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Surface functionalization of anodized tantalum with Mn$_3$O$_4$ nanoparticles for effective corrosion protection in simulated inflammatory condition

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**ABSTRACT**

The study highlights the corrosion behavior of untreated and treated tantalum with addition of trimanganese tetraoxide (Mn$_3$O$_4$) nanoparticles in simulated inflammatory media. The anodic layer was produced on pure tantalum by anodization in electrolytes composed of ammonium fluoride, ethylene glycol, and water. Nanoparticles were deposited uniformly on the surface of the anodized tantalum with the electrophoretic deposition (EPD) method. The results revealed that the anodic/EPD coating possessed more compact microstructure and higher bond strength than the anodic coating. Simulated inflammatory medium was based on phosphate-buffered saline with additions of H$_2$O$_2$ and HCl. Potentiodynamic polarization and electrochemical impedance spectroscopy studies showed that the anodic and Mn$_3$O$_4$ layers protected the tantalum from corroding in an acidic inflammatory condition. Finally, the corrosion protection mechanism of Mn$_3$O$_4$ NPs in inflammatory condition was presented.

1. Introduction

Tantalum and its alloys are widely used in orthopedics and dentistry fields due to their good biocompatibility and corrosion resistance, proper elastic modulus and high damping capacities [1]. The corrosion resistance of tantalum is secured by its ability to form a spontaneous passive oxide film on the surface, protecting it against the corrosive biological medium [2,3]. This passive film is usually only a few nanometers thick, so it may not be sufficient for protection in an acidic medium [2]. During inflammatory conditions after implantation cells release highly reactive oxygen species (ROS), such as hydrogen peroxide (H$_2$O$_2$), hydroxyl radical (•OH), superoxide (O$_2^{-}$), and hypochlorous acid (HOCl), as part of their response to infection, foreign bodies, and other inflammation-inducing conditions [4]. In parallel, osteoclast involved in bone remodeling express HCl for bone resorption which significantly drops local pH values together with the ROS release (from 7.4 to 5.5 and even down to 2.0–3.0), create an aggressive environment for the implant materials. Prior studies have demonstrated that simultaneous exposure to H$_2$O$_2$ and HCl can accelerate the degradation and corrosion rate of titanium [5], stainless steel [6], magnesium [7], and cobalt-chrome alloy [8]. However, the features of the corrosion behavior of tantalum in such inflammatory conditions still remain undiscovered. It is expected that by providing a proper surface treatment to tantalum its corrosion properties could be significantly enhanced. This could be done by controlled anodization and introduction of nanoparticles working against the ROS release.

Metal oxide nanoparticles have been used in a variety of medical applications, and in particular it was reported that trimanganese tetraoxide nanoparticles (Mn$_3$O$_4$ NPs) may possess excellent ROS-scavenging activities [9,10], eliminating H$_2$O$_2$, •OH, and O$_2^{-}$ up to nearly 75%. Moreover, the antibacterial activity and biocompatibility of the Mn$_3$O$_4$ NPs were reported by researchers in these years [11,12]. To date, several studies were carried out to incorporate manganese into the coatings matrix on the metallic implants [13], however, without sufficient evidences of the existence of the manganese oxide over the coating.

Recently Zhu et al. [14] have demonstrated that electrophoretic deposition (EPD) technology can be applied to deposit Mn$_3$O$_4$ micro-particles on Ni-coated steel for high-temperature applications.
EPD has also already been utilized for producing bioceramics coatings on the surface of metallic biomaterials [15,16]. EPD is based on an electrophoretic movement of charged particles in a suspension (containing an electrolyte, solvent, particles, additives, and dispersant) towards the opposite polarity electrode under an electrical field’s influence [17]. This technique presents significant advantages in synthesizing thin films from charged colloidal particles due to its short processing time, high deposition rate, environmentally friendly processing, and easy control of the thickness and uniformity of deposited particles through simple producing apparatus [15–17]. Usual drawback of the EPD for ceramic coatings is the insufficient bonding strength between coating and substrate for the requirements of clinical applications. To achieve high adhesion performance and corrosion resistance, pretreatment operation is required before the EPD process success on metallic substrates [18].

