Fabrication and Electrochemical Properties of Hierarchical Titanium Dioxide Nanoflower-Calcium Phosphate Composites

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The biological properties of implants can be improved by modifying calcium phosphate (CaP)/TiO$_2$ thin films on dental implants by controlling the structure, morphology, and thickness of the TiO$_2$ layer. Hierarchical TiO$_2$ nanoflowers (TNFs) were successfully fabricated on titanium substrate via hydrothermal reaction of titanium tetraisopropoxide and hydrochloric acid aqueous solution at 180°C for 3 h. The TNF films were soaked in modified simulated body fluid (m-SBF) for 1 to 7 days to form CaP crystals. The crystalline structure, shape and size of the prepared composites were characterized by X-ray diffractometry and scanning electron microscopy (SEM). The nucleation and growth of calcium phosphate coating on TNF in m-SBF solution were investigated using SEM, XPS, and FT-IR surface analytical techniques. The density of CaP increased with increase of soaking time in m-SBF. The CaP crystallites coated on TNF were obtained as spherical agglomerates with nano-sized calcium phosphate particles exhibiting low β-TCP crystallinity. The CaP/TNF coatings showed significant improvement in corrosion resistance compared with TNF coating.

Keywords: TiO$_2$ nanoflower; Hydrothermal method; Modified-simulated body fluid; Calcium phosphate, Corrosion resistance

1. INTRODUCTION

Titanium oxide (TiO$_2$) has been proposed as a substitute for the currently used biomedical coatings due to its chemical stability, nontoxicity, and biocompatibility. The biological response to titanium depends on the surface chemical composition and the ability of TiO$_2$ to interact with adsorbed molecules and incorporate elements [1]. Surface topography plays a fundamental role in regulating the cell behavior, including cellular shape, orientation, and adhesion [2, 3]. The topography of TiO$_2$ nanostructure is characterized by a more defined, reproducible, and reliable roughness result in enhanced bone cell function. The vacant TiO$_2$ nanostructures can be filled with bioactive species to provide an
interface for anchoring connective tissue. The development of biocompatible coatings is intended primarily to develop a new surface topography or alter the chemical composition of the surface layer [4]. However, selecting nanocoatings with optimal surface structure to reduce the osteointegration period on titanium implants is a challenge.

Nanostructured TiO$_2$ materials with various morphologies such as nanoparticles, nanorods, nanowires, nanotubes, and other hierarchical nanostructures have been produced by different techniques, including hydrothermal/solvothermal processes [5-7], sol-gel method [8], anode oxidation [9], vapor deposition [10], and microwave techniques [11]. Hydrothermal technique is one of the most convenient and effective methods for the preparation of metal oxide nanostructures like TiO$_2$. The properties can be enhanced easily by varying the hydrothermal conditions. TiO$_2$ nanostructures have been extensively investigated in biomedical applications. Calcium phosphates are the most important inorganic constituents of biological hard tissues in bone and teeth occurring in the form of hydroxyapatite [(HA), (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$)] [12]. Calcium phosphates/TiO$_2$ nanoflower (TNF) composites were prepared by immersing the TNF/Ti substrates in m-SBF solution. The TiO$_2$ nanostructures enhance apatite formation compared with common native oxide layer on titanium. Functionalized TiO$_2$-based nanostructures are effective in many biomedical applications such as bone scaffolds, vascular stents, drug delivery systems, and biosensors. Nano-TiO$_2$ scaffolds accelerate the rate of apatite formation and enhance osteoblast adhesion, proliferation, and differentiation [13-15]. TNF films ensure adequate blood compatibility and anti-coagulation characteristics, and thereby represent promising materials for vascular implants, and nanostructured TiO$_2$ has been widely used as a drug carrier [16].

