

Short communication

Fabrication, degradation behavior and cytotoxicity of nanostructured hardystonite and titania/hardystonite coatings on Mg alloys



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ABSTRACT

In this study, nanostructured hardystonite (HT) and titania (TiO₂)/hardystonite (HT) dual-layered coatings were deposited on biodegradable Mg–Ca–Zn alloy via physical vapor deposition (PVD) combined with electrophoretic deposition (EPD). Although a single layer nano-HT coating can decrease the corrosion rate from 1.68 to 1.02 mm/year, due to the presence of porosities and microcracks, the nano-HT layer cannot sufficiently protect the Mg substrate. In contrast, the corrosion resistance of nano-HT coating is further improved by using nano-TiO₂ underlayer since it was a smooth, very uniform and compact layer with higher contact angle (52.30°). In addition, the MTT assay showed the viability of MC3T3-E1 on the nano-HT and nano-TiO₂/HT coatings. The results demonstrated that the two-step surface modification improved both corrosion resistance and the cytocompatibility of the Mg alloy, hence making it feasible for orthopedic applications.

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Magnesium (Mg) as a biodegradable material possesses high biocompatibility, biodegradability and non-toxicity providing a great potential for implant applications [1–3]. In addition, Mg alloys have higher mechanical strength compared to the biodegradable polymers and it is the cofactor for many enzymes and structures stabilizer of the DNA and RNA [1]. However, the use of magnesium is hindered by its poor corrosion resistance which causes the remarkable deterioration of mechanical properties of the implant resulting in the inability of the tissue to heal [4–6]. Apart from alloying, surface coating methods such as physical vapor deposition (PVD) [7] and electrophoretic deposition (EPD) [8] are suitable for delaying the corrosion of magnesium alloys [9]. Thus, for the sake of increasing the corrosion resistance of the Mg alloy, the present work used PVD, as one of the most green methods for coating of nano-titania (TiO₂), and EPD as a simple technique [8] for nanostructured hardystonite (HT; Ca₂ZnSi₂O₇) coating. Several researchers demonstrated that TiO₂ coating enhances the corrosion resistance via the formation of a barrier film on the substrate

[10,11]. However, titania coating is bio-inert and is barely attached directly to the bone right after implantation [12,13]. Hence, addition of bioactive materials such as calcium phosphate and calcium silicate to TiO₂ coating is an appropriate way to enhance the bioactivity of the implants [14]. Hardystonite as a calcium silicate-based ceramics can induce biological fixation and tissue in-growth at the tissue/implant interface [15,16]. In addition, hardystonite is more chemically stable compared to calcium silicate-based ceramics such as dicalcium silicate Ca₂SiO₄, diopside CaMgSi₂O₆, merwinite Ca₃Mg(SiO₄)₂, bredigite Ca₇MgSi₄O₁₆ and akermanite Ca₂MgSi₂O₇ [14,16]. Furthermore, HT ceramics can improve the bone marrow stem cell proliferation and differentiation as well as its ability to induce proper bone remodeling [15]. Therefore, in present study, the PVD coupled with EPD methods was conducted for the first time to prepare nano-TiO₂ coating as an underlayer and nano-HT coating as an overlayer on magnesium alloy in order to assess its potential for orthopedic applications.

In this study, samples of Mg-1wt% Ca-4wt% Zn alloy with dimensions of 15 × 10 × 10 mm were used as substrates. The HT powders were prepared by the sol–gel process according to [16]. The nanostructured HT coating was deposited through the electrophoretic deposition method, accompanied by the conventional

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cell with a graphite rod as the anode and the Mg alloy as the cathode. The electrolyte was prepared by dissolution of nano-structured HT in methanol at a total concentration of 10 g solid/100 mL at room temperature. The solution concentration was kept uniform using a magnetic stirrer controlled at 120 rpm for 1 h. The HT coating was produced via electrodeposition at the applied voltage of 100 V for an hour with the electrode distance of 15 mm. For the nano-TiO₂ coating, a hybrid ion beam deposition system, consisting of a linear ion source and magnetron sputtering source with a TiO₂ target, was selected. An ion source with Ar gas was used to clean the surface of the Mg alloys for 40 min. This pre-treatment was performed when the base pressure of the chamber was below 2.55×10^{-3} Pa. PVD was performed at room temperature with argon as the sputtering gas. The process used a sputtering pressure of 0.24 Pa, an RF sputtering current of 200 W, the deposition time of 90 min, and a bias voltage of -150 V. X-ray diffractometry (Siemens-D500) was used for phase identification using Cu-K α radiation generated at 40 kV and 35 mA. Microstructural observation was performed using scanning electron microscopy (SEM; JEOL JSM-6380LA) and transmission electron microscopy (TEM; HT7700 Hitachi). A three-electrode cell was used for potentiodynamic polarization tests (PARSTAT 2263) and electrochemical impedance spectroscopy (EIS) in SBF solution according to [11]. The immersion test was carried out according to ASTM G1-03 in the SBF at 37 °C and the pH value of the uncoated and coated samples were monitored with a pH meter. The surface hydrophobicity of the samples was measured by static contact angles of a water droplet placed on the sample surfaces using an automatically video-based optical contact angle measurement (VCA Optima, AST Products Inc., USA) at the ambient temperature with a water droplet of about 1 μ L. The Methylthiazolyldiphenyl-tetrazolium bromide (MTT) method was used to evaluate the MC3T3-E1 cell toxicity of the uncoated and coated Mg samples. The details of the MTT test are in accordance with [17].