The anodizing technique is a cost-effective and efficient approach to increase the performance of metallic materials [19]. The primary aim of the anodizing is to generate a homogeneous, thick porous layer on the surface of a substrate [20]. It has been reported that an anodic oxide layer can act as an intermediate layer to reduce not only the corrosion rate of substrate but also to enhance the adhesion of the EPD coating [21,22]. For example, Askhab raja et al. [21] have reported the development of rGO-incorporated bioglass with 2 μm thickness via EPD on the titanium dioxide (TiO2) anodic layer of 6 μm thickness on titanium substrate.

Most literature has studied tantalum anodization using electrolytes composed of hydrofluoric (HF) and sulfuric (H2SO4) acids. Such electrolytes are very harmful to the environment and require specific safety measures for volume production [23]. There are very few studies focusing on tantalum anodization in HF-free electrolytes [24]. Fialho et al. [25] developed a pentavalent tantalum oxide (Ta5O3) layer on tantalum by anodizing in two different voltages and processing time using HF-free electrolytes. They studied the effect of the mentioned parameters on morphologies, structure, and chemical composition of the produced oxide layers, but did not address the effect of the anodization process on the corrosion behavior of tantalum.

The main aims of the current study are to design and make an anodic layer on tantalum in HF-free media as an intermediate layer for the EPD of Mn3O4 NPs on the tantalum surface and to discover the effects of these layers on the corrosion behavior of tantalum under normal physiological and simulated inflammatory conditions containing H2O2 and HCl.

2. Materials and methods

2.1. Coatings preparation

Rectangular plates (15 × 10 × 2 mm) of pure tantalum (BIMO Metals) were polished successively with 800, 1000, and 1200 grit SiC emery papers and were subjected to chemical etching in 4 M H2SO4 (98%, Sigma-Aldrich) for 2 min, following ultrasonic cleaning with ethanol (99.8%, Sigma-Aldrich) and drying in air.

The anodization process was performed using a two-electrode configuration with a direct-current (DC) power supply (Zhaoxin, KXN-6020D), comprising the tantalum sheet as the anode and the stainless steel as the cathode. The distance between the electrodes was kept constant at 1.5 cm, and the electrolyte was magnetically stirred. The anodic layer was achieved at 40 V for 20 min in an aqueous electrolyte containing ethylene glycol anhydrous (EG; 99.8%, Sigma-Aldrich), 3 vol % deionized (DI) water, and 1.2 g L−1 ammonium fluoride (NH4F; 98%, Sigma-Aldrich) [25]. The temperature of the anodization electrolyte was kept below 40 °C by using a cooling water circulation. The anodized sample was then ultrasonically cleaned with ethanol and subsequently dried by airflow.

For the preparation of the EPD suspension, 10 g L−1 of Mn3O4 NPs (99.95%, average particle size 30 nm, US-Nano) and 1.2 g L−1 iodine (I2; 99.8%, Merck) as a dispersant were added into the 125 mL ethanol and ultrasonically were mixed for 30 min. It was reported that Mn3O4 NPs are positively charged in the prepared suspension [14], so the anodized-tantalum should be connected as cathode and two stainless steel sheets electrodes as anodes. The distance between the parallel anodes and the cathode was set to be about 1 cm. The EPD process was carried out at 1 mA cm−2 using a DC voltage source at 45 °C [14]. The deposition process was conducted for 1 min. The suspension was magnetically stirred during the deposition. After deposition, the samples were dried in air at room temperature for 24 h. A schematic illustration of layers preparation by anodization and EPD techniques is shown in Fig. 1.

2.2. Materials characterization

The surface morphology, cross-sectional microstructure, and elements of the coatings were observed by field emission scanning electron microscope (FESEM; TESCAN, MIRA III) coupled with energy dispersive spectroscopy (EDS; Oxford INCA-energy 300). The transmission electron microscopy (TEM; Phillips, EM208S) of Mn3O4 NPs was carried out at an acceleration voltage of 100 kV. To examine the surface profile on the layers, three-dimensional (3D) pictures were acquired with microscopy atomic force (AFM; Ara Research Co). The layers phase analysis was analyzed using X-ray diffraction (XRD; Siemens D5000) with copper (Cu) Kα radiation source (λ = 1.5417 Å) and a monochromator at 40 kV, 30 mA in the 2θ range of 20–80° and 0.03° step per second. Fourier transform infrared spectroscopy (FT-IR; PerkinElmer, Spectrum 100) in the range of 4000–400 cm−1 with the resolution of 2 cm−1 was used to investigate the chemical compositions of surfaces. The bonding strength of the anodized- and EPD-coated samples was measured according to ASTM C-633 standard using universal testing machine (Instron 5569) with the 1 mm min−1 cross-head displacement rate and a 10 kN load cell [26].