In recent years, the various properties of both natural and artificial titanium oxide layers have been extensively investigated to elucidate the benefits of TiO$_2$ in bone bonding [17]. CaP/TiO$_2$ nanocoatings on a titanium surface were used in biomedical application by creating TiO$_2$ surface geometry and coating the TNF surface layer with CaP. TNF synthesis is thus the first step in the formation of calcium phosphate layer on the TNF/Ti substrate. The heterogeneous nucleation and growth of CaP on TNFs has been investigated due to its orthopedic and dental applications [18-22].

In this study, XPS, FT-IR, and transmission electron microscopy (TEM) techniques were used to evaluate the characteristics of CaP/TNF composite. A hydrothermally synthesized TNF layer has been shown to facilitate CaP deposition from m-SBF solution. The corrosion resistance of CaP/TNF composite was investigated using AC impedance and potentiodynamic polarization.

### 2. EXPERIMENTAL

2.1. Preparation of TiO$_2$ nanomaterials

Commercially pure titanium disks (cp-Ti, grade 2) measuring 12 mm in diameter and 1.4 mm in thickness were polished using #400 to #2000 SiC papers. The polished discs were ultrasonically cleaned in acetone, ethanol, and deionized water for 15 mins and then dried under atmosphere. Titanium isopropoxide [Ti(OCH(CH$_3$)$_2$)$_3$, 97%] and hydrochloric acid (HCl, 37 wt%) were acquired from Sigma-Aldrich (Sigma-Aldrich Korea) and used as received. The mixture of 0.75 mL of titanium isopropoxide
and 30 mL of HCl solution was placed in a Teflon-lined stainless-steel autoclave and stored in furnace at 180°C for 3 h. After the reaction was completed at the desired temperatures and times, the autoclave was cooled to room temperature. Based on the conditions used to control the hydrolysis of precursor, we found that a 5:5 v/v ratio of water to HCl was optimal for reproducing surface morphology and obtaining TNF structures.

2.2. Preparation of calcium phosphate coatings

TNF samples were immersed in 50 mL of m-SBF solution for 1 to 7 days at 37°C. The m-SBF solution was changed every 2 days. The m-SBF was prepared by dissolving NaCl, KCl, MgSO₄, MgCl₂, NaHCO₃, CaCl₂·2H₂O, KH₂PO₄ and tris-hydroxymethyl aminomethane in ultra-pure water and titrated at pH 7.4 using 1 M HCl, which was almost comparable to ion concentrations (Na⁺ 141.0 mM L⁻¹, K⁺ 4.0 mM L⁻¹, Mg²⁺ 1.5 mM L⁻¹, Ca²⁺ 5.0 mM L⁻¹, Cl⁻ 145.0 mM L⁻¹, HCO₃⁻ 4.2 mM L⁻¹, SO₄²⁻ 0.5 mM L⁻¹, H₂PO₄⁻ 2.0 mM L⁻¹) in human blood plasma used to estimate bioactivity [23]. All the samples were immersed under static conditions in a biological incubator at 37°C for 1 to 7 days and then removed from solution, followed by rinsing with distilled water for further studies and analyses. The products obtained under different immersion times in m-SBF solution were denoted as TNF-m₁d, TNF-m₃d, and TNF-m₇d, where m₁d to m₇d denote the immersion periods of 1, 3 and 7 days, respectively.

2.3. Characterization of TNF and calcium phosphate coatings

The surface morphology of the samples was analyzed with a field emission scanning electron microscope (FE-SEM; S-4700, Hitachi). The crystalline structure of TiO₂ nanostructures grown on different substrates was determined from the XRD pattern obtained using an XRD-6000 (Japan) X-ray diffractometer in the diffraction angle range of 5 – 80° with Cu-Kα radiation (λ=1.54 Å). Raman spectroscopy (FLEX G, Tokyo instruments, Inc.) with a double monochrometer was used to characterize the CaP coatings on TNF/Ti and Ti surfaces. The scan rate was 2 cm⁻¹ s⁻¹, and the integration time was 1 s. The samples were illuminated with about 50 mW of 532 nm radiation using a laser-diode pumped laser. All the spectra were recorded under a backscattering geometry with an 80 × microscope objective. The laser beam was focused on a 1 μm spot using a confocal microscope.

