Materials Research Express

PAPER

Optimizing parameter for electrophoretic deposition of hydroxyapatite coating with superior corrosion resistance on pure titanium

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Keywords: coating, corrosion, hydroxyapatite, titanium, electrophoretic deposition

Abstract

Bioactive hydroxyapatite (HA) coating is applied on a commercially pure Ti by electrophoretic deposition (EPD). Optimizing the coating structure is necessary to obtain a stable layer and the best corrosion protection. The EPD was conducted at a constant voltage of 20, 30, and 40 V for 30 min in a HA/DMF (dimethylformamide) suspension. Uniform HA layers with a Ca/P ratio of 1.82 were successfully deposited on the Ti surface. The layers, which consisted of HA grains with the size of 1–5 μm, exhibited a gradual increase in thickness of 32, 50, and 60 μm with formation voltage. For the biomedical application, the suitable coating thickness was at least 50 μm. The high compaction of HA grains deposited at 30 V led to an order magnitude higher polarization resistance and ten times lower corrosion current density relative to the other specimens. The porous HA layer formed at 20 V, and the presence of cracks in the 40 V-coating led to a lower corrosion resistance relative to the 30-V coating. The 20 V- and 30 V-coatings remained intact and triggered the deposition of HA during immersion in simulated body fluid for 28 days, while the 40 V-coating dissolved into the solution. The optimum EPD voltage for depositing a stable HA coating with reasonable coating thickness and the best corrosion resistance was 30 V.

1. Introduction

Titanium (Ti) and its alloys are used as materials for orthopedic and dental implants due to their high strength compared to polymeric materials and toughness compared to ceramic materials [1]. Ti has a modulus elasticity of 105 GPa, close to the human bone of 10–30 GPa [2]. The ideal material used for bone replacement must be biocompatible, initiate osteogenesis, simulate the mechanical properties of bone, and exhibit good corrosion resistance [3]. Liberation of the metallic ions from an implant may cause an allergic reaction in a patient. Moreover, a high corrosion rate destroys the stability of an implant [4]. Implant instability leads to implant failure, thereby increasing the chance of repeated surgery and high healing costs. Implant stability is obtained from the structural and functional relationship of the interface between the implant and human bone tissue to produce optimal interactions [5]. Corrosion resistance and bioactivity determine the success of implant materials [6]. A simple method to improve the corrosion resistance of an implant material while enhancing the surface bioactivity is by coating it with bioactive material. Many studies [7–9] have been carried out to introduce the osteoconductive properties of bioactive ceramics as a coating for implant materials. Hydroxyapatite (HA) is a bioceramic material commonly used as a coating for bone implant applications. The composition and structure of HA are similar to human bone and exhibit good biocompatibility properties [8].

Several coating techniques were explored in applications, including plasma spraying, sputtering, sol-gel, pulse laser deposition, and electrophoretic deposition (EPD) [10]. The long-term stability of the plasma spray is problematic due to its high porosity, poor bond strength, small amounts of amorphous phases with non-
stoichiometric composition, and non-uniformity [11, 12]. The sol-gel method produces a significant amount of chemical waste [13]. Electrophoretic deposition (EPD) is a two steps method to deposit HA from a colloidal suspension on a metallic surface by applying direct current [14]. In the first step, the suspended charge migrates to the electrode having an opposite charge under the influence of the electric field. In the second step, the particles are deposited on the electrode surface to form a layer. EPD is a relatively simple method and low cost. The microstructure of the HA layer can be controlled by varying the processing parameters such as deposition time, voltage, and suspension concentration [15, 16].

The problems identified in the EPD process are cracks in the deposited HA layer, aggregation of HA particles, high porosity, and inhomogeneous thickness [17]. Optimizing the electrical parameters of EPD is necessary to improve the layer morphology, which contributed significantly to the corrosion resistance of the specimen. The potential range for synthesizing the HA coating on Ti alloys using HA/ethanol suspension falls between 3–7 V for 3–7 min [18]. There was a close correlation between the voltage-time and the surface morphology-thickness of the HA layer. More mass was deposited with increasing voltage and time, which resulted in a thicker HA layer. Despite ethanol, various groups of alcohols can also be used as the solvent [19]. The surface roughness of HA coating increases in the following order methanol > ethanol > isopropanol [20]. The type of suspension greatly affects the quality of the coating. Stable suspension having suitably charged surface particles results in uniform distribution of particle deposition [21]. An EPD study [22] using nanopowder HA in DMF (dimethylformamide) suspension reported cracks in the HA layer deposited for 5 min at 30, 40, and 60 V. In comparison, a relatively free crack layer was obtained at 20 V. The DMF is a good solvent for HA with a wide range zeta potential value of 10–23 mV (for 1 g HA), depending on the pH [22]. The potential increased with decreasing pH. This work aims to clarify the effect of the applied voltage between 20–40 V at a longer deposition time of 30 min on the morphology of the HA layer and its relation to the electrochemical corrosion behavior.