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests were performed using potentiostat/galvanostat (EG&G, PARSTAST 2263A). All electrochemical measurements were conducted in a typical three-electrode cell of 500 mL at 37 °C with the treated- and untreated tantalum as the working electrode, graphite as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode [5–8]. Phosphate-buffered saline (PBS; pH = 7.4, Sigma-Aldrich) was used to simulate normal physiological conditions; and a 150 mM H2O2 (30%, Merck) solution in PBS titrated to pH 5.2 with hydrochloric acid (HCl; 37%, Merck) was considered to simulate inflammatory conditions around the metallic implants [5–7]. Before electrochemical measurements, the samples were soaked in the normal and inflammatory solutions for 24 h to stabilize the soaked sample’s open-circuit potential (OCP). The samples to be examined in solutions were soaked to a surface of 1 cm². Polarization studies were carried out at a sweep rate of 1 mV s−1 and were analyzed with CorrView (version 2.8) software (Scribner Associates). With a 10 mV sinusoidal potential in amplitude around Ecorr, the EIS plots were obtained across a frequency range of 0.01 Hz–100 kHz. The EIS plots were examined and fitted by the ZView (version 3.1) software (Scribner Associates). The thermodynamic calculations were performed using HSC Chemistry software (Chemistry Software Ltd).

3. Results and discussion

Fig. 2a shows the FESEM images of the untreated tantalum surface after polishing and etching, used as the reference sample during the electrochemical measurements. Fig. 2b and 2c depict the micrographs of anodized-tantalum in different magnifications. These exhibited a compact anodic layer with randomly distributed small diameter pores. No visible delaminations and crack was observed on the surface. Fig. 2d shows a representative TEM image of the Mn3O4 NPs and the insert’s corresponding selected-area electron-diffraction (SAED) pattern. It indicates that the Mn3O4 NPs have a spherical shape and...
Mn₃O₄ NPs successfully deposited [32]. Continuous, smooth, and well-bonded layer-substrate interfaces. At the viewing of the anodic layer. It has a uniform thickness, and it appears tetrahedral and octahedral sites, respectively [34]. The weak absorption peaks at 512 and 625 cm⁻¹ spectrum, the two 

The positively charged Mn₃O₄ NPs continuously migrate toward the NPs EPD layer on anodized-tantalum, shown in two magnifications in average diameter of ~35 nm. The FESEM micrographs of the Mn₃O₄ NPs EPD layer on anodized-tantalum, shown in two magnifications in Fig. 2f, indicate that the layer was uniform and homogenous. The positively charged Mn₃O₄ NPs continuously migrate toward the anodized tantalum substrate under the application of an electrical field, as shown schematically in Fig. 1 [17]. The porous structure increases the contact area between NPs and the anodized layer during the EPD. As it can also be seen in Fig. 2f, the Mn₃O₄ NPs are more or less evenly deposited on the surface of the anodic layer. The presence of some particles with a larger size in the coating is due to higher agglomeration behavior of NPs [27,28].

The AFM surface topography of anodized- and EPD coated-tantalum is shown in Fig. 2g and 2h, respectively. The root mean square (RMS) values of anodic and anodic/EPD coatings were 1.24 μm and 0.58 μm, respectively. The measured topography parameters indicate that the anodic layer has become rougher compared to the EPD coating. It has been reported that the rougher surface of the interlayer is beneficial for EPD coating adhesion to the metallic substrate [18,21,22].