The morphology and structure of TNF and the nano-crystallites formed in m-SBF solution were examined using TEM, selected area electron diffraction (SAED) pattern and high-resolution transmission electron microscopy (HRTEM; TECNAI F20 Philips, Netherlands) operated at 200 kV. The TEM sample was prepared by dispersing powders in water and drying on a carbon-coated Cu grid. The chemical composition of the sample surface, TNF and CaP/TNF formed via immersion in m-SBF solution, was characterized using X-ray photoelectron spectroscopy (Microlab 350) using AlKα non-monochromated radiation (1486.6 eV; 300 W) as the exciting source and a pressure of 10⁻⁹ mbar. The binding energy of the target elements (Ti 2p, O 1s, C 1s, Ca 2p, and P 2p) was determined at a pass energy of 40 eV, with a resolution of 0.83 eV, using the binding energy of carbon (C 1s: 285 eV) as reference. A linear or Shirley background subtraction was used to obtain XPS signal intensity. The peaks
were fitted using the mixed Gaussian-Lorentzian function.

Electrochemical measurements were carried out using a classical three-electrode cell, with platinum as the counter electrode, saturated calomel electrode (SCE, +0.242 V vs. SHE) as the reference electrode, and the CaP/TNF samples as the working electrode. The impedance spectra were acquired in the frequency range of 100 kHz to 1 Hz with a modulation amplitude of 10 mV. Electrochemical impedance data were fitted to an equivalent circuit model using Zview software. The potentiodynamic polarization studies were performed using a Wonatech potentiostat (model SP1) in the range of –0.75 to 1.5 V at a scan rate of 1 mVs\(^{-1}\).

3. RESULTS AND DISCUSSION

Figure 1. FE-SEM micrographs of CaP particles formed on hydrothermally grown TNF under varying immersion times in m-SBF solution. (a) TNF; (b) TNF-m1d; (c) TNF-m3d; (d) TNF-m7d. The inside of (b) represents the cross-sectional view of TNF-m1d.

Figure 1 displays the FE-SEM images of TNF and CaP particles formed under different immersion times in m-SBF solution on hydrothermally grown TNF. The synthesized TNFs shown in Fig. 1a consist of a bunch of aligned nanorods with different orientations. Notably, the nanorods are
tapered at the tip and separated from each other as hierarchical flower-like nanostructures. The TNF were immersed in m-SBF solution and, the surfaces were covered with CaP crystallized from the m-SBF solution. Fig 1b displays the SEM images of TNF with CaP coatings after 1 day of immersion. The cross-section reveals the formation of approximately 2-μm-thick CaP deposits mainly on the surface of TNFs. Upon prolonged immersion for 3 days, the small nanoparticles rapidly agglomerated into compact microspheres (300–400 nm, Fig. 1c). Numerous small protuberances appeared on the surface of the microspheres as the reaction progressed (Fig. 1d). A significant increase in thickness was observed following immersion from 3 to 7 days.

After biomimetic deposition, the surfaces of the TNFs were covered with CaP crystallized from the m-SBF solution. Each TNF/Ti substrate exhibited a CaP-related XRD peak. The XRD patterns of the calcium phosphate precipitate obtained in the calcium phosphate deposition experiment showed broad and low-intensity peaks that matched the index card of β-TCP (Fig. 2). It was difficult to identify the exact species formed on the surface. However, the CaP deposited on TNF was poorly crystallized β-TCP. The as-prepared TNFs resulted in a rutile structure, which was confirmed using XRD.