2. Method

2.1. Specimen preparation
A plate of commercially pure (CP) Ti grade 2, with a purity of 99.5%, having a thickness of 1 mm, is used. The plate was cut into a square shape of 15 mm × 15 mm using a CNC wire-cutting machine. The specimen was molded in epoxy resin to give one open surface. Grinding of the specimen surface was done using silicon carbide (SiC) sandpaper with grit #400, #1000, #1500, and #2000 consecutively using a Tegramin-25 grinder/polisher. The specimen was then polished using alumina paste. Finally, the specimen was washed using an ultrasonic cleaner (KLS 303363) in a solution of acetone and ethanol for 3 min.

2.2. Suspension preparation
The colloidal suspension was prepared by suspending 1 g of hydroxyapatite powder in 100 ml of N, N-Dimethylformamide (DMF, Merck) and stirred with a magnetic stirrer at 250 rpm for 1 h. The HA powder was synthesized in our laboratory. The HA powder was filtered using #650 mesh paper to get a relatively homogenous particle size of 20–25 μm. Detailed fabrication and analysis of the HA powder are described in ref [23]. DMF is chosen because of its inertness to the HA powder. The suspension was stabilized for a few hours in the ambient laboratory. After a few hours, sediment was precipitated at the basal of the glass beaker. The stable suspension was separated from the sediment and used for EPD.

2.3. Electrophoretic deposition (EPD)
The EPD process was performed using a two-electrodes configuration. The CP-Ti specimen as a working electrode was placed as the cathode, and a platinum foil used as a counter electrode was placed as the anode. The constant distance between the flat electrodes was 20 mm. The EPD process was carried out for 30 min in at a constant voltage of 20, 30, and 40 V using a DC voltage power supply (Dekko PS-1200Q series) in the colloidal suspension at a temperature of 25 °C. To enhance the coating compaction, the as deposited HA was exposed to warm air stream from a hair drier for an hour and then cooled down to room temperature for 24 h in ambient air.

2.4. Surface characterization and compositional analysis
Surface observation in both plane and cross-sectional views was done using a digital microscope (Keyence VHX 7000). The morphology of the resulting HA coating was investigated using Field Emission Scanning Electron Microscopy (FE-SEM) and Energy Dispersive Spectroscopy (EDS) analysis (FEI Inspect F-50 series and EDAX analyzer). The phase that existed in the specimen was detected by an x-ray diffractometer (Panalytical X’Pert Pro...
MPD). The data was analyzed by using X’Pert Highscore software. The composition of HA particles was also tested using Fourier transform infra-red (FTIR) spectroscopy (Thermo Scientific Nicolet iS50).

2.5. Electrochemical test
The electrochemical corrosion test was performed in the Ringer solution at 37 °C. The ion concentration in Ringer solution was similar to that reported in our earlier work [24]. The tests included electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization using a potentiostat (CorrTest CS310). The test uses three electrodes, silver/silver chloride (Ag/AgCl) in KCl as a reference electrode, a platinum mesh as a counter electrode, and the sample as a working electrode. The solution was stirred at a constant rate of 300 rpm using a magnetic stirrer, and the temperature was kept at 30 °C ± 1 °C. For the potentiodynamic polarization test, the potential was swept at a speed of 0.5 mV s\(^{-1}\) from −100 mV below OCP to 100 mV above OCP. The corrosion potential and current density were determined from the polarization curve by the Tafel extrapolation method. The EIS data were collected by conducting the test at potential ±10 mV from OCP, at a frequency range of 10\(^{-2}\) to 10\(^{6}\) Hz.

2.6. Immersion test
The specimen was immersed in simulated body fluid (SBF) at pH 7.4 and temperature 37 C for 28 days. Each specimen was placed in a hanging configuration in a sealed polyethylene (PE) bottle containing 100 ml SBF. The bottle was immersed inside water bath equipped with temperature regulator.

