A FACILE ELECTRODEPOSITION OF POLY (3,4-ETHYLENEDIOXYPYRROLE)/STRONTIUM, MAGNESIUM SUBSTITUTED HYDROXYAPATITE BILAYER COATING ON SURGICAL GRADE STAINLESS STEEL FOR BIOMEDICAL APPLICATIONS

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Abstract—Hydroxyapatite (HA) is the most commonly used calcium phosphate based coating material for metallic implants like 316L SS due to its excellent biocompatibility and similar composition and structure to the human hard tissues. The biological performance of HA might be improved by the addition of bioactive ions such as strontium, magnesium, etc. Though the coating of strontium, magnesium substituted HA (Sr,Mg-HA) on 316L SS improves the biocompatibility, the component metal ions of the substrate may be oxidised and will release toxic ions. In order to improve the corrosion resistance and biological performance of the implant, we have fabricated the PEDOP/Sr,Mg-HA bilayer on 316L SS by electrodeposition. The as-developed bilayer coatings were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), high resolution scanning electron microscopy (HRSEM) and energy dispersive X-ray analysis (EDAX). The corrosion resistance of the obtained coating is also investigated in Ringer's solution by electrochemical techniques. Also, the mechanical property of the PEDOP/Sr,Mg-HA bilayer coating is analyzed. The in-vitro bioactivity of the bilayer coating was investigated. Thus, the PEDOP/Sr,Mg-HA bilayer coated 316L SS can serve as a prospective biomaterial for orthopaedic applications.

Index Terms—Electropolymerization, Poly (3,4-ethylenedioxypyrrole), Stainless steel; Substituted hydroxyapatite.

I. INTRODUCTION

Surgical grade stainless steel (316L SS) is widely used as an implant material in orthopaedic applications owing to its excellent mechanical properties, availability at low cost and ease of fabrication [1]. However, since the 316L SS are not bioactive, in order to ensure the biocompatibility and corrosion resistance of these kinds of materials, the surface of the metallic implants are usually treated with biomaterials such as calcium phosphate ceramics [2]. Among these bioceramic materials, hydroxyapatite [HA, $Ca_{10}(PO_4)_6(OH)_2$] seems to be the most investigated bioceramic material during the last decade and it has excellent biocompatibility, similar composition and structure to human tissues. Also, the biological performance of HA based bioceramic materials might be improved by the addition of divalent ions that has stimulated a number of studies on ion- substituted HA coatings [3].

Strontium (Sr) is an important trace element in human body and enhances preosteoblast proliferation and decreases bone resorption. In addition, strontium substituted HA (Sr-HA) can exhibit better mechanical properties than pure HA [4-6]. Magnesium ions (Mg^{2+}) plays an important role in preventing osteoporosis in human bone and also has its own significance in the calcification process. In particular during the early stages of osteogenesis it stimulates osteoblast proliferation, and its depletion causes bone loss and bone fragility with an effect comparable to that of insulin [7,8]. Among 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 [3].

The aim of this work was to electrochemically deposit the porous strontium, magnesium substituted hydroxyapatite [Sr,Mg-HA, $Ca_8Sr_1Mg_1(PO_4)_6(OH)_2$] on 316L SS. But, it has been reported that the bonding between the coating and substrate is very poor [3]. Therefore, in order to enhance the adhesion of HA with the metallic substrate and also to prevent leach out through pores various polymeric coatings have been used [9]. Recently, poly (3,4-Ethylenedioxypyrrole) (PEDOP) is one of the most gifted conductive polymers due to its numerous advantages such as relatively easy synthesis, good mechanical stability, corrosion protection etc., [9-14]. The coating of PEDOP was deposited as a first layer on 316L SS substrate in the presence of sodium salicylate followed by the deposition of additional layer containing Sr,Mg-HA with excellent mechanical properties, biocompatibility and corrosion resistance.