The XRD patterns of anodized and EPD-coated samples are depicted in Fig. 3a. The Ta peaks in both patterns are attributed to the contribution from the substrate. The diffraction peaks revealed Ta₂O₅ (JCPDS card No. 25-0922) as the main components of the anodic layer [29]. The following mechanism can be suggested for the formation of an anodic layer on the tantalum, analogous to data [30,31]: (i) formation of a thin passive layer, (ii) transfer of OH⁻ and O²⁻ ions through the oxide layer to the oxide/metal interface and their reaction with tantalum, (iii) appearance of local nano- and micropores due to the local dissolution of the Ta₂O₅ layer. The XRD pattern of anodized/EPD coating shows Mn₃O₄ peaks (JCPDS card No. 75-1560) along with Ta peaks, indicating Mn₃O₄ NPs successfully deposited [32].

Fig. 3b represents the FT-IR analysis of samples surfaces. The absorption bands at 534 and 658 cm⁻¹ are corresponding to Ta–O–Ta and Ta–O stretching vibrational modes, indicating the formation of Ta₂O₅ during anodization [33]. In the EPD-coated sample’s spectrum, the two peaks at 512 and 625 cm⁻¹ are attributed to Mn–O stretching modes of tetrahedral and octahedral sites, respectively [34]. The weak absorption band at 1675 cm⁻¹ ascribed to the bending vibration of O–H groups joined with Mn₃O₄ NPs during EPD in an ethanol-based electrolyte [35]. A band relating to the vibration of adsorbed water was observed in 3400 cm⁻¹ (stretching mode mode) [33,34].

Fig. 4a and 4b show the FESEM micrographs of the cross-sectional view of the anodic layer. It has a uniform thickness, and it appears continuous, smooth, and well-bonded layer-substrate interfaces. At the lowest magnification in Fig. 4b it is seen that each roughly cylindrical pore extending from the interface is connected to the tantalum substrate by a thin barrier layer of around ~50 nm thickness [36]. The FESEM analysis of the cross-section of the EPD layer (Fig. 4c) indicated that Mn₃O₄ NP coating is rather dense and adherent to the underlying anodized layer. The lowest magnification in Fig. 4d shows the detail of some Mn₃O₄ NPs included on the surface of coatings near the epoxy, which has been formed during mounting. As seen in Fig. 4a and 4c, the anodic layer and EPD coating thickness were about 4.6 μm and 17.8 μm, respectively.

The elemental maps for EPD coating’s cross-section in high magnification are shown in Fig. 4e. The presence of Ta, O, and F elements from the porous Ta₂O₅ layer underneath the Mn₃O₄ coating is also confirmed from the EDS mapping. The existence of F and C is attributed to the presence of NH₄F and EG in the anodization electrolyte composition [25]. Moreover, the O and Mn elements mappings suggest a well distribution of the Mn₃O₄ NPs on the anodized layer.

The bonding strength of coatings is a crucial factor that directly affects the coated implants’ service life [37]. The bonding strength of the anodic layer was 13.1 MPa. However, the bonding strength of the anodized/EPD coated sample was 23.4 MPa which meets the orthopedic implant industry’s necessary standards (15 MPa) according to the standard ISO 13779–2 [38]. By introducing the porous Ta₂O₅ layer on the tantalum surface, the coating/substrate interface bondimproves.

Fig. 5a and 5b show the polarization curves of the as-polished and surface-treated tantalum in normal and inflammatory media solutions, respectively. Anodic branches reveal that the as-polished tantalum exhibited strong passivation behavior in both conditions [39,40]. Regardless of the imposed conditions, the anodization and EPD treatments of the tantalum improved its corrosion resistance, as can be observed from the shift of potentials towards the anodic side, compared to the as-polished tantalum [41]. The corrosion current density (icorr) can be obtained by Tafel curve extrapolation, as shown in Fig. 5c [42]. When the as-polished tantalum is exposed to an inflammatory medium, the icorr shows an increase, indicating an increase in corrosion rate. These results show that the passive film is increasingly unstable in acidic conditions when H₂O₂ is present in the environment. For coated samples immersed in inflammatory conditions, the icorr values were insignificantly increased by simultaneous presence of H₂O₂ and HCl. On the contrary, compared with that of the as-polished sample, the icorr of the anodic and anodic/EPD coatings decreased, which demonstrated that the coated samples were thermodynamically stable against corrosion in both conditions [43,44]. It can also be seen from Fig. 5c that the icorr of
the anodic/EPD sample is the lowest among the three samples, which is one and two orders of magnitude lower than that of anodized and as-polished tantalum in inflammatory medium, respectively. It can be said that through the deposition of the Mn_3O_4 NPs on the anodic layer, the increasing coating thickness and decreasing surface roughness eventually lead to the most protective composite coatings on tantalum [45].

