deteriorated partly owing to fracture at the HA–titanium interface, due to the poor adherence between the ceramic film and the substrate. Thus, improvement of chemical bonding between the HA and Ti implant is mostly desirable particularly for clinical applications. Over the past decades, hydroxyapatite–titania (HA–TiO_2) nanocomposites have been widely used as Ti-based implant coatings. The addition of TiO_2 is a possible method for improvement the bonding of coated HA to Ti implants (Lim et al., 2001).

Most recently, for tissue engineering applications the trend is to develop nanosized apatites with properties closer to those of living bone (Cunniffe et al., 2010). In natural tissues or organs, cells directly interact with nanostructures extracellular matrices (ECM), which are mainly composed of nanofibrous collagen fibrils. Nanomaterials, resembling the natural ECM in some features and possessing unique physiochemical properties, play a key role in stimulating cell growth as well as guide tissue regeneration (Zhang and Webster, 2009). In a biomimetic viewpoint, the three-dimensional CNTs resembles the nanofibrous network of natural ECM (Lin et al., 2004). Also, the extraordinary mechanical properties of CNTs are expected to have a contribution for improvement the poor mechanical properties of apatite coatings when used as reinforcement in novel apatite/CNT composites (Kaya et al., 2008). However, pristine CNTs tend to bundle up and are insoluble in most types of solvents, making them difficult to be used in biological systems (Worsley et al., 2009). Recently, Smart et al. (2006) reported that unrefined CNT possess some degree of toxicity (in vivo and in vitro), predominately due to the presence of transition metal catalysts, while chemically functionalized CNT applicable for drug delivery have not demonstrated any toxicity (Smart et al., 2006). Therefore CNTs need to be functionalized and purified by the removal of residual metal catalysts to improve their solubility and biocompatibility properties.

The controlled functionalization and decoration of metal nanoparticles onto CNTs were done for reduction its toxicity as well as prevention of aggregation (Wang et al., 2006). The success and long-term survival of the biomaterials are also dependent on the prevention of bacterial putrefaction after implant placement. In the case of dental implants, complications derived from an implant-associated infection lead to a harm in the patient quality of life and satisfaction because it is one of the reasons for early failures by lack of osseointegration and the major cause of late failures (Chen and Darby, 2003). The antiseptic activity of antibacterial nanoparticles is influenced by their size. The smaller particles, lead to the greater antibacterial effect (Panacek et al., 2006; Chen et al., 2006) although the problems of aggregation can not be neglected. A common solution to avoid this disadvantage is to support the nanoparticles on the surface of different substrates. Decoration of carbon nanotubes with antibacterial metals such as silver and copper are of considerable interest for their application in the biotechnology. In fact, the decoration of MWCNTs with antibacterial agent can prevent from carbon nanotubes and antibacterial nanoparticles agglomeration. The present study were investigated the preparation and characterization of FA–TiO_2–CNT nanocomposite coatings containing antibacterial agent by sol–gel process. Ti–6Al–4V as substrate was subjected to a sol–gel spin coating process. The aims of this study are to investigate the role of decorated CNTs in the microstructural and nanomechanical evolution of FA-based composite coatings. This has been carried out by XRD analysis and SEM observations. The effect of CNTs modified microstructure on elastic modulus and Hardness of the composite coatings is also elucidated.

2. Materials and methods

2.1. Decoration of MWCNTs

Carbon nanotubes with outside and inside diameters 40–60 nm and 10–20 nm respectively were used as starting material. Mean length of MWCNTs reported by manufacture was about 2–10 μm. Nitric acid (HNO_3, Merck, Purity ≈ 64.3–66.4%) was used for modification of surface of carbon nanotubes. 0.1 g of as-received MWCNTs were added to 50 ml of HNO_3. The mixture was mixed ultrasonically for 2 h and then refluxed for 24 h at room temperature. After 24 h refluxing, the reaction mixture was diluted with distilled water and then filtered through a filter paper (Watchman, 42). Dilution was repeated until the pH of mixture reached to pH of distilled water about 6. The functionalizing process followed by drying in a vacuum oven at 90 °C for 24 h (Hiang et al., 2001). These conditions have been employed to non-covalently functionalize CNTs for binding the nanoparticles. In fact the final products may be nanotube fragments whose ends and sidewalls are decorated with mainly carboxyl groups. About 0.03 g of functionalized MWCNTs was added to 50 ml of ethanol (Purity ≈ 96%) and then the solution was stirred for 2 h. Also, the solution of copper acetate (CuAc) in ethanol with 1 g/10 ml concentration was prepared and mixed for 2 h. The mixtures was added together and mixed ultrasonically until the ethanol was evaporated completely. This process leads to impregnation of MWCNTs with copper acetate. The weltered MWCNTs then heat treated at 200 °C temperatures at air atmosphere for 30 min (Lin et al., 2012). The suitable temperature for heat treatment was determined from thermogravimetric analysis.

2.2. Preparation of FA–TiO_2–CNT (Cu) composite sol–gel

The sol–gel process started with the preparation of a TiO_2 sol. Tetraethylorthotitanate ($C_8H_{20}TiO_4$, Merck, Purity ≥ 98%) was first diluted with isopropanol (Dr. Mojallali chemical laboratories, Purity ≥ 99%), and then a small amount of distilled water mixed for hydrolysis, followed by vigorous stirring for 24 h. Subsequently, the mixed sol was aged for 24 h. For preparation of fluorapatite sol–gel, controlled amounts of triethyl phosphate