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# To improve corrosion resistance and hemocompatibility of magnesium alloy via cathodic plasma electrolytic deposition combined with surface thiol-ene photopolymerization

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ABSTRACT

To improve corrosion resistance and hemocompatibility of magnesium alloy (Mg alloy), a polymerized 2-methacryloyloxyethyl phosphorycholine (PMPC) coating was fabricated via surface thiol-ene photopolymerization onto Mg alloy treated by cathodic plasma electrolytic deposition (CPED). Surface morphology, chemical composition and phase composition of CPED layer and CPED/PMPC composite coating were investigated by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), respectively. Potentiodynamic polarization test and electrochemical impedance spectroscopy (EIS) illustrated that the corrosion resistane of Mg alloy in simulated body fluid (SBF) was significantly enhanced after the formation of CPED/PMPC composite coating. Platelets adhesion measurement indicated that CPED/PMPC treated Mg alloy possesses promising hemocompatibility. The approach presented here affords an effective alternative for surface modification of Mg alloy to meet the requirements of vascular scaffold materials.

## 1. Introduction

Magnesium alloy (Mg alloy) possesses great application potential acting as vascular scaffold materials due to its attractive features, including exceptional light weight, excellent mechanical properties and ability to degrade *in vivo* [1,2]. However, poor corrosion resistance of Mg alloy remains a key challenge in clinical applications. The high degradation rate under physiological conditions can cause a reduction in the mechanical integrity of the scaffolds before the vascular sufficiently repairs [3–5]. Moreover, the hemocompatibility, such as thrombus formation due to platelets adhesion, is also a vital problem for Mg alloy as vascular scaffold materials. In this respect, surface modification can be employed to solve the above problems of Mg alloy without damaging its bulk properties [6–8].

Cathodic plasma electrolytic deposition (CPED) is a novel liquid phase plasma process, in which the plasma discharge occurs in liquid precursors at atmospheric pressure and the plasma is confined to the cathode in a superheated vapor sheath surrounded by the liquid phase. CPED can be utilized to fabricate kinds of coatings on Mg alloy, Ti alloy and other metal substrates owing to the advantages of relative simple devices and moderate reaction conditions compared with that of gas phase plasma. Especially, the coatings prepared by CPED on Mg alloy substrates can improve the materials' corrosion resistance to some extent, which recently was confirmed by our group [9,10].

Despite the good performance of CPED, the coatings prepared by this method often present micropores, which may decrease the anticorrosion ability of CPED treated Mg alloy under long-term application. Therefore, it is necessary to manufacture a protective layer on CPED treated Mg alloy to seal the micropores to further improve the anticorrosion ability. Certainly, desirable sealing coatings for vascular scaffold materials should be hemocompatible. Polymers, particularly biocompatible macromolecules, can be selected as proper candidates to fabricate sealing layers on CPED treated Mg alloy [11,12]. Fabrication of polymer coatings on substrates can be realized by several chemical reactions, in which surface thiol-ene photopolymerization proceeds under benign conditions with specific selectivity, good efficiency and fast kinetics, which make it an optimal candidate [13].

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Herein, polymerized 2-methacryloyloxyethyl phosphorycholine (PMPC) coating was perpared onto CPED treated Mg alloy via surface thiol-ene photopolymerization using (3-mercaptopropyl) trimethoxysilane (MPTS) self-assembled layer as spacer. PMPC is well-known for its antithrombogenic nature [14]. Meanwhile, PMPC coating also can seal the micropores of CPED coating to further enhance the Mg alloy's anticorrision ability. Therefore, we hoped that the combination of CPED and surface thiol-ene photopolymerization would be helpful for improving anticorrosion property and hemocompatibility of Mg alloy.

## 2. Materials and methods

Commercial AZ31D Mg alloy (composition: 2.98% Al, 0.88% Zn, 0.38% Mn, Mg rest) was machined into cuboids with dimensions of 20 mm × 10 mm × 1 mm and polished (the final polishing paper was 5000 grit paper) until the surface became smooth, then cleaned in an ultrasonic bath of acetone for twice (each for 5 min).

CPED process was performed with the instrument and the protocol previously reported [9]. Mg alloy as cathode was discharged for 15 min with graphite as the anode. The electrolyte employed in this work was the solution of NaCl (4.8 g/L) and mixed solvent (ethanol and water, 5:1 v/v). The electrolyte temperature was controlled by circulating water (5 °C) during the treatment. The applied voltage, pulse frequency and duty cycle were fixed at 450 V, 100 Hz and 30%, respectively. Subsequently, CPED treated Mg alloy samples were immersed in 3% MPTS solution (solvent mixed with ethanol and water, 1:1 v/v) for 3 h to assemble MPTS molecules, then rinsed with ethanol and dried at 110 °C for 1 h. For surface thiol-ene photopolymerization, the above Mg alloy samples were placed in a 0.2 mol/L 2-methacryloyloxyethyl phosphorylcholine (MPC) solution (ethanol as solvent) with 4 mol% initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) under nitrogen atmosphere, and exposed to UV irradiation (500 W, $\lambda=365$ nm) for proper period to form PMPC coating, denoted as CPED/PMPC treated Mg alloy.