The Nyquist plots related to the normal and inflammatory conditions are displaced in Fig. 5d and 5,e, respectively. The impedance modulus (|Z|) values at a lower frequency (0.01 Hz) are shown in Fig. 5, f. Generally, larger semicircles and higher |Z|_{0.01Hz} reflect a higher corrosion resistance [46,47]. It could be found that the distinct difference among the Nyquist plots was the size of the capacitive semicircles. Moreover, the Nyquist plots of anodic and anodic/EPD coatings exhibit two semicircles. The low-frequency semicircle traced by the anodic and anodic/EPD coated sample suggests the higher dielectric constant and considerable resistance to the corrosive ion diffusion than other samples. As presented in Fig. 5,f, the |Z|_{0.01Hz} value of all samples quickly dropped, indicating the anti-corrosion performance of the samples is greatly reduced during the inflammatory condition. In this condition, the anodic/EPD coating shows the largest |Z|_{0.01Hz} about 19.2 \times 10^3 \, \Omega \, cm^2 and the substrate is about 5.1 \times 10^3 \, \Omega \, cm^2. This result suggests that anodic/EPD can improve efficiently the substrate corrosion resistance, which is consistent with the polarization results.

Fig. 5,g depicts the equivalent circuit for as-polished tantalum in both conditions. It made of a charge transfer resistance (R_{ct}) in parallel with a double layer capacitance (Q_{dl}). To simulate the structure of the anodic and anodic/EPD coatings, a two-constant type equivalent circuit was considered (Fig. 5,h). Compared with the circuit in Fig. 5,g, it contains anodic and Mn_3O_4 coatings' resistance in parallel with a constant phase element (Rc/Qc elements) for the low-frequency loop that reveals a large capacitive behavior observed. In both circuits, R_s denotes the electrolyte resistance between the working and reference electrodes. The fitted values of the circuit elements are summarized in Table 1. At angular frequency \( \omega \) (rad s^{-1}), the impedance (Z_{\omega}) of a constant phase element is defined by Refs. [44,48]:

![Fig. 2. FESEM micrographs of the (a) as-polished tantalum, (b and c) anodic coating in different magnifications, (e) TEM micrograph of Mn_3O_4 NPs with SAED pattern, (e and f) FESEM micrographs of anodic/EPD coating in different magnification, (g and h) 3D APM images of (g) anodic coating and (h) anodic/EPD coating.](image-url)
Fig. 3. (a) XRD patterns, and (b) FTIR spectra of anodic and anodic/EPD coatings.

Fig. 4. (a) The cross-sectional FESEM image of the anodic coating, (b) the framed area at an increased magnification of the anodic coating with dashed-line, (c) the cross-sectional FESEM image of the anodic/EPD coating, (d) the framed area at an increased magnification of the anodic/EPD coating with dashed-line, and (e) EDS elemental maps of the cross-sectional FESEM image of the anodic/EPD coating.
\[ Z_\omega = \frac{1}{Q_0 \omega} \] (1)

where \( Q_0 \) is \( (|Z|)^{-1} \) at frequency 1 rad \( s^{-1} \) and \( i = \sqrt{-1} \). The value of \( n \) varies between 0 and 1, representing the amount to which the element deviates from its ideal capacitive nature. When \( H_2O_2 \) and \( HCl \) are added to the solution, \( R_{ct} \) decreases from \( 5.9 \times 10^3 \) to \( 2.8 \times 10^3 \) \( \Omega \cdot \text{cm}^2 \) for as-polished tantalum, evidencing a higher electrochemical activity in inflammatory medium. A lower \( R_{ct} \) implied more efficient charge transfer across the substrate/solution interface, which could decrease the possibility of charge recombination and thus diminish the corrosion resistance [35,41]. In Table 1, in both conditions, the \( R_c \) values of anodic/EPD coating are higher than anodic coating, indicating that duplex coating efficiently protects the tantalum substrate.