II. EXPERIMENTAL

A. Materials

316L SS specimens obtained 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 substrate material [3]. All the chemicals used were of analytical grade reagents without further purifications and deionized water was employed as the solvent throughout the experiments. The electrolyte used for electropolymerisation of EDOP was prepared using EDOP (monomer) and sodium salicylate (oxidising agent).

The electrodeposition of Sr,Mg-HA was carried out in the electrolyte containing calcium chloride dihydrate ($CaCl_2.2H_2O$, 99.9% purity, Sigma–Aldrich, USA), strontium chloride hexahydrate ($SrCl_2.6H_2O$, 99.8% purity, Sigma–Aldrich, USA), magnesium chloride hexahydrate ($MgCl_2.6H_2O$, 99.8% purity, Sigma–Aldrich, USA) and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, 99.9% purity, Sigma–Aldrich, USA).

B. Preparation of 316L SS samples

The 316L SS samples were cut into 10×10×3 mm^3 dimensions and were embedded in epoxy resin leaving area of 1 cm^2 for exposure to the electrolyte [3]. The as-prepared 316L SS samples were mechanically ground with various silicon carbide (SiC) abrasive sheets (400, 500 up to 1200 grit) to obtain homogeneous roughness. After grinding the specimens, they were ultrasonically cleaned using anhydrous ethanol, deionized water and acetone for 10 min. Finally, the cleaned 316L SS samples were dried under an air pressure steam for 5 min and then used for further studies.

C. Electrodepostion

The electrolyte solution for Sr,Mg-HA deposition was prepared by dissolving the analytical grade reagents. In brief, for the preparation of Sr,Mg-HA electrolyte, solutions of 0.40 M $CaCl_2.2H_2O$, 0.05 M $SrCl_2.6H_2O$, 0.05 M $MgCl_2.6H_2O$ and 0.3 M $(NH_4)_2HPO_4$ were separately adjusted at pH-4.5 by the addition of 0.1 M NH_4OH or HCl. The above electrolyte solution is the appropriate molar ratio to produce the (Ca + Sr+Mg)/P target ratio of 1.67 to use as precursor for Sr,Mg-HAP coating on 316L SS. The electrolyte was then de-aerated with nitrogen (N_2) for 25 min during the electrodeposition process in order to reduce the amount of dissolved carbon dioxide (CO_2) and thus to minimize the formation of calcium carbonate ($CaCO_3$) deposits.

In the present work, we have deposited porous Sr,Mg-HA on 316L SS at constant current density of 9 $mA.cm^{-2}$ for the duration of 30 min which has been proved as the best current density to produce uniform porous coating [3]. After the electrodeposition, the Sr,Mg-HA coated 316L SS specimens were gently rinsed with deionised water and dried for 12 h.

D. PEDOP coating on 316L SS

The polymerisation of EDOP on 316L SS was carried out in a regular three electrode cell arrangement by cyclic voltammetry method using an electrochemical workstation (CHI 760C (CH Instruments, USA)) in which the 316L SS and saturated calomel electrode (SCE) served as the working and reference electrodes and platinum electrode served as the counter electrode, respectively. The electropolymerisation of EDOP on 316L SS was performed in 0.1 M EDOP containing 0.5 M of sodium salicylate solution. The applied potential was scanned between -0.5 V and +1.5 V vs SCE for 60 cycles at a fixed scan rate of 20 $mV.s^{-1}$ [3]. All the potential in this experimental work is quoted on the SCE scale.

E. Sr,Mg-HA coating on PEDOP coated 316L SS

The same procedure of the Sr,Mg-HA coating on 316L SS was adopted for the coating of Sr,Mg-HA on PEDOP coated 316L SS for 30 min at a constant current density of 9 $mA.cm^{-2}$. After the electrodeposition process, the PEDOP/Sr,Mg-HA bilayer coating was gently rinsed with deionised water and then dried for 24 h.