The SEM micrographs in Fig. 1 a,d shows that the eutectic Mg₂Ca and Ca₂Mg₆Zn₃ are formed within the matrix of the uncoated Mg–Ca–Zn alloys with a typically longitudinal morphology. The XRD patterns of the uncoated sample illustrate the formation of the Mg₂Ca₆Zn₃ and Mg₂Ca compounds besides α -Mg (Fig. 1g). It can be observed that the HT coating has a rough and porous surface (Fig. 1b,e). It is known that roughness and porosity of surfaces are advantageous for cell attachment, propagation and tissue growth

on the bone implants [18]. However, the porosity and cracks of the surface are not beneficial for corrosion resistance. This structure leads to penetration of the electrolyte into the substrate which accelerates the corrosion attack [19]. The XRD analysis of the HT coating confirms the presence of hardystonite (Ca₂ZnSi₂O₇). The calculated crystallite size of the HT powder was 78 nm according to the Scherer equation [11]. The bi-layer TiO₂/HT coating showed a smaller pore size compared to the single-layer HT coating because of the incorporation of TiO₂ as an inner layer, which may affect the porosity of the hardystonite in the top layer, as they might be embedded inside these pores (Fig. 1c,f). The XRD pattern of TiO₂ coated specimens indicated peaks at 2 θ values of 26.7° corresponding to the strong peak of rutile TiO₂ (110), besides very weak diffraction peaks related to the anatase TiO₂ (101), (004), according to the JCPDS file No. 84-1286 (Fig. 1g). The expected crystallized size of titania based on the Scherer equation [11] was 38 nm. Meanwhile, in the pattern of TiO₂/HT coating, in addition to the weak diffraction peaks of TiO₂, the diffraction peaks of hardystonite were observed. Moreover, it can be observed that the water contact angle of the uncoated sample is 46.70°, while the HT and TiO₂/HT coatings presented a contact angle of 33.40° and 37.10°, respectively, indicating that the coating has a hydrophilic surface, as the water droplet easily wets and spreads out over the coated surface which means that it is more favorable for the attachment of cells.

The cross section morphology of the bi-layer TiO₂/HT coating indicated two distinct layer structures, the HT layer at the top with a thickness of around 5–6 μ m and TiO₂ layer underneath it (Fig. 2a). The strong adhesion between the deposited coating and the underlying substrate could also be observed. The TiO₂ coating as underlayer had a thickness of around 1–1.5 μ m with a developed columnar structure (Fig. 2b). However, the surface of the nano-TiO₂ coating possesses a uniform surface dispersed with nanometer-sized particles (40–50 nm) and the contact angle of 52.30°.

The electrochemical polarization curves in Fig. 3a show that the corrosion potential (E_{corr}) of the uncoated samples (-1735.1 mV_{SCE}) shifted to the nobler direction after single-layer HT coating (-1618.2 mV_{SCE}), single-layer TiO₂ coating (-1620.7 mV_{SCE}) [11] and bi-layer TiO₂/HT coating (-1535.4 mV_{SCE}). The uncoated alloy presented the higher corrosion current density (i_{corr}) compared to the coated alloys owing to the formation of a micro-galvanic cell between the secondary phase and the α -Mg phase. However, the bi-layer TiO₂/HT coating sample presented a lower i_{corr} (5.11 μ A/

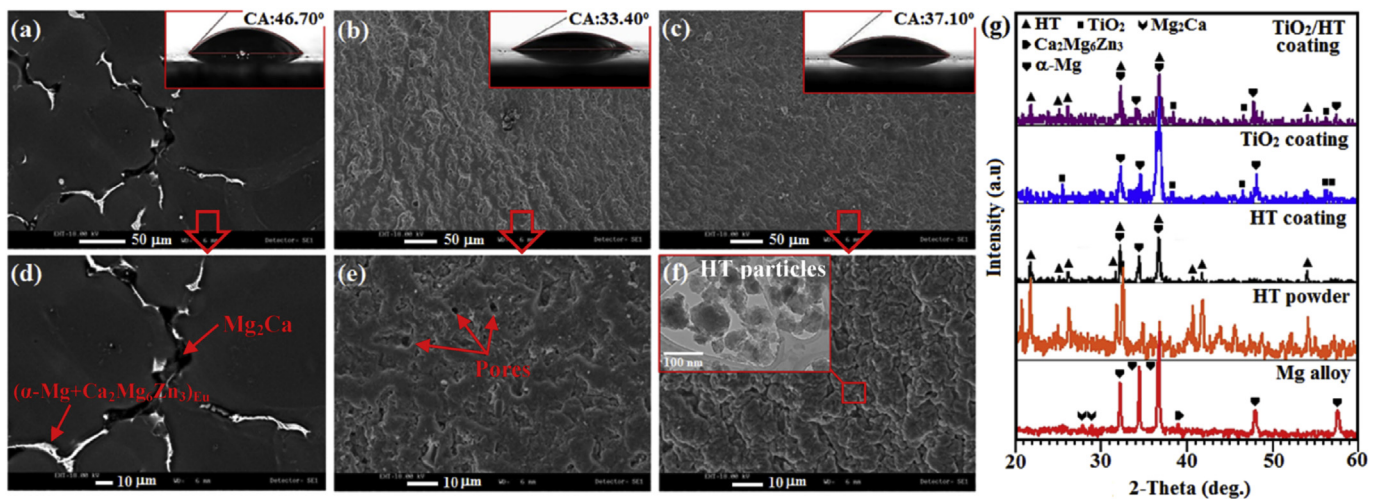


Fig. 1. Surface morphology of (a,d) uncoated Mg alloy, (b,e) single-layer HT coated and (c,f) bi-layer TiO₂/HT coated and (g) X-ray diffraction patterns of uncoated and coated Mg alloy samples.

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