Therefore, it can be said that the deposition of \( \text{Mn}_3\text{O}_4 \) NPs has increased the barrier performance of the anodic coating [49,50]. Furthermore, its \( R_{ct} \) values increase noticeably, indicating the improvement of corrosion resistance of composite coatings. The anodic/EPD coating has lower \( Q_c \) and \( Q_{dl} \) values due to fewer pores and defects in the coating’s structure, which trap reaction products inside the pores [44]. Moreover, the \( n_c \) values for anodic/EPD coating are higher than \( n_c \) for the anodic layer. By deposition of \( \text{Mn}_3\text{O}_4 \) NPs, \( n \) values are typically increased, resulting in a smoother surface with decreased roughness, which matches the AFM study in Fig. 2 [7]. The \( \text{Mn}_3\text{O}_4 \) coated sample had the highest corrosion resistance in both media. This can be due to the formation of a low-defect and diffusion-less layer.

The corrosion protection mechanism of the anodic/EPD coated tantalum in the inflammatory condition is shown schematically in Fig. 6. The anti-corrosion mechanism can be mainly influenced by the following factors: the physical barrier effect and corrosion inhibition of \( \text{Mn}_3\text{O}_4 \) NPs based on catalytic activities. Due to the high surface area of NPs, the pores could be sealed by depositing \( \text{Mn}_3\text{O}_4 \) NPs on top of the anodic coating, inhibiting the penetration of corrosive molecules and ions via pores, resulting in a significant level of protective property for the tantalum, as seen in the left part of Fig. 6 [7,50]. The corrosion behavior of the \( \text{Mn}_3\text{O}_4 \) coating in acidic inflammatory medium can be also affected by its excellent catalytic ROS removal efficacy.

A variety of catalyst nanomaterials with ROS scavenging activities have been reported for the surface functionalization of biomedical implants. Recently Li et al. [51] demonstrated that catalase-mimetic

### Table 1

| The condition of EIS test | Samples      | \( R_s \) (\( \Omega \cdot \text{cm}^2 \)) | \( Q_{dl} \) \( (\text{F} \cdot \text{cm}^{-2}) \) | \( n_s \) | \( R_{ct} \) (k\( \Omega \cdot \text{cm}^2 \)) | \( Q_c \) \( (\text{F} \cdot \text{cm}^{-2}) \) | \( n_c \) | \( R_c \) (k\( \Omega \cdot \text{cm}^2 \)) |
|--------------------------|--------------|----------------------------------|-----------------|------|-----------------|-----------------|------|-----------------|
| Normal                   | As-polished Ta | 8.15                             | 2.61 \times 10^{-6} | 0.85 | 5.9             | --              | --   | --              |
|                          | Anodized Ta   | 7.73                             | 1.03 \times 10^{-7} | 0.91 | 6.3             | 2.88 \times 10^{-7} | 0.85 | 15.5            |
|                          | EPD-coated Ta | 9.12                             | 9.71 \times 10^{-8} | 0.94 | 9.9             | 6.20 \times 10^{-8} | 0.91 | 25.7            |
| Inflammatory             | As-polished Ta| 10.93                            | 7.29 \times 10^{-7} | 0.79 | 2.8             | --              | --   | --              |
|                          | Anodized Ta   | 12.44                            | 9.77 \times 10^{-7} | 0.88 | 2.4             | 8.31 \times 10^{-7} | 0.83 | 9.1             |
|                          | EPD-coated Ta | 11.29                            | 5.36 \times 10^{-8} | 0.90 | 5.3             | 2.16 \times 10^{-8} | 0.95 | 18.6            |

**Fig. 5.** (a and b) Potentiodynamic polarization curves, (c) \( i_{corr} \) values, (d and e) Nyquist plots, (f) \( |Z|_{0.01 \text{ Hz}} \) values, (g and h) equivalent circuits employed to fit the impedance data of (g) As-polished tantalum and (h) anodic and anodic/EPD coated tantalum.
activities of cerium oxide (CeO₂) NPs, which deposited by magnetron sputtering on acid-treated titanium, can scavange the ROS and create an anti-inflammatory microenvironment. It is also known that a range of ROS produced by bone tissue cells during inflammatory response can participate in Fenton reactions, resulting in large quantities of radical species [52]. In Fenton-like reactions, the metal ion provides an electron to H₂O₂ and creates the •OH radical through following equation:

\[ \text{M}^{n+} + \text{H}_2\text{O}_2 \rightarrow \text{M}^{(n+1)+} + \text{OH}^- + \cdot\text{OH} \]  
(2)

where \( n \) is the valence state and \( M \) represents a transitional metallic catalyst (e.g., FeS₂, Fe₂O₃, Fe₃O₄, and FeOOH), Mn₃O₄ possesses many outstanding advantages such as superior chemical stability, high adsorption ability for H₂O₂, and very low manganese ion leaching [53].

