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# Preparation and characterization of nanostructured dibasic calcium phosphate coating on magnesium alloy wire

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ABSTRACT

In this study, nanostructured dibasic calcium phosphate (DCP) coating was prepared on the surface of magnesium alloy via hydrothermal method. The nanomorphology of coating was characterized by scanning electron microscopy (SEM). Raman spectroscopy and X-ray diffraction (XRD) confirmed the DCP phase of coating. The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) results prove that the nanostructured DCP coating can greatly enhance the anticorrosion performance of AZ31B Mg alloy in PBS solution.



## 1. Introduction

As a lightweight metal with mechanical properties similar to natural bone [1–4], magnesium-based implants have the potential to serve as biocompatible, osteoconductive, degradable implants for load-bearing applications [1,5–8]. However, two major drawbacks of magnesium and its alloys in many applications are low corrosion resistance and poor wear resistance [9]. At present, the widely used coatings on Mg alloys are prepared by electrochemical treatment method in solution of silicate, phosphate, aluminate, zirconate, sodium hydroxide, or their mixed solution, and the coatings prepared are usually composed of MgO, $MgSiO_3$, or $MgAl_2O_4$ [10,11].

Calcium phosphate is one of the promising coating materials, which has high biocompatibility, good fracture toughness property, excellent wear resistance, and corrosion resistance [12,13]. Hydrothermal method has been widely used in recent years to directly generate coatings on Mg, Al, Ti, and many other metals and alloys [2]. The coatings prepared by hydrothermal method had excellent corrosion resistance, anti-abrasion property, and decorative property, which may therefore be useful in many fields like metallurgy, aerospace, medicine, and textiles industry [10]. Presently, there are seldom research works about calcium phosphate coatings on Mg alloy prepared by hydrothermal technique. In this study, for the first time, we prepared dibasic calcium phosphate (DCP, $CaHPO_4$) coating on AZ31B Mg alloy wire by hydrothermal technique in modified simulated body fluid and characterized its structure by SEM, XRD, FTIR and Raman spectroscopy. The corrosion behaviors of DCP coated magnesium alloy sheet in phosphate buffered saline (PBS) solution were studied by polarization curve measurement, and alternating current impedance spectroscopy respectively.

## 2. Materials and methods

### 2.1. Experimental materials

Concentrated sulfuric acid (98%), $H_2O_2$ (30%), sodium nitrate, potassium permanganate (AR, Beijing Chemical Co., Ltd), and trihydroxy methyl amino methane (AR, Sigma Aldrich, USA).

Plate samples of AZ31B (Mg-0.03Al-0.01Zn) Magnesium alloy wire (Kunyao Metal Material Company, Luoyang, China) were cut into 4 cm long and then polished with # 600, # 800 and # 1200 abrasive paper, then rinsed with deionized water and dried in air.

### 2.2. Preparation of magnesium alloy wire with DCP coating

The polished magnesium alloy wires were put in the reaction kettle and added into simulated body fluid [14] immediately under 105 °C for 24 h, then rinsed with deionized water and dried in air.

### 2.3. Structure characterization

The Mg alloy wires and DCP coated Mg alloy wires were immersed in PBS buffer at room temperature and consequent

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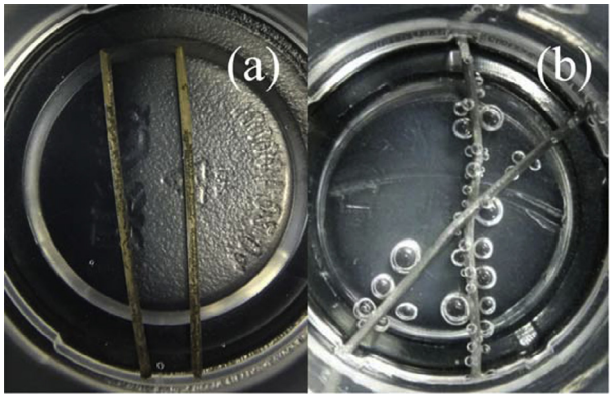


**Fig. 1.** (a) DCP coated Mg alloy wire and (b) bare Mg alloy wire after 6 weeks' immersion in PBS buffer at room temperature.

formation of hydrogen gas bubbles was assessed graphically after 6 weeks. The particle size and morphology of the bare magnesium alloy wire and DCP coating were observed by field-emission scanning electron microscopy (FE-SEM, S4800II, Japan). The crystalline phase of the samples was examined by X-ray diffraction (XRD, D8 ADVANCE, Bruker-AXS, Germany) with graphite monochromatized Cu Kα radiation operating at 40 kV and 40 mA at room temperature. The molecular structure was characterized by Fourier transform infrared spectrometry (FTIR, ALPHA, BRUKER, USA). The molecular structure was further analyzed by Raman spectroscopy (DXR, GX-PT-2412, Thermo, USA) with 532 nm laser as excitation wavelength.