3. Results and discussion

Figure 1 shows the raw HA powders used for the suspension preparation. The HA particles, which exhibited a polyhedral shape with an average size of 20 μm (figure 1(a)), consisted of smaller grains with a size of 1–5 μm (figure 1(b)). The grains, which exhibited a rough surface, were attached each other. Few particles with the size of 1–5 μm distributed randomly among the bigger particles. Agglomeration of HA particles is unavoidable when using micron or nano-size HA powder. A previous report [9] has shown observation using electron microscope results in a ten times larger grain size of HA than stated in the MSDS of a commercial product. The water or hydroxide content in the HA particles gave the tendency of the particles to attach to the nearest particles.

The 2D digital microscope images of the deposited HA coating on the Ti substrate are displayed in figure 2. Following the EPD process, the metallic CP-Ti surface turned to matte white due to surface coverage by the HA deposit. The entire surface was successfully enclosed by the HA coating resulting from EPD for 30 min at the formation voltage of 20, 30, and 40 V. The HA coating appeared as a solid and uniform white layer on the Ti substrate. The results indicated that the suspension for EPD was stable, and the HA particles were fully suspended in DMF. Unstable suspension tended to result in a non-homogeneous layer [21]. The layer thickness was approximately 40 μm for all the coatings. The limitation in the magnification restricted the accurate thickness measurement using the digital microscope images. Few cracks were observed in the layer formed at 40 V (figure 2(f)), while no crack was observed in the coatings formed at lower voltages. Cracks might form during the drying of the specimen after EPD. We have also tried to sinter the coated specimen to enhance the coating compaction. However, sintering tended to induce many opening cracks in the coating resulting in a grainy HA layer. Therefore, the characterization and tests in this work were only for the green coating.
The morphology of HA coating on CP-Ti substrate is displayed in figure 3 on both surface and cross-sectional views. The HA coating consisted of a stack of HA grains with a size of 0.5–3 μm, as shown in figures 3(a), (c), (e). There was no significant difference in the granule size with the variation of formation voltage. The HA granule deposited on the Ti surface was significantly smaller than that of the raw powder (figure 1). The results indicated that most of the agglomerated particle was dispersed into individual grains in the suspension medium. The smaller the HA grain size is better for application. The use of nano-grain HA as implant base materials showed a better healing response of host tissue [25]. Local thickening of the HA layer observed in figure 3 gave bright contrast. Although the surface view showed a granular structure, the cross-sectional views showed a compact structure.

The bulk coating formed at 20 V showed a more porous structure (figure 3(b)) than that formed at higher voltages (figures 3(d) and (f)). The cross-sectional images revealed that the HA layers consisted of fine grain, giving a rough morphology in the 20 V-coating, while higher compaction of grains led to smoother layers in the 30 V- and 40 V-coatings. The higher the applied voltage during EPD increased the electric field developed across the layer, enhancing bonding between the HA grains. Crystallization of HA grains during coating formation at 30 and 40 V yielded in coarsening of HA particles. The particle size increased with the applied voltage. The biggest HA particles reached the size of 50 μm in the coating formed at 40 V. Unfortunately, the coarse HA particles induced cracks in the surrounding matrix, as observed in figures 3(d) and (f). Similar to the previous finding [18] that revealed cracks in the HA layer deposited by EPD at a high voltage, higher than 50 V. Moreover, the coating formed at 20 and 30 V attached better to the metal surface, as noticeable from the smoother interface relative to those formed at a higher voltage. The coating thickness can be measured more accurately from the cross-sectional images to complement the observation by digital microscope image in figure 2. The average thickness for the coating formed at 20, 30, and 40 V was 32.2, 50.5, and 60.6 μm, respectively. The thickness increased linearly with the formation voltage. The higher the applied voltage, the more charged particles are

Figure 2. Digital microscope images from the (a), (c), (e) surface view and (b), (d), (f) cross-sectional view showing the HA coatings formed at (a) and (b) 20 V, (c) and (d) 30 V, and (e) and (f) 40 V.
attracted to the cathode, resulting in a faster deposition rate. The HA coating thickness for an implant application typically falls about 50–100 μm [26].