F. Surface characterisation of the bilayer (PEDOP/ Sr,Mg-HA) coating

To identify and confirm the functional groups, the as-coated samples were characterised by Fourier transform infrared spectroscopy (FT-IR; Impact 400D Nicholet Spectrometer) 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 morphological features and the elemental composition of the as-deposited coatings were observed after gold sputtering using a high resolution scanning electron microscopy (HRSEM; JEOL JSM-6400, Japan) equipped with an energy dispersive X-ray analysis (EDAX).

G. Adhesion tests

The adhesion strength can offer precious information on the mechanical properties of the surrounding coating and metallic implant. Adhesion strength of the Sr,Mg-HA, PEDOP, and PEDOP/Sr,Mg-HA coated 316L SS specimens were studied by pull-out test according to the American Society for Testing Materials (ASTM) international standard F1044, with at least six measurements for each specimen. The as-coated 316L SS cylindrical samples (25 mm in diameter) were bonded to counter 316L SS cylinder surface using quick set epoxy adhesive. All the experimental samples were cured in an oven at 100 ºC during 60 min and the fixtures were subjected to pull-out test using a universal testing machine (Model 5569, Instron) at a crosshead speed of 1 $mm.min^{-1}$.

H. Electrochemical investigation of the coatings

Electrochemical measurements using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were performed in

Ringer's solution (NaCl-8.6 $g.L^{-1}$, $CaCl_2.2H_2O$-0.66 $g.L^{-1}$ and KCl 0.6 $g.L^{-1}$) to assess the corrosion resistance of uncoated and as-coated 316L SS samples. The pH of the Ringer's solution was maintained at 7.4. The electrochemical experiments were carried out in a 20 mL Ringer's solution at a generally accepted human body temperature of 37 ± 1 ^oC.

The electrochemical studies were conducted using a three-electrode cell (CHI 760C, USA), using the 316L SS samples as the working electrode, saturated calomel electrode (SCE) as the reference electrode and platinum electrode as the counter electrode. The potentiodynamic polarization measurements were performed from -1000 mV to +1000 mV vs. SCE with a scan rate of 0.1 $mV.s^{-1}$.

The EIS studies were performed in the same setup as that of potentiodynamic polarization studies and the applied ac perturbation signal was about 5 mV vs SCE within the frequency range 10^{-2} Hz to 100 kHz at an open circuit potential (OCP) condition. The record of obtained electrochemical data was taken using internally developed software. All the electrochemical tests were repeated three times to ensure for the reliability and reproducibility.

I. In vitro studies of PEDOP/Sr,Mg-HA bilayer in simulated body fluid.

The bone-bonding ability of the as-coated PEDOP/Sr,Mg-HA bilayer sample can be evaluated by investigative apatite formation on its surface in simulated body fluid (SBF) at 37 $^{\circ}C$ for 7 and 21 days. The preparation and composition of SBF solution, which was buffered with hydrochloric acid (HCL) to maintain a pH of 7.4, has been described in the literature [5]. Then, the PEDOP/Sr,Mg-HA bilayer coated 316L SS samples were soaked in 25 ml of SBF solution in 100 ml beaker with airtight lids where the temperature was maintained at 37 ± 1 $^{\circ}C$ in an incubator for various days like 7 and 21 days. The SBF solution was renewed every two days for a period of 7 and 21 days to avoid any change in cationic concentration that can occur owing to degradation of the PEDOP/Sr,Mg-HA bilayer coated sample. The immersed bilayer sample was then gently rinsed with deionized water and the formation of bone-like apatite was evaluated by SEM.