![Figure 2. XRD patterns of CaP particles deposited on hydrothermally grown TNF at various immersion times in m-SBF solution. (a) cp-Ti; (b) TNF; (c) TNF-m1d; (d) TNF-m3d; (e) TNF-m7d.](image)

In Fig. 3, the Raman spectra of these TNFs show strong Raman bands due to the δ(TiO₂) bending vibration (455 cm⁻¹ for rutile) and the symmetric v(TiO₂) stretching vibration (617 cm⁻¹ for rutile). The Raman bands of rutile phase appear at 250, 455, and 617 cm⁻¹, which can be attributed to the B1g, Eg, and A1g modes, respectively [24, 25]. As shown in Fig. 3, the Raman spectra of CaP tribasic reveal several intense Raman bands. The three bands were assigned to the v(PO) stretching vibrations at 934, 966 and 974 cm⁻¹ [26]. The main peak was observed at 974 cm⁻¹. Other frequencies are detected forming
a broad peak at 934 cm\(^{-1}\) and a shoulder at 966 cm\(^{-1}\). As the internal bands are centered at about the same frequencies for both \(\beta\)-TCP and HA, the wider frequency range of the \(\beta\)-TCP \(\nu_2\)- and \(\nu_4\)-type modes apparently shorten the distance between the two bands in the \(\beta\)-TCP spectrum. The spectra of all samples with a rapidly deposited CaP coating showed low-intensity peaks at 934, 966, and 974 cm\(^{-1}\). The intensity of peaks at 966 cm\(^{-1}\) increased significantly after immersion in m-SBF, indicating higher levels of CaP was present on the sample surface after 7 days of immersion.

**Figure 3.** Raman spectra of CaP particles formed on hydrothermally grown TNF at various immersion times in m-SBF solution. (a) cp-Ti; (b) TNF; (c) TNF-m1d; (d) TNF-m3d; (e) TNF-m7d.

As shown in Fig. 4a, a TEM image of the TNFs on cp-Ti substrate was obtained at different magnifications. Densely packed nanorods of TiO\(_2\) appeared in TEM image and typical HR-TEM images of TNF obtained via hydrothermal method. The as-synthesized TNF exhibit a three-dimensional nanoflower structure. The phase and crystal structures of TNF were confirmed by lattice image of Fig. 4b. The distance between lattice fringes was assigned to (110) and (001) of the rutile TiO\(_2\) phase. The crystalline distances were strongly consistent with \(d_{110} = 3.2\ \text{Å}\) and \(d_{001} = 2.9\ \text{Å}\) of the tetragonal rutile TiO\(_2\) phase, suggesting growth of TNFs along the (001) axis. The diffraction pattern of TiO\(_2\) was obtained and the lattice spacing \(d\) of TiO\(_2\) was calculated. The results showed a \(d_{001}\) of 0.23 nm along the longitudinal axis pertaining to the \(d\)-spacing of the rutile TiO\(_2\) (001) crystal planes. The HR-TEM image shows \(d\)-spacing of 0.325 nm corresponding to the (110) plane of rutile TiO\(_2\) structure (Fig. 4b). The c-axis is parallel to the (110) face, and therefore, the TNFs were grown along the (001) direction. The SAED pattern revealed that the sample was a single crystalline rutile TiO\(_2\) structure as shown in Fig.
4c. The spotted SAED indicates single crystals of rutile TNFs. It is believed that the synthesized films are composed of single crystals of rutile TiO$_2$ nanorods growing in the (001) direction.

![TEM images and SAED pattern of hydrothermally grown TNF on cp-Ti substrate. (a) TEM image; (b) HR-TEM image; (c) Corresponding SEAD pattern.](image)

**Figure 4.** TEM images and SAED pattern of hydrothermally grown TNF on cp-Ti substrate. (a) TEM image; (b) HR-TEM image; (c) Corresponding SEAD pattern.