The composition of HA coating shown in figures 3(a), (c), and (e) was analyzed by EDS. The results are displayed in figure 4. The coatings were composed of elements C, O, P, and Ca. The signal of Ti originated from the underlying substrate. The coatings exhibited a relatively similar composition independent of the formation voltage. The Ca and P concentrations were 20 at% and 11 at%, respectively. The Ca/P ratio of the coatings was 1.82. The ratio is close to the stoichiometric apatite, 1.67 [27]. The slightly higher ratio indicated high purity of HA.

The FTIR analysis was performed to investigate the chemical composition of HA. Figure 5 shows the FTIR graph for the HA powder, DMF/HA suspension, and HA coating. The peaks and the corresponding chemical bonding are listed in table 1. The analysis revealed the fingerprint of HA detected in all the specimens, as shown by the peaks corresponding to the functional group of hydroxyls (OH$^-$), phosphate (PO$_4^{3-}$), and carbonate (CO$_3^{2-}$). The result was similar to that obtained by earlier work [22]. The number of peaks for each functional group became numerous in the suspension. The hydrated OH$^-$ ion in the HA particles was detected in the band range of 3000–3600 cm$^{-1}$. The sharp peak at 1955 cm$^{-1}$ in the HA/DMF spectra was also related to the stretching vibration of OH$^-$ ions. The characteristic for PO$_4^{3-}$ ions appeared in a wide range of bands from
400–1300 cm\(^{-1}\). The carbonate signal increased in the colloidal suspension, as shown by more peaks appearing in the graph due to the dissolved CO\(_2\) from the ambient air. Less number of carbonate peaks were displayed for HA powder and HA coating. The dissolved CO\(_2\) may be unintentionally included in the EPD process or during the drying of the specimen [22]. Apart from the incorporation of carbonate, no phase change of HA occurred either during suspension preparation or during EPD.

The phase that existed in the coating was analyzed by XRD. Figure 6 shows the XRD pattern of the HA coatings as compared to the bare Ti substrate. The patterns revealed \(\alpha\)-Ti peaks, which came from the substrate, and a series of HA peaks in the wide range of 2\(\theta\) angles from 20\(^{\circ}\)–50\(^{\circ}\). The HA coating was successfully deposited on the Ti surface by EPD at 20, 30, and 40 V. The characteristic peaks for HA were similar to that reported [19] for HA coating on Ti-Al-V alloy. The peaks for Ti remained detected in the coated specimen due to the presence of defects such as porosity and cracks in the coatings allowing the x-ray to penetrate down to the underlying substrate. The intensity of \(\alpha\)-Ti peaks at 38.2\(^{\circ}\), 39.9\(^{\circ}\), and 52.7\(^{\circ}\) decreased significantly in the pattern of 30V-coating, indicating high coating density. Most of the apatite peaks were tiny compared to the substrate peak, indicating the small size of HA crystallite in the coatings. The XRD analysis confirmed the presence of crystalline HA, which stated that no phase transformation occurred either during the preparation of the suspension or EPD process, in agreement with the FTIR analysis.

The corrosion resistance of the HA coatings was examined by EIS measurement in Ringer solution. EIS is a powerful technique for analyzing the impedance of a coating-metal system. Figure 7 displays the EIS spectra in Nyquist, bode magnitude, and bode phase plots. The Nyquist diagram in figure 7(a), which plots the real and imaginary impedance, shows that the coating exhibits capacitive behavior. The diameter of the capacitive loop varied depending on the formation voltage. The largest loop was obtained in the 30 V-coating, while the 40 V-coating demonstrated the smallest. The largest loop diameter represented the highest impedance magnitude. The bode magnitude of 30 V-coating, particularly at the low-frequency range, was significantly higher at
300 kΩ.cm² than other specimens, as shown in figure 7(b). The coatings developed at 20 and 30 V exhibited similar behavior that the impedance increased as going to the low frequency. On the contrary, the bode magnitude of the 40 V-coating decreased at the low-frequency range. The low-frequency range represents the response of the interface between coating and metal. The cracks in the layer lowered the corrosion resistance because the solution easily penetrated the coating. The bode phase graph displayed the capacitive behavior, which revealed the broad peak of the phase angle at −80°.