III. RESULTS AND DISCUSSION

A. Electropolymerisation of EDOP on 316L SS

The electropolymerisation of EDOP on 316L SS was carried out by cyclic voltammetry from sodium salicylate solution at a fixed scan rate of 20 $mV.s^{-1}$ and for 60 cycles in the potential range between -0.5 V and 1.5 V (vs. SCE) as shown in Fig. 1**.** The anodic peak observed around 1 V (vs. SCE) was attributed to the polymerisation of monomer (EDOP) as well as the oxidation of sodium salicylate forming passive film underneath the PEDOP coating on 316L SS sample. Separate peaks cannot be detected owing to overlapping of oxidation peaks of sodium salicylate and PEDOP. The oxidation of sodium salicylate which forms a passive film is advantageous for the electropolymerisation of EDOP and formation of PEDOP layer on 316L SS. With the increasing cycle numbers, the intensity of the oxidation peak of PEDOP decreases while a slight increase in current density was observed at the end of each cycle.

The drop of the peak intensity is a result of PEDOP being involved in the passivation process and the decrease in current intensity continues in repetitive cycles. The slight increase in current at the end of each cycle is ascribed to the development of PEDOP oxidation that occurs in a step by step manner which leads to the growth of PEDOP layer with increasing thickness.

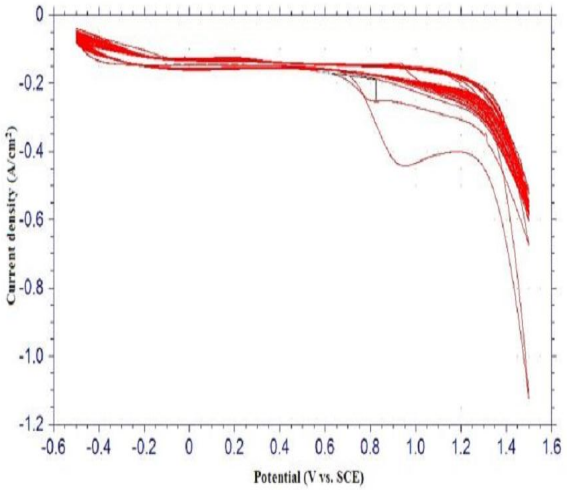


Fig. 1. Cyclic voltammogram for PEDOP coating on 316L SS for cycle numbers 1-60 at a scan rate of 20 mV/s in 0.1 M EDOP containing 0.5 M sodium salicyclate.

B. Surface characterisation FT-IR analysis

The FT-IR spectrum of the PEDOP/Sr,Mg-HA bilayer coated 316L SS sample is shown in Fig. 2. The characteristics peaks found at 3442, 1521 and 1443 cm^{-1} are ascribed to the stretching vibration of N-H, C-C and C-N groups in the PEDOP ring, respectively. Whereas, the peak appeared at 1573 cm^{-1} is due to the formation of metal-salicylate complex. Apart from these, the peaks located at 1019 cm^{-1} (ν_3), 591 cm^{-1} and 558 cm^{-1} (ν_4), 471 cm^{-1} (ν_2) as well as the bands at 1082 cm^{-1} (ν_3) and 949 cm^{-1} (ν_1) are assigned to the phosphate groups [3]. The broad stretching band at 3442 cm^{-1} and a bending band at 1636 cm^{-1} are attributed to the stretching and bending mode of hydrogen-bonded water molecules, while the absorption bands at 3592 cm^{-1} and 637 cm^{-1} are assigned to the stretching and bending vibration of hydroxyl groups of Sr,Mg-HA, respectively. The peaks found in both PEDOP and Sr,Mg-HA is present in Fig. 2 which strongly reveals the formation of PEDOP/Sr,Mg-HA coating on 316L SS sample.

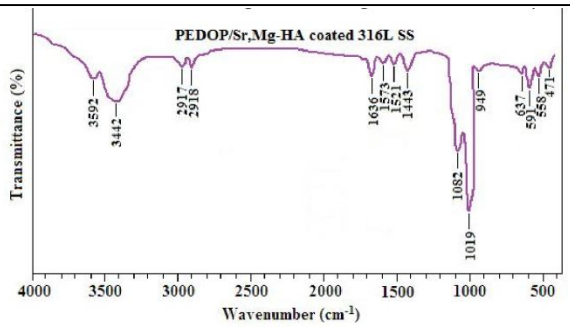


Fig. 2. The FT-IR spectrum of PEDOP/Sr,Mg-HA bilayer coated 316L SS.

