



# Improving the bioactivity and corrosion resistance properties of electrodeposited hydroxyapatite coating by dual doping of bivalent strontium and manganese ion

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## ABSTRACT

The key property in the preparation of a biomaterial is to facilitate the regeneration and/or replacement of injured organs and tissues. To obtain such a biomaterial, strontium and manganese co-substituted hydroxyapatite (SrMnHA) ceramic coatings on commercially pure titanium (CP-Ti) were successfully prepared by a cathodic electrodeposition method. The formation of SrMnHA coating was investigated using Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis and inductively coupled plasma. Co-doping of Sr<sup>2+</sup> and Mn<sup>2+</sup> ions decreased hydroxyapatite unit cell volume and grain sizes. Obtained coatings were crack-free and dense, which led to the decrease in the corrosion current densities of CP-Ti in physiological solutions. The dissolution tests performed on SrMnHA resulted in the leaching of Sr<sup>2+</sup> and Mn<sup>2+</sup> at low levels. SrMnHAs have moderately hydrophilic surfaces with a contact angle of 23.8°. Additionally, the MC3T3-E1 cells show better cell morphology, adhesion, spreading, proliferation and expression of alkaline phosphatase on SrMnHA than on HA. The excellent biocompatibility of SrMnHA is mainly attributed to a probable effect of a combination of good surface wettability and ion release (Sr<sup>2+</sup> and Mn<sup>2+</sup>). Results suggest that SrMnHA composite-coated CP-Ti can be a potential candidate for orthopaedic applications.

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## 1. Introduction

Annually, 2.2 million bone grafting operations are carried out worldwide in the fields of neurosurgery, orthopaedics and dentistry to repair bone defects [1]. These data forecast the huge potential demand for bone implants. However, instability, infection, aseptic loosening and dislocation of surgical implants result in >10% revisions in hip implants [2]. Given that life expectancy is increasing and more implants are being placed in younger patients, the revision surgery rate will also increase over time. Accordingly, demand for new technologies to prolong the life of load-bearing medical implants *in vivo* is increasing [3].

Orthopaedic implants, which are essential for the internal fixation of fractures, are traditional metal materials as they need to maintain reliable strength, resistance to wear and corrosion and biocompatibility

for the duration of the bone repair period [2]. In particular, titanium and its alloys are extensively adopted in the orthopaedic fields due to their prominent mechanical properties [4,5]. However, a fibrotic encapsulation is often generated around the titanium implants, affecting the long-term prosthesis stability [6]. Moreover, titanium is unable to elicit a biologically functional material/bone interface [7]. Therefore, the application of biocompatible surface films is aimed to enhance the osteointegration of titanium-based implants. In particular, given its outstanding cytocompatibility and osteoconductivity, artificial hydroxyapatite (HA, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) has been widely studied as a coating material for metallic implants [1,8]. The bone mineral is idealised as HA and is associated with minor groups and elements (e.g., CO<sub>3</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup> and Mg<sup>2+</sup>) as well as trace elements (e.g., Sr<sup>2+</sup>, K<sup>+</sup>, Cl<sup>-</sup> and F<sup>-</sup>); some of these elements are at the ppm level [9]. These minor groups and elements play a key role in the physiological reactions associated with bone metabolism.

Furthermore, the HA structure can lightly adopt minerals to imitate bone-like material, and addition of bioactive ions into the HA-based bioceramic material might improve the biological activities of the implants [10]. In particular, the favourable effect of bioactive ions, such as Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>, Sr<sup>2+</sup>, Ce<sup>3+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Si<sup>4+</sup>, Cl<sup>-</sup>,

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F<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, in HA-based coatings on metallic substrates has been reported [9–12]. More recently, the probability to implement the substitution with at least two distinct bioactive ions has been put forward [12–15]. Among the divalent cations, Sr<sup>2+</sup> has been shown to play a significant role in bone formation [2,4,7]. This effect is due to the fact that Sr stimulates the calcium sensing receptor, which promotes the proliferation and differentiation of osteoblastic cells [9,11]. The incorporation of Sr<sup>2+</sup> into HA instead of Ca<sup>2+</sup> reveals enhanced bioactivity, biocompatibility, biodegradable rate and compressive strength compared with the traditional Sr-free HA bone cement [10,11]. Several studies report the effects of SrHA coating in improving the bioactivity and biocompatibility of implants [7].