**Table 1.** Chemical group for peaks in FTIR spectra of HA.

| Wave number (cm⁻¹) | HA powder | HA/DMF suspension | HA coating | Chemical bonding |
|-------------------|-----------|--------------------|------------|-----------------|
| 3400              | 1955, 3332, 3547 | 3345              | OH⁻        |
| 419, 471, 564, 603, 962, 1029 | 405, 565, 1063, 1088, 1152, 1255 | 471, 563, 603, 963, 1029, 1263 | PO₄³⁻ |
| 874, 1420         | 637, 865, 1384, 1403, 1438, 1504 | 801, 875, 1420, 1454 | CO₃²⁻ |
|                   |           | 1595              | H₂O        |
The EIS data were fitted following the equivalent circuit in the inset image in figure 7(a). The fitting parameters are listed in table 2. The electronic circuit consisted of solution resistance (Rs) connected in series with polarization resistance and constant phase element (Rp-CPEp). The constant phase element (CPE) was used to compensate for the deviation from capacitive behavior because the loop was not fully half-circle. The n value is a constant with a value between 0 and 1, which indicates the deviation from capacitive behavior. The n values obtained for the three coatings are close to 1 (0.86–0.93), indicating the proximity to the capacitive characteristic. The polarization resistance (Rp) represented the corrosion resistance of the specimen. The highest resistance ($2.00 \times 10^5 \text{ k}\Omega \cdot \text{cm}^2$) was obtained for the 30 V-coating, while the lowest, about an order magnitude lower, was obtained for the 40 V-coating. The polarization resistance of the 20 V-coating was not significantly different than that of the 40 V-coating. The EIS results inferred the best corrosion resistance on the 30 V-coated specimen.

Figure 8 shows the results of the potentiodynamic polarization test of the HA-coated specimen in Ringer solution at 37°C. The polarization curve of CP-Ti was not included in the graph as it was already reported elsewhere. An earlier study [28] revealed that the corrosion potential of CP-Ti in Ringer solution ranged between $-0.65$ and $-0.50 \text{ V}_{\text{SCE}}$ in the replicated specimens, and the corrosion current density was 1 $\mu\text{A cm}^{-2}$. Converting the potential to $\text{V}_{\text{Ag/AgCl}}$, the corrosion potential of CP-Ti was between $-0.61$ and $-0.46 \text{ V}_{\text{Ag/AgCl}}$. The analysis by Tafel extrapolation is presented in table 3, which tabulates the corrosion potential and current density data. The corrosion potential of the HA-coated specimens was in the range of $-0.15$ to $-0.08 \text{ V}_{\text{Ag/AgCl}}$. The lowest corrosion potential was obtained for the 30 V-coated specimen, while the highest was for the 40 V-coating.

### Table 2. EIS fitting parameters.

| EPD Voltage | Rs (Ω.cm²) | Rp (Ω.cm²) | CPEp (F.cm⁻²) | n       |
|-------------|------------|------------|---------------|---------|
| 20 V        | 10.0       | $4.09 \times 10^4$ | $8.50 \times 10^{-5}$ | 0.86    |
| 30 V        | 16.1       | $2.00 \times 10^5$ | $6.05 \times 10^{-5}$ | 0.93    |
| 40 V        | 13.0       | $2.18 \times 10^4$ | $5.02 \times 10^{-5}$ | 0.91    |
V-coated specimen. However, the corrosion current density of the 30 V-coated specimen was approximately an order magnitude lower than that of the other specimens. Moreover, the anodic current of the 30 V curve was significantly lower than the other two curves. The anodic current density of the 40 V-specimen increased faster as it departed from the corrosion potential relative to the other two specimens. The corrosion potential represents the susceptibility to corrosion initiation, while the corrosion current density was directly related to the corrosion rate\(^2\). The high corrosion potential obtained in the 40 V-specimen was likely attributed to the thickest HA layer formed at 40 V, which delayed the solution penetration. The cracks in the coating remained to expose the cathodic sites on the substrate, as demonstrated by the cathodic current density, which was as high as the bare specimen. Significant suppression of cathodic current in the 30 V curve, indicated effective coating coverage, relative to the 20 and 40 V curves, shifted the corrosion potential to the negative direction. Higher coating compaction in the 30 V-coating inhibits penetration of the corrosive solution to the underlying metal surface, hence, improving the corrosion resistance of the specimen. Meanwhile, defects such as pores in the 20 V-coating and crack in the 40 V-coating became an easy path for the corrosive solution to infiltrate the coating and initiate corrosion on the Ti metal surface. The polarization result was consistent with the EIS result and the FE-SEM observation that the optimum formation voltage for obtaining optimum corrosion protection was 30 V.