Scanning electron microscopic investigations

The microstructure information of the Sr,Mg-HA, PEDOP and PEDOP/Sr,Mg-HA bilayer coatings are shown in Fig. 3(a-c), respectively. It can be seen in Fig. 3(a), the coating exhibited an interconnected porous network microstructure of Sr,Mg-HA on 316L SS. The Fig. 3(b) represent the morphology of PEDOP coated 316L SS which exhibits the formation of granular and uniform microstructure. The morphological feature of the as-formed bilayer coating shown in Fig. 3(c), exhibits more compact, porous and uniform structure. The porous nature of the Sr,Mg-HA coating on uncoated and PEDOP coated 316L SS is a consequence of the H_2 bubbles evolved at the cathode surface. It is attractive to note that most of the pores are interconnected which can be favourable for the initiation of bone formation [15]. The interconnected pores can allow the proliferation and attachment of diverse cell types responsible for the growth of osseous tissue or organ.

The elemental composition of the PEDOP/Sr,Mg-HA bilayer coating is shown in Fig. 3(d). This spectrum indicates the presence of Ca, Sr, Mg, C, N, O and P there by confirming the existence of PEDOP/Sr,Mg-HA bilayer coating on 316L SS sample.

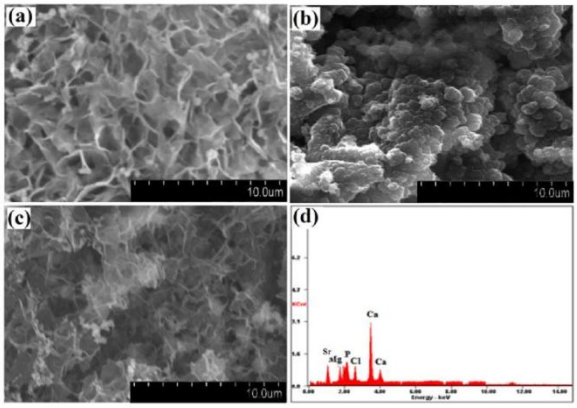


Fig. 3. HRSEM images of (a) Sr,Mg-HA, (b) PEDOP, (c) PEDOP/Sr,Mg-HA coated 316 L SS and (d) EDAX spectrum of PEDOP/Sr,Mg-HA bilayer coated 316L SS.

C. Adhesion strength

Adhesion of the PEDOP/Sr,Mg-HA bilayer coating with the 316L SS substrate is one of the most important properties for *in vivo* implantation. The adhesive strength of the PEDOP/Sr,Mg-HA bilayer coating on 316L SS was 12.0 ± 1.1 MPa where as the individual coatings of Sr,Mg-HA and PEDOP coated 316L SS exhibited 9.7 ± 0.5 MPa and 13.2 ± 0.7 MPa, respectively. This adhesion strength of the as-coated bilayer coating will make it suitable for orthopaedic applications.

D. Electrochemical characterization

Potentiodynamic cyclic polarization studies

The potentiodynamic polarization of the uncoated, Sr,Mg-HA, PEDOP and PEDOP/Sr,Mg-HA coated 316L SS in Ringer's solution are shown in Fig. 4. The corrosion potential (E_{corr}), breakdown potential (E_b) and repassivation potential (E_{pp}) for the uncoated 316L SS were found to be at -870, +449 and -90 mV (vs. SCE), respectively. The polarization curves obtained reveals that the E_{corr} , E_b and E_{pp} values for Sr,Mg-HA coated 316L SS were found to be -591,463 and 39 mV vs. SCE, respectively. While the E_{corr} , E_b and E_{pp} values recorded for the PEDOP coated 316L SS were -494, 492 and 125 mV vs. SCE, respectively. Thus, the E_{corr}, E_b and E_{pp} values obtained for PEDOP coated 316L SS were found to be nobler than that of the Sr,Mg-HA coated 316L SS sample. Hence, this higher E_{corr}, E_b and E_{pp} values obtained for PEDOP coated 316L SS is ascribed to the formation of a passive film underneath the PEDOP layer owing to the salicylate. The polarization curve for bilayer coated 316L SS sample exhibited E_{corr}, E_b and E_{pp} values of -446, 582 and 199 mV vs. SCE, respecctively.