### 2.4. Electrochemical evaluation

The electrochemical experiments were carried out through potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in phosphate buffered saline (PBS) solution at pH 7.4 and at 37 °C. We prepared two AZ31B square metal sheets ($1 \times 1$ cm$^2$) with thickness of 0.5 mm, which are made of exactly same AZ31B material from the same company as AZ31B alloy wire. The electrochemical measurements were performed with a three-necked cell using the CHI 760 electrochemical workstation (Shanghai Chenhua Instrument, Inc., Shanghai, China), consisting of a saturated calomel electrode (SCE), bare magnesium alloy sheet and platinum electrodes as the reference, working and counter electrodes. The potential was measured at a scan rate of 1 mV/s in the potential range between −2.5 and 0 V (vs. SCE). The EIS

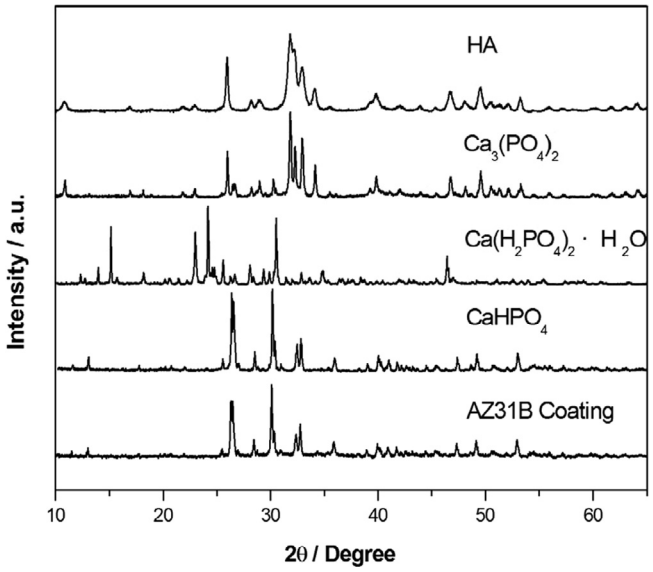


**Fig. 3.** X-ray diffraction patterns of hydroxyapatite (HA), $Ca_3(PO_4)_2$, $Ca(H_2PO_4)_2 \cdot H_2O$, $CaHPO_4$ and coating on the surface of AZ31B Mg alloy wire.

experiments were performed in the frequency range of 10 mHz to 100 kHz with a perturbation amplitude of 5 mV. The $I_{corr}$ was determined by Tafel extrapolation methods. The potentiodynamic polarization and EIS were repeated at least three times to ensure the reliability of the experiments.

## 3. Results and discussion

Light weighted Magnesium (Mg) alloys have excellent physical and mechanical properties. However, Mg alloys are highly susceptible to corrosion in aqueous physiological environment, which has limited its use in the biomedical applications. In vitro biodegradation of the Mg alloy and DCP coated Mg alloy in PBS buffer and consequent formation of hydrogen gas bubbles was assessed graphically at 6 weeks. As shown by Fig. 1, the DCP coating changed the color of Mg alloy wire from gray to metallic gold. There is no gas bubbles formed on DCP coated Mg alloy wire (Fig. 1a) while numerous bubbles were observed on the surface of Mg alloy wires (Fig. 1b) after 6 weeks' immersion in PBS buffer at room temperature. The experiment results show the DCP coating on the surface Mg alloy significantly slows down the degradation of Mg alloy

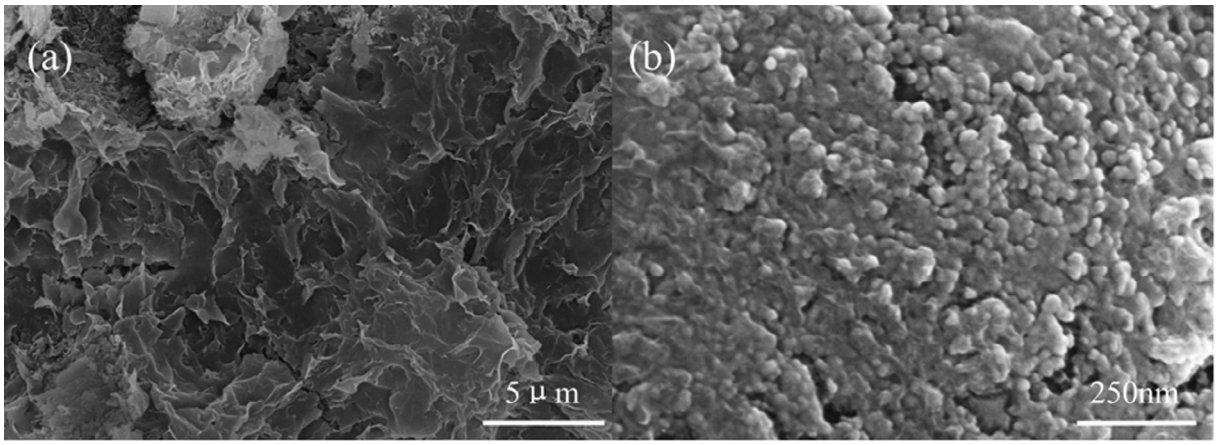


**Fig. 2.** (a) SEM images of DCP coating on Mg alloy wire; (b) high-resolution SEM images of DCP coating on Mg alloy wire.