However, to date, only limited studies focused on manganese in the field of implant materials [16]. Mn is a trace mineral that is essential for the growth and development of bones [15–17]. The radius of Mn<sup>2+</sup> (0.90 nm) is very close to that of Ca<sup>2+</sup> (0.99 nm), which enables Mn ion to enter osteoblasts through calcium ion channel. Mn<sup>2+</sup> affects bone metabolism by adjusting the osteoblast differentiation and bone resorption. In the work of Miola et al. [18], cytocompatibility tests manifested a good osteoblast adhesion and proliferation on Mn-doped bioglass; most Mn-doping can stimulate the expression of alkaline phosphatase (ALP) and some bone morphogenetic proteins. The existence of Mn in calcium phosphate can also promote the generation of osteocalcin in osteoblasts, which is more efficient than Mg and Sr [19–21]. To the best of our knowledge, few reports focused on Mn and Sr co-doped HA (SrMnHA) coating on CP-Ti for improving the mechanical capacities, corrosion resistance and biological activity of the HA coating [21].

A large number of coating approaches are available for the development of ion-substituted HA surfaces, including cathodic electrodeposition (CED), plasma spraying, radio frequency magnetron sputtering, pulsed laser deposition, sol–gel methods, co-blasting and micro-arc oxidation [3]. Of the technologies highlighted here, CED has unique technical advantages due to its comparatively low deposition temperature, process simplicity, capability of forming a uniform coating on porous substrates (or) complex shapes of substrate and the availability and low cost of equipment [2,13–15]. CED is established as one of the most promising approaches for fabricating coating on CP-Ti [22]. Several studies have reported the electrodeposited co-substitution of two distinct ions, such as (Sr, Mg), (Cu, Zn), (Na, Si) and (F, Sr), into HA coating [23–26]. Recently, Gopi et al. succeeded in the CED of ball flower such as manganese and strontium-substituted HA/cerium oxide dual coatings on the AZ91 Mg alloy on AZ91 Mg alloy [15]. We hypothesise that surface modification of Ti implants with co-substituted HA improves their stability and osteoconductivity, prolonging implant lifetime *in vitro*.

Considering the advantages of both the electrodeposited HA coating technology and the Mn/Sr co-doped HA coating material, the current work focused on the CED of SrMnHA bioceramic coatings on CP-Ti to enhance its corrosion resistance and mechanical and biological properties. The surface morphological and elemental compositions, topographical and phase structural properties, ionic substitution level and thermal stability were assessed using XRD, FTIR, SEM and EDS. The *in vitro* corrosion behaviour of the SrMnHA bioceramic coatings on sodium hydroxide-treated CP-Ti has been assessed in simulated body fluid (SBF), and the mechanical capacity of the composite was studied in relation to adhesion strength. Finally, the MT3C3-E1 preosteoblast cells were cultured on the SrMnHA composite coating to evaluate the proliferation and differentiation by MTT and ALP activity cell assays.

## 2. Materials and methods

### 2.1. Coating process

A sheet of commercially pure titanium (CP-Ti) (purity > 99.98%) was used and cut into small stripes of dimensions of 10 mm × 10 mm × 1 mm (width × length × thickness). To obtain homogeneous