The E_b and E_{pp} values of PEDOP/Sr,Mg-HA coated 316L SS shows a maximum shift in the noble direction. This shift in the E_{corr}, E_b and E_{pp} values towards the noble direction is an indication that the bilayer (PEDOP/Sr,Mg-HA) coating has high corrosion resistance in Ringer's solution than that of the PEDOP and the Sr,Mg-HA coated 316L SS samples.

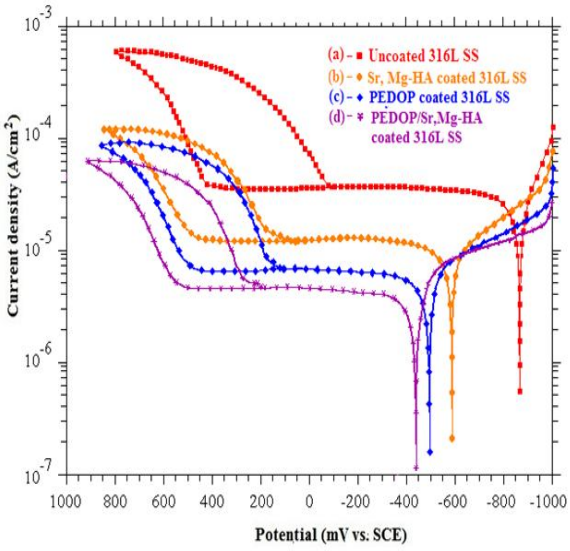


Fig. 4. Potentiodynamic polarization curves for uncoated, Sr,Mg-HA, PEDOP and PEDOP/Sr,Mg-HA coated 316L SS in Ringer's solution.

Electrochemical Impedance Spectroscopic studies

The Nyquist plot obtained for the uncoated, Sr,Mg-HA, PEDOP and PEDOP/Sr,Mg-HA coated 316L SS in Ringer's solution are shown in Fig. 5. For uncoated 316L SS sample the polarization resistance (R_p) value was found to be 41 Ω.cm^2 (Fig. 5.). The R_p value obtained for the Sr,Mg-HA coated 316L SS sample was found to be greater as 982 Ω. cm^2 than that of the uncoated 316L SS.

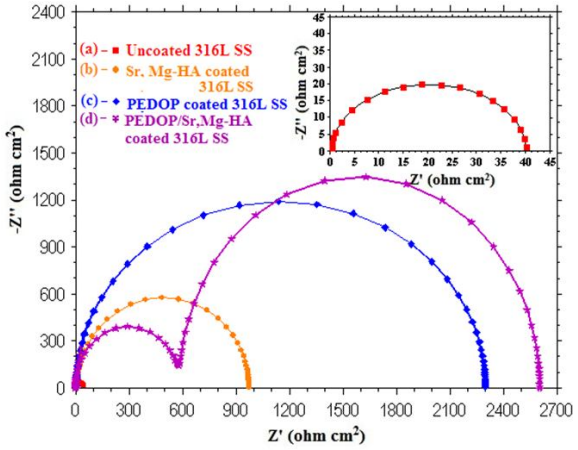


Fig.5. Nyquist plots for uncoated, Sr,Mg-HA, PEDOP and PEDOP/Sr,Mg-HA coated 316L SS in Ringer's solution.