The coated specimens were soaked in simulated body fluid (SBF) for 28 days to investigate the coating stability in physiological solution. Figure 9 shows the surface appearance and the EDS analysis of the corresponding surface after immersion. The coatings formed at 20 and 30 V were stable and remained attached to the metal surface after immersion. However, the P concentration increased to 15 at%, which is 4 at% higher than that of the green coating. The concentration of O was about the same as before immersion. In addition, magnesium (Mg) was detected in the coating at 1 at%. The surface appearance of 30 V-coating was denser and more homogenous than the 20 V-coating after the immersion. The stable coatings protect the metal surface from corrosion. On the contrary, the coating formed at 40 V detached entirely from the surface during immersion. EDS analysis detected a very high C concentration indicating the presence of an organic substance that led to the charging effect under electron beam exposure. The elements Ca and P were not detected on the surface (below 1 at%). The O concentration also dropped to half of the concentration before immersion. The results indicated that the coating formed at 40 V was not stable during exposure to the physiological environment.

The surface layer of the coated specimen exhibited different morphology after immersion in SBF for 28 days. Figure 10 shows the higher magnification images of the specimen showing the HA morphology before and after immersion. Prior to immersion, all the HA coating exhibited a granular structure. After immersion, the HA grains in the 20 V- and 30 V-coatings exhibited a spongy structure, as shown in figures 10(b) and (d). Thickening of the HA layer might have occurred during immersion in SBF. The HA layer formed in SBF was reported\(^3\) to have a scallop and spongy structure with a size range of 5–10 μm. The Ca/P ratio of the surface layer after immersion in SBF for 28 days decreased to 1.46. The result indicated that the HA layer developed in SBF was a Ca-deficient HA compound. Meanwhile, the 40 V-coated specimen exhibited a rough surface with a little HA.

Figure 8. Potentiodynamic polarization curves of HA coated specimens at formation voltage of 20, 30, and 40 V in Ringer solution.
Figure 9. EDS analysis on the surface area of HA coatings after immersion in simulated body fluids for 28 days.

Table 3. Corrosion current density and corrosion potential data from potentiodynamic polarization curves.

| Specimen     | $i_{corr}$ (A cm$^{-2}$) | $E_{corr}$ (VAg/AgCl) |
|--------------|--------------------------|------------------------|
| Coated-20 V  | $1.67 \times 10^{-7}$    | $-0.11$                |
| Coated-30 V  | $8.71 \times 10^{-8}$    | $-0.15$                |
| Coated-40 V  | $8.53 \times 10^{-7}$    | $-0.08$                |
coating residue (figure 10(f)). The material that can induce the natural growth of the Ca-P compound in a physiological solution is classified as bioactive material [31]. The HA coating developed by the EPD method at 20 and 30 V enhanced the surface bioactivity of Ti.

4. Conclusion

Hydroxyapatite (HA) coatings were deposited uniformly on the CP-Ti surface using electrophoretic deposition (EPD) at 20–40 V. The compositional analyses by FTIR, XRD, and EDS revealed no phase change of HA particles when dissolved as HA/DMF suspension or during EPD. The ratio of Ca/P of the HA coatings was 1.82, close to the stoichiometric HA. The coating thickness increased linearly from 32 to 60 μm with increasing formation voltage. The thick coating did not necessarily provide better corrosion protection. The highest corrosion resistance was attained at 30 V formation voltage, resulting in a layer with an order magnitude higher polarization resistance and ten times lower corrosion current density than the other two specimens. The coating formed at 30 V exhibited fewer defects (pores and cracks) and higher compaction, which resisted corrosion attack better than the other two specimens. Crystallization of big HA particles at 40 V induced cracks in the coating. Consequently, the layer was dissolved entirely from the surface, while the coatings developed at 20 and 30 V remained intact during immersion in SBF for 28 days. The optimum voltage for depositing HA coating by EPD at a suitable thickness (≥ 50 μm) for biomedical application was 30 V considering the coating stability and high electrochemical corrosion resistance in physiological solution.

Acknowledgments

This research is funded by Directorate of Research and Development, Universitas Indonesia through Hibah Publikasi Terindeks Internasional (PUTI) Q2 (No. NKB-639/UN2.RST/HKP.05.00/2022).

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.
Declaration of competing interest

The authors declare no competing financial interests.

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