Crystals of CaP obtained from m-SBF were further analyzed via TEM. Figure 5 a & b present the typical TEM image and SAED pattern of β-TCP crystals extracted from the CaP surfaces after immersion in m-SBF for 3 days. Also, β-TCP was identified from the SAED pattern in TEM with B (beam direction) of (110) (Fig. 5b). The interplanar spacing of 0.652 nm corresponds to the (104) plane of β-TCP, while 0.829 nm corresponds to the (012) plane of β-TCP, which is consistent with previous XRD and Raman results.
Figure 5. HR-TEM image (a) and SAED pattern (b) of CaP particles on hydrothermally grown TNF on day 3 of immersion in m-SBF solution are shown.

Figures 6a~6d display the XPS spectra of C 1s, O 1s, Ca 2p, and P 2p signals identified from individual TNF and CaP/TNF samples. The BEs of the main XPS peaks and the relative chemical composition of the TNF surface and after immersion in SBF are presented in Table 1. As shown in Fig. 6a, all the peaks representing C 1s are asymmetric, with a small shoulder appearing at higher BE. The C 1s spectrum of TNF was fitted by three peaks at 284.8, 286.1, and 288.6 eV, which were assigned to C atoms in C–C/C–H, C–O, and O–C=O bonds, respectively. The BE of the C-O bonds increased when the samples were incubated for extended duration in the m-SBF solution. Incubation longer than 3 days did not result in significant variation in the C 1s spectral intensity.

Figure 6b illustrates the O 1s XPS spectra of the TNF and CaP/TNF samples. Comparison of the TNF spectrum indicates an increase in the O 1s XPS peak as a function of incubation time up to 7 days. The O 1s signal is fitted with the three peaks at 530.3, 531.4 and 532.5 eV. The signal at 530.0 eV corresponds to rutile titanium oxide, and the peaks at 531.2 and 532.5 eV are attributed to hydroxides and adsorbed water or C- and O-contaminants, respectively [27]. The signal at 531.2 eV corresponding to phosphate-containing components was clearly enhanced and predominant after 3 days of immersion in m-SBF.

Figure 6c displays the Ca 2p XPS spectra derived from all the CaP/TNF samples, suggesting CaP coating on the TNF/Ti substrates. Each of the Ca 2p peaks displays a doublet band, which is typical of calcium oxide in inorganic calcium-oxygen compounds. Ca 2p3/2 and Ca 2p1/2 peaks emerged at 347.2 and 350.8 eV, respectively, in the TNF-m1d. The intensity of the XPS peak of representing calcium appeared to increase under prolonged incubation, indicating increased levels of calcium incorporated into the CaP/TNF samples. Concurrently, this result may indicate an increase in the thickness of CaP coating with increasing incubation time.

The P 2p XPS spectra are presented in Figure 6d. The P 2p XPS peak is already visible on the surface prepared after incubation in m-SBF. The peak intensities of the P 2p XPS spectra obtained from
the CaP/TNF samples were altered similar to those of calcium. The shape of the P 2p peak appears to be broad, suggesting the presence of two subpeaks in the P 2p band. The presence of the P 2p XPS spectra in addition to that of calcium suggests the formation of CaP coatings. The intensity of the P 2p\textsubscript{3/2} peak increased with incubation times up to 7 days. However, incubation time did not appear to elicit any significant change in BE.

**Table 1.** XPS spectral components of CaP particles formed on hydrothermally grown TNF at various immersion times in m-SBF solution