As it can be seen from the Fig. 5, the PEDOP coated 316L SS showed higher R_p value of 23820 Ω.cm^2 which is due to the effective protection of 316L SS by PEDOP coating. When compared with the Sr,Mg-HA coated 316L SS, the R_p value of the PEDOP coated 316L SS showed higher R_p value owing to its uniform granular microstructure. Two capacitive semicircles, that is the first semicircle at higher frequencies that can be attributed to the Sr,Mg-HA layer and the second semicircle at low frequencies to the compact PEDOP layer are observed for bilayer (PEDOP/Sr,Mg-HA) coated 316L SS samples.

The R_p value was found to be 2620 Ω.cm^2 for bilayer coated 316L SS, which shows more R_p than that of the individual coatings of Sr,Mg-HA and PEDOP on 316L SS samples. From these results, it could be well ascertained that the as-formed bilayer (PEDOP/Sr,Mg-HA) coating on 316L SS sample is corrosion protective and hence potential for biomedical applications.

E. In vitro apatite forming ability of PEDOP/Sr,Mg-HA bilayer coating in SBF.

In the present study, the evaluation of the apatite forming ability of PEDOP/Sr,Mg-HA bilayer coating on 316L SS for various days (7 and 21 days) at 37 ± 0.5 °C was carried out. Figure 6(a-b) shows the morphology of the PEDOP/Sr,Mg-HA bilayer coating on 316L SS after being soaked in SBF for various days like 7 and 21 days. The morphology of the PEDOP/Sr,Mg-HA bilayer coated specimen showed the bone-like apatite formation at various days of immersion in SBF but the amount of apatite formation and the surface coverage varied particularly. Fig. 6a is ascribed to bone-like apatite, demonstrating that the granular structured coating formed on 316L SS could induce the nucleation and growth of bone-like apatite on coated 316L SS after7 days of immersion in SBF. As it can be evident from Fig. 6b, the bone-like apatite forming ability of the PEDOP/Sr,Mg-HA bilayer coating at 21 days of immersion in SBF is observed to be excellent and the surface was fully covered with bone-like apatite. This apatite layer formed on the PEDOP/Sr,Mg-HA bilayer coating can develop the osteointegration and osteoconduction properties.

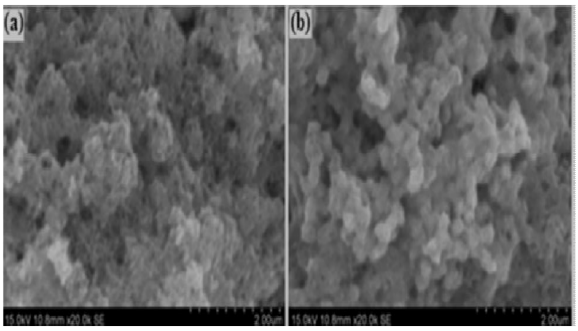


Fig. 6. HRSEM images of the PEDOP/Sr,Mg-HA bilayer coating after soaking in SBF solution for various (a) 7 and (b) 21 days

CONCLUSIONS

The reported study recognized the possibility and effectiveness of fabricating the bilayer (PEDOP/Sr,Mg-HA) coated 316L SS by electrodeposition for enhanced corrosion resistance and biological activity. The surface morphological evaluation of the as-developed PEDOP/Sr,Mg-HA bilayer coating on 316L SS exhibited an uniform and adherent coating with porous morphology which indicated that the bilayer coatings could protect 316L SS effectively. The corrosion protection performance of all the as-formed coatings evaluated using potentiodynamic polarization and EIS studies revealed that the bilayer (PEDOP/Sr,Mg-HA) coatings significantly improved the corrosion resistance of 316L SS sample. The *in-vitro* studies of the coated 316L SS implant in SBF at 21 days of immersion confirms that the bilayer coating of PEDOP/Sr,Mg-HA exhibited excellent bone-like apatite formation. Hence, the bilayer coated 316L SS appears to be prospective in orthopedic applications.

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