Scanning electron microscopy (SEM, FEI Quanta 200) was utilized to observe surface morphology of pristine and modified Mg alloy samples. Surface chemical composition and phase composition of the samples were investigated by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra) using monochromatic Al Kα radiation and X-ray diffraction (XRD) with Cu Kα radiation (MiniFlex600, Japan). A three-electrode electrochemical workstation (CHI660C, Shanghai Chenhua Co., China) was used for electrochemical measurements. The counter electrode was made of platinum and a reference electrode was saturated calomel electrode. Pristine and modified Mg alloy samples were allowed to equilibrate for several minutes to reach a stable open circuit potential before measurements, respectively. Potentiodynamic polarization curve was measured at a scanning rate of 0.5 mV/s. Electrochemical impedance spectroscopy (EIS) test was carried out in a frequency range from 100 kHz to 1 Hz. Platelets adhesion test was done as previously reported [15]. Briefly, fresh platelet-rich plasma was dropped onto the pristine and modified Mg alloy samples, placed in a tissue culture plate. Then the samples were incubated for 60 min at 37 °C, and they were carefully rinsed with PBS (pH 7.2), subsequently immersed in 2.5 wt% glutaraldehyde for 1 h at room temperature. Finally, the above samples were dehydrated with a series of ethanol/water mixtures and characterized by SEM.

## 3. Results and discussion

### 3.1. Surface morphology, chemical composition and phase composition

SEM images of different samples were showed in Fig. 1. Pristine Mg alloy displayed visible scratches (Fig. 1A), which were attributed to polishing abrasion. The CPED treated Mg alloy surface appeared rough structure with micropores (Fig. 1B). After the fabrication of PMPC coating on CPED treated Mg alloy, the surface presented smooth and neat feature without obvious micropores (Fig. 1C). This phenomenon could be interpreted by the formation of uniform PMPC coating on Mg alloy via surface thiol-ene photopolymerization, thus resulting in a relatively smoother surface.

XPS spectra and XRD patterns of different samples were shown in Fig. 2A and B, respectively. The appearance of C and O on pristine Mg alloy surface (Fig. 2A-a) was attributed to the hydrocarbon contamination and oxidation of the sample. After CPED treatment (Fig. 2A-b), the relative intensity of Mg1s and O1s peaks increased obviously. Furthermore, as shown in Fig. 2B, the XRD pattern of CPED coating presents phase compositions assigned to MgO (JCPDS no. 45-0946) and $Mg(OH)_2$ (JCPDS no. 07-0239), which is consistent with the results of XPS. For the MPTS treated sample (Fig. 2A-c), the presence of Si2s, Si2P, S2s and S2p peaks was ascribed to the successful assembly of MPTS spacer. After surface thiol-ene photopolymerization of MPC, new signals assigned to N1s, P2s and P2p were observed (Fig. 2A-d), illustrating the triumphant fabrication of PMPC coating on CPED treated Mg alloy.

### 3.2. Corrosion behavior

The corrosion resistance of the CPED/PMPC treated Mg alloy was evaluated through potentiodynamic polarization test and EIS measurement in SBF solution, respectively. In a typical potentiodynamic polarization curve, lower corrosion current density ($i_{corr}$) and positive corrosion potential ($E_{corr}$) correspond to lower corrosion rate and better corrosion resistance [16]. As shown in Fig. 3A, the $E_{corr}$ of pristine Mg alloy was $-1.682$ V and its $i_{corr}$ was $7.652\times10^{-4}$ A/cm$^2$, and the $E_{corr}$ of CPED treated Mg alloy was $-1.580$ V and its $i_{corr}$ was $2.235\times10^{-5}$ A/cm$^2$, which indicated the thermodynamic tendency of the corrosion decreased. After the fabrication of PMPC coating, the $E_{corr}$ of CPED/PMPC treated Mg alloy was $-1.545$ V and its $i_{corr}$ was $4.605\times10^{-6}$ A/cm$^2$, showing a positive shift of $E_{corr}$ about 137 mV and a decrease of $i_{corr}$ about

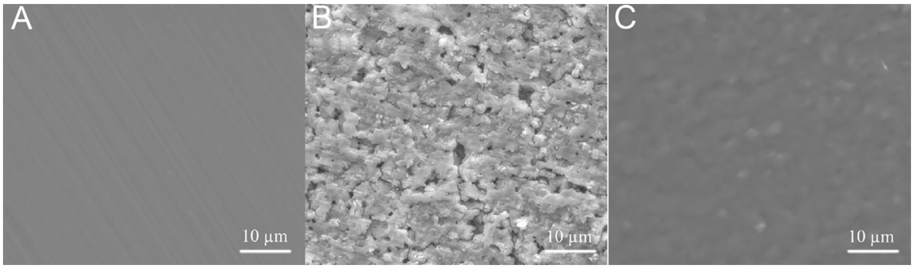

**Fig. 1.** SEM images of (A) pristine, (B) CPED treated and (C) CPED/PMPC treated Mg alloy.