<table>
<thead>
<tr>
<th>Samples</th>
<th>Carbon</th>
<th>Oxygen</th>
<th>Calcium</th>
<th>Phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C\textsubscript{1s}</td>
<td>C\textsubscript{1s}</td>
<td>O\textsubscript{1s}</td>
<td>O\textsubscript{1s}</td>
</tr>
<tr>
<td>TNF</td>
<td>248.8</td>
<td>286.1</td>
<td>288.6</td>
<td>530.0</td>
</tr>
<tr>
<td>TNF-m1d</td>
<td>284.7</td>
<td>286.3</td>
<td>288.5</td>
<td>530.0</td>
</tr>
<tr>
<td>TNF-m3d</td>
<td>285.0</td>
<td>286.4</td>
<td>288.6</td>
<td>530.0</td>
</tr>
<tr>
<td>TNF-m7d</td>
<td>284.8</td>
<td>285.9</td>
<td>288.8</td>
<td>530.3</td>
</tr>
</tbody>
</table>
Figure 6. XPS spectra of CaP particles fabricated on hydrothermally grown TNF at various immersion times in m-SBF solution. (a) C 1s; (b) O 1s; (c) Ca 2p; (d) P 2p.

Figure 7. Nyquist plots of CaP particles formed on hydrothermally grown TNF at various immersion times in m-SBF solution at 37°C. (a) TNF; (b) TNF-m1d; (c) TNF-m3d; (d) TNF-m7d.
The Nyquist plots of TNF and CaP/TNF coated at various immersion times in m-SBF solution are shown in Fig. 7. As shown in Fig. 7, the plot for the CaP/TNF coating exhibits two capacitive semicircles at higher and middle frequencies, suggesting that the oxide layer formed on the TNF/Ti substrate comprises a porous outer layer and a barrier inner layer [28]. The impedance increased with immersion time, demonstrating that the nanoporous layer of TNF facilitated the entry of calcium and phosphate ions from m-SBF solution and filled the pores in the outer porous layer, and thereby increased the stability of the passive film. The increased surface area of the TiO$_2$ accelerates bone growth in dental implant coating. Among the CaP/TNF coatings, a dramatic increase in impedance was observed in the TNF-m3d coating after immersion for 3 days in m-SBF solution at 37°C, which suggests a nobler electrochemical behavior of the deposited coatings impeding the ion diffusion and reducing the corrosion rate of the substrate. In order to illustrate these results, the Nyquist plots were fitted using the equivalent circuit presented in Fig. 7 insert. As shown in Table 2, the CaP/TNF coatings exhibit lower capacitance ($Q_o$, $Q_i$) and higher porous resistance ($R_o$, $R_i$) than the TNF. Low capacitance and high resistance indicate the formation of a highly stable film on the cp-Ti substrate in the electrolyte. Low capacitance is associated with an increase in the thickness of passive layer. The outer layer containing TNF-m3d resulted in the best corrosion resistance, as observed in Figure 7. The fitting quality was evaluated by chi-squared ($\chi^2$) values of about $10^{-3}$ and the EIS parameters are presented in Table 2.

Fig. 8 displays the potentiodynamic polarization curves of TNF and CaP/TNF coatings under different immersion times in m-SBF solutions. As shown in Fig. 8, the corrosion potential of the CaP/TNF coating was increased and the corrosion current density was decreased compared with that of TNF. The TNF acts as a barrier and blocks the porosity of the CaP layer. The stable CaP/TNF-based ceramic structure provides a dual protection for the substrate. Both these results are attributed to the increased thickness of the CaP/TNF coating.

