



Development of strontium and magnesium substituted porous hydroxyapatite/poly(3,4-ethylenedioxythiophene) coating on surgical grade stainless steel and its bioactivity on osteoblast cells



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ABSTRACT

The present study deals with the successful development of bilayer coatings by electropolymerisation of poly(3,4-ethylenedioxythiophene) (PEDOT) on surgical grade stainless steel (316L SS) followed by the electrodeposition of strontium (Sr) and magnesium (Mg) substituted porous hydroxyapatite (Sr, Mg-HA). The bilayer coatings were characterised by Fourier transform infrared spectroscopy (FT-IR) and high resolution scanning electron microscopy (HRSEM). Corrosion resistance of the obtained coatings was investigated in Ringer's solution by electrochemical techniques and the results were in good agreement with those obtained from chemical analysis, namely inductively coupled plasma atomic emission spectrometry (ICP-AES). Also, the mechanical and biological properties of the bilayer coatings were analyzed. From the obtained results it was evident that the PEDOT/Sr, Mg-HA bilayer exhibited greater adhesion strength than the Sr, Mg-HA coated 316L SS. *In vitro* cell adhesion test of the Sr, Mg-HA coating on PEDOT coated specimen is found to be more bioactive compared to that of the single substituted hydroxyapatite (Sr or Mg-HA) on the PEDOT coated 316L SS. Thus, the PEDOT/Sr, Mg-HA bilayer coated 316L SS can serve as a prospective implant material for biomedical applications

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1. Introduction

Among the various implant materials, 316L SS is widely used as a biomedical implant material, particularly for orthopaedic and dental implants [1]. More specifically, it has unique property of low cost, good biocompatibility, adequate corrosion resistance and mechanical properties [2]. But the formation of passive chromium oxide layer on the 316L SS surface was unable to tolerate with the biological environment and hence the release of metallic ions such as iron, chromium and nickel are evidenced in the human body [3]. Moreover, as the metals and their alloys are not bioactive and in order to ensure the corrosion resistance, osteointegration, and biocompatibility of these kinds of materials, the surface of the metallic implants are usually treated with osteoconductive or osteointegrating biomaterials such as calcium phosphate ceramics [4,5]. Hydroxyapatite [HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] is the most commonly used calcium phosphate based biomaterial for coating metallic implants due to its excellent biocompatibility and similar composition and structure to the human hard tissues [6–8].

The biological performance of the HA based bioceramic materials might be improved by the addition of bioactive ions that has stimulated a number of studies on the ion-doped (or) ion-substituted HA coatings [9]. In particular, the beneficial effect of magnesium (Mg^{2+}), strontium (Sr^{2+}), manganese (Mn^{2+}), silicon (Si^{2+}) and carbonate (CO_3^{2-}) in the HA based coatings deposited on metallic substrates has been demonstrated [10–13]. These ionic substitutions play an important role in the bone formation and also affect bone mineral characteristics, such as bioactivity, biocompatibility, osteoconductivity, degradation behaviour and mechanical properties [14–16].

Among the various substituting ions, Sr^{2+} is one of the most abundant and nutritionally essential trace elements in the human body. Sr^{2+} plays a special role in bone remodelling with the stimulation of bone formation and a reduction in bone resorption. It also enhances the osteoblast proliferation and has various effects on bone metabolism depending on its level of dosage used [17–20]. Low dose of Sr^{2+} , enhances the replication of pre-osteoblastic cells, and stimulates bone formation. In contrast, high dose of Sr^{2+} induces bone mineralization defect and also alters the mineral profile in rats. So, the dose of Sr^{2+} is an important factor for bone formation [21,22]. Capuccini et al., reported that the partial substitution of Ca^{2+} by Sr^{2+} can apparently

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improve the biological properties of the HA based materials [23].

Mg²⁺ is also undoubtedly one of the most important divalent ion associated with biological apatites [24,25]. Bone, enamel and dentin contain 0.44 wt%, 0.72 wt%, 1.23 wt% of Mg²⁺, respectively [26,27]. It is well known that Mg²⁺ is strongly associated with the mineralization of calcified tissues, in particular during the early stages of osteogenesis where it stimulates osteoblast proliferation, and its depletion causes bone loss and bone fragility with an effect comparable to that of insulin [28–31]. Due to the biological relevance of Mg²⁺, many research teams have worked on the preparation of calcium phosphate implant materials containing low level of Mg²⁺, which has been shown to improve their bioactivity [32].

Thus Sr²⁺ and Mg²⁺, as essential elements, were found to be very effective in enhancing the structural stability and biological properties of HA. Both *in vivo* and *in vitro* studies have also clearly indicated that Sr²⁺ and Mg²⁺ influence the mineral metabolism during the bone remodelling process and enhance preosteoblastic cell proliferation [33]. However, there are very few reports on the deposition of Sr²⁺ and Mg²⁺ substituted HA on metallic substrate [34].

Among the various coating methods, we preferred electrochemical deposition which is an attractive method because of the advantages in the coating fabrication such as low process temperature, process simplicity, uniformity of deposition, and the control over the thickness and porosity of the coatings. Recently, Gopi et al., have achieved the electrodeposition of HA on implant materials and the coatings exhibited uniform morphology with desired structure [2,5,35]. Though the coating of HA on implant materials improves the biocompatibility, the component metal ions of the substrate may be oxidised and will release toxic ions such as chromium leach out through pores. Moreover, it has been reported that the bonding between the coating and substrate is very poor. Therefore, various polymeric coatings have been used in order to enhance the adhesion of HA with the metallic substrate and also to prevent the leach out of metal ions through pores [4].

