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Supporting Information

Catechol/Polyethyleneimine Conversion Coating with Enhanced Corrosion Protection of Magnesium Alloys: Potential Applications for Vascular Implants

Hao Zhang,[a] Lingxia Xie,[a] Xiaolong Shen,[a] Tengda Shang,[a] Rifang Luo,*[b] Xin Li, [a] Tianxue You, [a] Jin Wang,*[a] Nan Huang,[a] Yunbing Wang[b]

[a]. *School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, China*

[b]. *National Engineering Research Center for Biomaterials, Sichuan University, Chengdu 610064, China*

Corresponding Authors

*E-mail: lrifang@scu.edu.cn. Tel: +86 28 85470537; Fax: +86 28 85470537

*E-mail: jinxxwang@263.net. Tel: +86 28 87634148; Fax: +86 28 87600625

EXPERIMENTAL SECTION

2.1 Materials

Mg-Zn (2 wt%)-Mn (2 wt%) alloy was used as substrates. For the analysis determination measurements of the elements in MgZnMn alloy, the inductively coupled plasma mass spectrometry ICP-MS (ICAP-QC, Thermo, USA) was employed. The results are summarized in Table. S1.

Table. S1. The composition of MgZnMn alloys detected by ICP-AES.

Ag	**Al**	As	Au	B	Ba	Be	Bi	Ca	Cd	Ce	Co
<0.0001	**0.0015**	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cr	Cu	Dy	Er	Eu	**Fe**	Ga	Gd	Ge	Hf	Hg	Ho
<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	**0.0013**	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
In	Ir	K	La	Li	Lu	**Mg**	**Mn**	Mo	**Na**	Nb	Nd
<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	**balance**	**0.18**	<0.0001	**0.0009**	<0.0001	<0.0001
Ni	P	Pb	Pr	Pd	Pt	Re	Rh	Ru	Sb	Sc	Se
<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Si	Sm	Sn	Sr	Ta	Tb	Te	Ti	Tl	Tm	V	W
0.0002	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0011	<0.0001	<0.0001	<0.0001	<0.0001
Y	Yb	**Zn**	Zr								
<0.0001	<0.0001	**2.01**	<0.0001								

2.3 The cross-cut tape test

The adhesion strength of the CA/PEI conversion coating on the MgZnMn was measured by the cross-cut tape test, according to ASTM 3359-02.[29] Grids of parallel cuts with 1 mm intervals were scratched on the coated samples, then scotch tape (3M Brand, USA) was attached firmly over the area of the grids for 90 s, after that the tape was torn abruptly off at about 180^{o} as possible. Damage of the coatings was evaluated by stereoscopic microscopy (OLYMPUS, SZX7-1093). The extent of damage is inversely related to the adhesion strength. The samples were scored with grades as follows: 5 = almost 0%; 4 = less than 5%; 3 = 5-15%; 2 = 15-35%; 1 = 35%-65%; 0 = over 65%.

2.4 Electrochemical corrosion test

Electrochemical corrosion tests consist of potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). The tests were conducted on an electrochemical workstation (IM6, Zahner, Germany) which consisted of a three-electrode unit: working electrode (the specimen), counter-electrode (platinum) and reference electrode (saturated calomel electrode SCE). Specimens with 10 mm in diameter and 1.5 mm thickness were molded into silicone rubber with one exposed side of 0.785 cm^2 served as working electrode. The electrochemical measurement was carried out in phosphate buffered saline (PBS) solution and the whole configuration was incubated in a water bath at 37 ± 0.2 ^oC. The samples were firstly exposed to deoxygenated PBS for 10 min prior to scanning to stabilize the open-circuit potential (OCP). Potentiodynamic polarization curves were scanned from -2.0 V to -1.0 V with a scanning rate of 1 mV s^{-1}. The natural corrosion potential (E_{corr}) and natural corrosion current density (i_{corr}) were determined by the Tafel extrapolation. The surface morphologies of the resultant specimens were observed by FE-SEM. The electrochemical impedance spectroscopy (EIS) measurements were tested on the same setup. The samples were stabilized for 30 min, then tested at the open-circuit potential in a frequency range from 10^{-2} to 10^5 Hz. The sinusoidal perturbing signal was 20 mV. The Nyquist plots were simulated using corresponding equivalent circuits. The tests were repeated no less than 3 times for statistical purpose.

2.5. Immersion degradation test.

Samples for immersion test were sealed by epoxy resin with an area of 0.785 cm^2 exposed to the PBS solution (pH = 7.4) at 37 ± 0.5 ^oC. Four sealed specimens with a total surface area of 3.14 cm^2 in 160 mL PBS and three groups were set up as parallel samples. The pH value of the solution and the hydrogen gas volume was recorded during the immersion process at different intervals. The pH value was recorded on a PHS-3C pH meter (Lei-ci, China). The hydrogen gas was collected by a eudiometer which was made of an upside-down graduated cylinder as a water-filled container. The corrosion resistance of MgZnMn alloys coated with the conversion coating was evaluated on the basis of the changed rate of pH and hydrogen evolved in comparison with the uncoated samples.

2.7 Whole blood test

Rabbit whole blood adhesion tests were conducted in a closed flow chamber using 50 ml of the citrated whole blood (0.5 U/mL) in vitro. All the samples were simultaneously exposed for 1 h to a flow of 65 mL/min at a temperature of 37 °C. At the end of this test, the samples in the chamber were rinsed with PBS at a slow flow rate of 10 mL/min. Then the samples were removed and fixed in glutaraldehyde solution, then incubated with rhodamine 123 (Sigma-Aldrich) for 15 min at 37 °C, washed with PBS five times for 5 min, and viewed by a fluorescence microscope. The samples also were dehydrated with 40, 50, 70, 90 and 100 vol. % in ethanol solutions ethanol/water solution for 15 min for each in sequence and observed by FE-SEM.

2.9 In vivo subcutaneous implantation studies

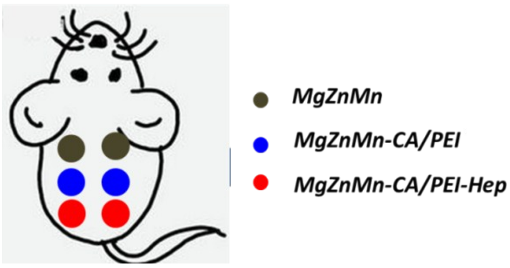

Figure.S1 The schematic diagram of the layout of samples implanted on the back of rats.

2.10 Intravascular implantation of MgZnMn wires

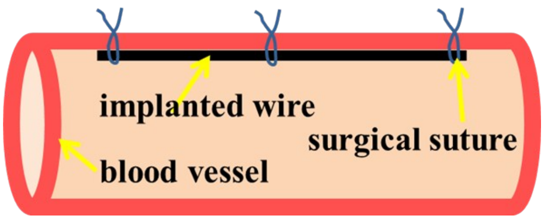

Figure.S2 The schematic diagram of the intravascular implantation of wires.