Table 2. Impedance parameters of CaP/TNF coatings on cp-Ti in 0.9% NaCl solution

<table>
<thead>
<tr>
<th>Samples</th>
<th>Solution</th>
<th>Rs (Ω)</th>
<th>$R_o$ (kΩ)</th>
<th>$Q_o$ (μS·s$^{-1}$)</th>
<th>$n_o$</th>
<th>$R_i$ (kΩ)</th>
<th>$Q_i$ (μS·s$^{-1}$)</th>
<th>$n_i$</th>
<th>$\chi^2$ ($\times 10^{-3}$)</th>
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</thead>
<tbody>
<tr>
<td>TNF</td>
<td></td>
<td>0.02</td>
<td>1.2</td>
<td>44.6</td>
<td>0.92</td>
<td>0.3</td>
<td>52.2</td>
<td>0.81</td>
<td>275</td>
</tr>
<tr>
<td>TNF-m1d</td>
<td></td>
<td>44.75</td>
<td>51.6</td>
<td>36.7</td>
<td>0.74</td>
<td>238.0</td>
<td>38.4</td>
<td>0.37</td>
<td>123</td>
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<tr>
<td>TNF-m3d</td>
<td></td>
<td>0.01</td>
<td>3.3</td>
<td>26.1</td>
<td>0.70</td>
<td>273.0</td>
<td>0.4</td>
<td>0.84</td>
<td>242</td>
</tr>
<tr>
<td>TNF-m7d</td>
<td></td>
<td>0.01</td>
<td>166.0</td>
<td>18.4</td>
<td>0.52</td>
<td>52.5</td>
<td>1.6</td>
<td>0.76</td>
<td>255</td>
</tr>
</tbody>
</table>

The corrosion parameters obtained using Zman software fitting are presented in Table 3. The CaP/TNF coating samples exhibit stable passive current densities under increased potential. The corrosion potentials ($E_{corr} = -0.078$V) of the TNF-m7d coating are more positive compared with those
of the TNF-m1d coating ($E_{corr} = -0.177$ V), TNF-m3d ($E_{corr} = -0.081$V) and TNF ($E_{corr} = -0.356$V). The corrosion current ($I_o = 18.4 \mu$A cm$^{-2}$) of the TNF-m7d coating is nearly three-fold lower than that of TNF ($I_o = 44.6 \mu$A cm$^{-2}$). Polarization curves of the CaP/TNF coating indicate lower degradation rates compared with that of the TNF, resulting in decreased corrosion current density and active surface for corrosion reaction.

![Polarization diagrams of CaP particles formed on hydrothermally grown TNF at various immersion times in m-SBF solution at 37°C. (a) TNF; (b) TNF-m1d; (c) TNF-m3d; (d) TNF-m7d.](image)

**Figure 8.** Polarization diagrams of CaP particles formed on hydrothermally grown TNF at various immersion times in m-SBF solution at 37°C. (a) TNF; (b) TNF-m1d; (c) TNF-m3d; (d) TNF-m7d.

**Table 3.** Corrosion parameters of CaP/TNF coatings on cp-Ti in 0.9% NaCl solution

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_{corr}$ (V)</th>
<th>$I_{corr}$ (µA cm$^{-2}$)</th>
<th>$\beta_c$ (mV/decade)</th>
<th>$\beta_a$ (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNF</td>
<td>-0.356</td>
<td>44.6</td>
<td>304</td>
<td>275</td>
</tr>
<tr>
<td>TNF-m1d</td>
<td>-0.177</td>
<td>36.7</td>
<td>249</td>
<td>123</td>
</tr>
<tr>
<td>TNF-m3d</td>
<td>-0.081</td>
<td>26.1</td>
<td>273</td>
<td>242</td>
</tr>
<tr>
<td>TNF-m7d</td>
<td>-0.078</td>
<td>18.4</td>
<td>259</td>
<td>255</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

Hierarchical rutile TNFs were successfully fabricated on titanium substrate via hydrothermal reaction between titanium isopropoxide and hydrochloric acid at 180°C for 3 h. The synthesized TNFs with a rutile structure consist of a bunch of aligned nanorods with different orientations. The TNF initially comprised nanorods formed on the cp-Ti substrate and separated from each other as hierarchical floral nanostructures. These TNF films were soaked in m-SBF for 1 to 7 days to induce the formation of CaP. The XRD and HR-TEM results of CaP synthesized on TNF showed that all peaks matched the index card of β-TCP, suggesting that the pre-deposited CaP acts as an effective nucleation surface to induce the formation of a biomimetic β-TCP coating on the TiO₂ surface. Compared with the TNF/Ti substrate, the CaP/TNF coatings showed significant improvement in corrosion resistance due to protective layers.

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