Recently, coating of conductive polymer (CP) has shown excellent anticorrosion properties [36–41]. PEDOT is a CP which has been investigated in many biomedical applications because of its unique properties, such as excellent environmental stability and high conductivity [42]. Moreover, the PEDOT has various bioengineering applications, because of its high aqueous stability and excellent biocompatibility [43,44]. The biocompatibility of the PEDOT which is essential for its application in implantable devices was reported by Luo et al. [45]. In the present work, we have chosen sodium salicylate as the most suitable candidate that allows the formation of an adherent and homogenous CP coating on active metals without any pre-treatments [46]. The formation of passive film is mainly due to the presence of sodium salicylate in the electrolyte which will be beneficial for the electropolymerization and formation of CP on the stainless steel substrate [5,47].

The objective of our work is the development of Sr, Mg substituted HA coating on PEDOT coated 316L SS. Here, the first layer PEDOT on 316L SS may prevent the release of toxic ions thereby enhancing the adhesion strength between the coating and the substrate. The second layer, *i.e.*, Sr, Mg-HA coating which is porous in nature will definitely pave the way for the growth of bone tissues through the pores in between them. So, it is aimed to evaluate the biocompatibility of the as-developed bilayer coatings.

To the best of our knowledge, there are no reports on the electrodeposition of Sr²⁺ and Mg²⁺ substituted HA coating on PEDOT coated 316L SS. Hence the present work is designed to achieve the PEDOT/Sr, Mg-HA coating on 316L SS with improved adhesion strength, bioresistivity and biological properties.

2. Materials and methods

2.1. Preparation of 316L SS specimens

Type 316L SS (procured from steel Authority of India Ltd., (SAIL), India) having elemental composition (wt%) C–0.0222, Si–0.551, Mn–1.67, P–0.023, S–0.0045, Cr–17.05, Ni–11.65, Mo–2.53, Co–0.136, Cu–0.231, Ti–0.0052, V–0.0783, N–0.0659 and rest Fe was used as the metal substrate for the electrodeposition [5,48]. The 316L SS substrates were cut into dimensions of 10 × 10 × 3 mm and were embedded in epoxy resin leaving area of 1 cm² for exposure to the electrolyte [35]. Prior to deposition, all the substrates were abraded with different grades of silicon carbide (SiC) sheets from 400 to 1200 grits. After polishing, the 316L SS substrates were thoroughly washed with deionised water and ultrasonically cleaned in acetone for 10 min, and then used for further studies.

2.2. Preparation of electrolyte

The electrolyte for the deposition was prepared by dissolving the analytical grade calcium chloride dihydrate (CaCl₂·2H₂O), strontium chloride hexahydrate (SrCl₂·6H₂O), magnesium chloride hexahydrate (MgCl₂·6H₂O) and diammonium hydrogen phosphate ((NH₄)₂HPO₄) in deionised water in the appropriate molar ratio to produce the target with (Ca + X)/P ratio of 1.67 (X = Sr + Mg). The electrolyte was then de-aerated with N₂ for 30 min during the electrodeposition in order to reduce the amount of dissolved carbon dioxide and thus to minimise the formation of CaCO₃ deposits. The pH of the above electrolyte was adjusted to 4.5 using dilute NH₄OH (or) HCl. The electrolyte used for the electropolymerization of 3,4-ethylenedioxythiophene (EDOT) was prepared using analytical grade sodium salicylate and monomer EDOT.

2.3. Electrochemical deposition

2.3.1. Electrodeposition of PEDOT on 316L SS

The electropolymerization of EDOT on 316L SS was carried out in a regular three electrode cell arrangement by cyclic voltammetry using an electrochemical workstation (CHI 760C (CH Instruments, USA)) in which the saturated calomel electrode (SCE) served as the reference electrode, 316L SS and platinum electrode as the working and counter electrode, respectively. The electrodeposition of PEDOT was performed in 0.5 M sodium salicylate solution containing 0.2 M EDOT. The applied potential was scanned between –0.5 V and 2.0 V vs. SCE for 10 cycles at a fixed scan rate of 100 mV/s [45]. All the potentials in this experimental work are quoted on the SCE scale.

2.3.2. Electrodeposition of Sr-HA, Mg-HA, Sr, Mg-HA on PEDOT coated 316L SS

The electrodeposition of Sr-HA, Mg-HA, Sr, Mg-HA on the PEDOT coated 316L SS was performed in the conventional three-electrode cell configuration by galvanostatic method using CHI 760C electrochemical workstation (USA). Three series of electrolytes were utilised for the electrodeposition, which are, Series 1 (Sr-HA): CaCl₂·2H₂O, SrCl₂·6H₂O and (NH₄)₂HPO₄; Series 2 (Mg-HA): CaCl₂·2H₂O, MgCl₂·6H₂O and (NH₄)₂HPO₄; and Series 3 (Sr, Mg-HA): CaCl₂·2H₂O, SrCl₂·6H₂O, MgCl₂·6H₂O and (NH₄)₂HPO₄.

Series 1: The electrolyte for the Sr-HA deposition on the PEDOT coated 316L SS was prepared in an aqueous solution containing 0.3 M CaCl₂·2H₂O, 0.2 M SrCl₂·6H₂O and 0.3 M (NH₄)₂HPO₄, under magnetic stirring at room temperature. The coating process was carried out in galvanostatic mode at a constant current density of 9 mA/cm² for the duration of 30 min [5]. After the deposition, the as-coated substrates were gently rinsed with deionised water and then dried at room temperature for 24 h.

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