roughness, the surfaces of the samples were mechanically polished with 500, 800, 1000, 1500 and 2000 grades of abrasive silicon carbide paper and then ultrasonically cleaned in acetone, ethyl alcohol and deionized (DI) water, respectively for 600 s. To increase surface roughness, the CP-Ti samples were etched with a solution consisting of 10% hydrochloric acid, 10% nitric acid, and 80% H<sub>2</sub>O for 20 s. Additionally, the specimens were alkali-treated by immersing in 40 mL of 5 M NaOH solution at 60 °C for 24 h. It is generally believed that the NaOH pretreatment process leads to the formation of a thin surface layer of Na<sub>2</sub>TiO<sub>3</sub> [27]. Previous studies have shown that the NaOH pre-treatment processing could produce excellent bond strength between the HA layer and the substrate [27]. The Na<sub>2</sub>TiO<sub>3</sub> layer assists HA deposition as it can actively exchange ions with Ca<sup>2+</sup> in solution, converting to CaTiO<sub>3</sub>. The CaTiO<sub>3</sub> represents a more beneficial surface for the formation of HA, as compared to the other calcium phosphates, and acts as a binding layer between the Ti substrate and the HA. Finally, all the specimens were rinsed in the DI water and then dried and employed for further experimental studies.

Analytical grade Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Sr(NO<sub>3</sub>)<sub>2</sub>, Mn(NO<sub>3</sub>)<sub>2</sub>, and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> were dissolved separately in DI water. The electrolyte solution was prepared from the mixture of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (2.2 × 10<sup>-2</sup> M), Sr(NO<sub>3</sub>)<sub>2</sub> (1 × 10<sup>-2</sup> M), and Mn(NO<sub>3</sub>)<sub>2</sub> (1 × 10<sup>-2</sup> M). To the above electrolytes, 2.5 × 10<sup>-2</sup> M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> solution was added dropwise under magnetic stirring for 10 min to produce the target (Ca + Sr + Mn)/P ratio of 1.67 at 65 °C. The pH of the electrolyte was regulated to 4.3 using nitric acid or ammonium hydroxide. A conventional three electrode cell configuration was used for the CED of SrMnHA composite using LK2005A electrochemical workstation (China), where CP-Ti substrate served as the working electrode, platinum electrode as the counter electrode and saturated calomel electrode (SCE) as the reference electrode [13,24]. The CED process was carried out in a constant current mode. The parameters were kept constant as per our previous study [27], SrMnHA coating was produced at a constant current density of 0.85 mA/cm<sup>2</sup>, at 65 °C, for 30 min. After the coating process, the specimens were removed from the electrolyte and sintered at 250 °C for 2 h to increase the purity, crystallinity, and bond strength of the apatite coatings. For comparison, pure HA coating was designated as a control.

### 2.2. Characterization

The topographical features of the bioceramic-coated samples were observed with field emission scanning electron microscopy (FESEM, JEOL JSM-7500F, Japan), this SEM apparatus is coupled with a system for microanalysis EDS (Energy-Dispersive X-ray Spectroscopy, GENESIS 2000 XMS, Japan). Before examination by FESEM, the specimens with the nonconductive HA coating were sputter-covered with a gold/palladium layer. The crystalline phase composition and structure of the bioceramic coatings were evaluated using an X-ray diffractometer (XRD, DX-1000, Dandong Fangyuan Instrument Co., Ltd., China) in with a monochromatic CuKα radiation source generated at 35 mA and 35 kV. The HA X-ray diffraction patterns (#9-0432) from the ICDD database were used as a reference. The scanning angle is ranged from 10° to 70°, with a scan rate of (2θ) 0.06° s<sup>-1</sup>. Fourier transform infrared spectroscopy (FTIR, Nicolet 670, USA) was used to identify the presence of OH<sup>-</sup> and SiO<sub>3</sub><sup>2-</sup> bonds formed in the bioceramic structure. Each spectrum was acquired in the reflectance mode by executing 32 scans at 4 cm<sup>-1</sup> resolution, in the range of 4000–400 cm<sup>-1</sup>.

### 2.3. The coating adhesion test

The HA coating on CP-Ti, the HA coating on alkali-treated CP-Ti and the SrMnHA coating on alkali-treated CP-Ti were evaluated for its adhesion strength by pull-out tests according to the American Society for Testing Materials (ASTM) international standard F 1044-05 [14]. Three replicate tests were conducted. All the coated specimens were cured

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