According to the Pourbaix diagram of manganese in water (Fig. 7), Mn₃O₄ is unstable in acidic pH and can react with the •OH radicals caused by the circulation processes of Mn³⁻/Mn²⁺, as described by Ref. [54]:

\[ \text{Mn}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Mn}^{3+} + \text{OH}^- + \cdot\text{OH} \]  
(3)

Besides, the pH of the biological medium influences the catalytic activity of Mn₃O₄ NPs, mostly dependent on whether the catalyst surface is H⁺/OH⁻ adsorbed. H₂O₂ prefers to interact with H⁺ in an acidic environment and decomposes into H₂O and •OH, according to theoretical calculations [55]:

\[ \text{Mn}^{2+} + \text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Mn}^{3+} + \text{H}_2\text{O} + \cdot\text{OH} \]  
(4)

As stated before, besides the Mn³⁻ compounds, the other dominant phase of the Mn₃O₄ in acidic inflammatory solution is MnO₂. MnO₂ is relatively easy to undergo reversible redox reaction between Mn³⁻ and Mn⁴⁺ state and produces the Mn₂O₃ [56]. As seen in Fig. 7, Mn₂O₃ is stable in acidic pH and can react with the •OH radicals released in equations (3) and (4) to scavenge the •OH radicals and produce Mn₃O₄ and H₂O₂ thermodynamically possible. The Gibbs free energy change (ΔG) for reactions 5 and 6 at 37 °C was calculated −69.51 and −7.71 kJ mol⁻¹ using the HSC Chemistry software, respectively. The H₂O₂ and the •OH radicals scavenging processes can be described below:

\[ 2\text{MnO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{Mn}_2\text{O}_3 + \text{H}_2\text{O} + \text{O}_2 \]  
(5)

\[ 3\text{Mn}_2\text{O}_3 + 2\cdot\text{OH}^- + \text{H}_2\text{O} \rightarrow 2\text{Mn}_3\text{O}_4 + 2\text{H}_2\text{O} \]  
(6)

By performing the reactions 5 and 6 cyclically, the manganese oxide phases could turn H₂O₂ into H₂O and O₂ again through equation (5) and, decreasing the risk of invasion of H₂O₂ [57]. It is also reported that the scavenging role of the manganese oxide phases is only efficient when the H₂O₂ decomposition rate be equal to or higher than the production rate [10]. Therefore, this study developed a novel implant surface coating using Mn₃O₄ NPs on tantalum surfaces that possessed excellent corrosion resistance and strong anti-inflammatory efficacy. The probable schematic diagram of the corrosion protection mechanism of Mn₃O₄ NPs based on catalytic activity is drafted in the right part of Fig. 6.

4. Conclusion

In the present study, we successfully proposed the EPD technique to prepare a corrosion-resistant Mn₃O₄ coating on tantalum when it is combined with an anodization process. Our results provide evidence that the corrosion rate of untreated and treated tantalum can be accelerated by inflammatory conditions. As the primary coating film on the substrate, the anodic layer can increase the corrosion resistance of tantalum in normal and inflammatory conditions. Combining anodic and EPD coatings makes it possible to develop compact, thicker, and well-adhered coatings on the tantalum surface. Electrochemical studies also revealed that the impedance modulus of the anodic/EPD coating was considerably higher than that of tantalum and anodic layer in normal and inflammatory conditions. We can propose that due to the sealing effect of Mn₃O₄ NPs, they act as a physical barrier against corrosive agents accessing the anodic layer in acidic inflammatory conditions. Importantly, the Mn₃O₄ coating protected tantalum from H₂O₂ oxidant-mediated damage by maintaining catalytic activity and suppressing ROS generation in acidic pH. Taken together, the Mn₃O₄ NPs could provide an opportunity to be utilized as a potential candidate for bone regeneration under ROS stress.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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