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Short communication

Preparation of hydroxyapatite coating on smooth implant surface by electrodeposition

Dong-Yang Lin *, Xiao-Xiang Wang

Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

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Abstract

A novel process for the deposition of a hydroxyapatite (HA) coating on a smooth implant surface has been developed. Specimens were firstly subjected to electrodeposition at −1.8 V (versus Ag/AgCl) in a mixed solution of 0.042 M $Ca(NO_3)_2 \cdot 4H_2O$ and 0.025 M $NH_4H_2PO_4$ at 85 °C for 5 s, and then post-treated in 1 M NaOH solution for 30 min. The experimental results showed the specimens prepared by the designed process to have better adhesion properties than those prepared by the traditional electrodeposition process.

Keywords: B. Surfaces; E. Biomedical applications

1. Introduction

The enhancement of the bioactivity of Ti implants by applying a hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) coating has attracted particular attention in the past few decades [1]. Shirkhanzadeh first reported the application of HA coatings by electrodeposition in 1991 [2]. Compared to other coating techniques, electrodeposition is conducted in solution at a mild temperature and can be applied to complex or porous structures with high efficiency, good flexibility, and economy [3]. Hence, electrodeposition of HA coatings has aroused great interest for biological applications [4–7]. However, the low adhesive strength of the deposited coatings (unlikely to rough surfaces common for implants in bone) limits clinical application.

To increase the adhesion strength of calcium phosphate layers, Roessler et al. combined cathodically assisted deposition with subsequent anodic polarization [8]. Their results showed that it is possible to create a compound layer of titanium oxide and HA at the interface to increase the adhesion strength. However, the introduction of a titanium oxide layer is not easily controllable. As part of our continuing research on preparing bioactive coatings on implant surfaces [9–12], we have now developed a fast and simple electrodeposition process for preparing HA coatings on smooth implant surfaces with good adhesivity.

2. Experimental

Sheets (10 mm × 10 mm × 1 mm) of commercial pure Ti were used as the cathode. Prior to electrodeposition, the cathode was mechanically ground on SiC papers from P120 to P800 grit before polishing, cleaned ultrasonically in acetone, and rinsed with deionized water.

Electrodeposition was carried out in a three-electrode macrocell. A Pt foil and an Ag/AgCl electrode were used as anode and reference electrode, respectively. The ELD was conducted with a CHI1140 (USA) potentiostat/galvanostat at a potential of $E = -1.8$ V (versus Ag/AgCl) in the electrolyte at 85 °C. Two groups of specimens obtained by different preparation processes (Table 1) were compared.

To evaluate the adhesivity of the electrodeposited coatings, the 1# and 2# specimens were each placed in beakers containing 100 mL of deionized water and subjected to ultrasonication at 120 W at 40 kHz for 3 min, rinsed with deionized water, and dried.

Mouse renal epithelial cells were cultured in RPMI-1640 medium and rat embryonic midbrain neuron cells were cultured in Dulbecco's modified Eagle's medium (DMEM) at 37 °C in a humidified atmosphere containing 5% CO_2. The cells (in culture medium) were dispensed into 24-well plates (2×10^4 cells per

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* Corresponding author.
E-mail address: dylin@yahoo.cn (D.-Y. Lin).

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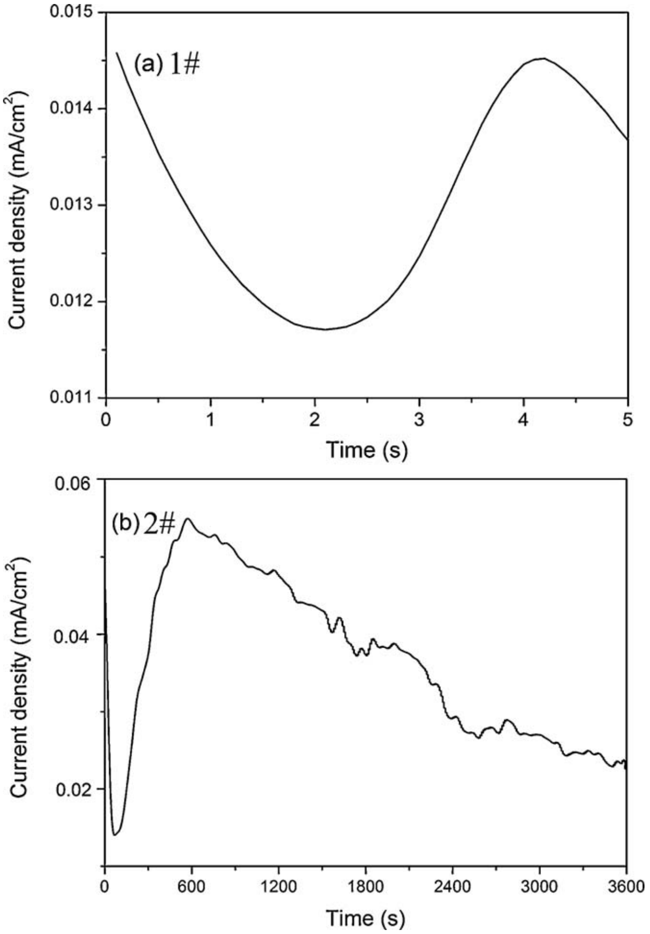

Fig. 1. Current density versus time during the electrodeposition on Ti at −1.8 V (versus Ag/AgCl).

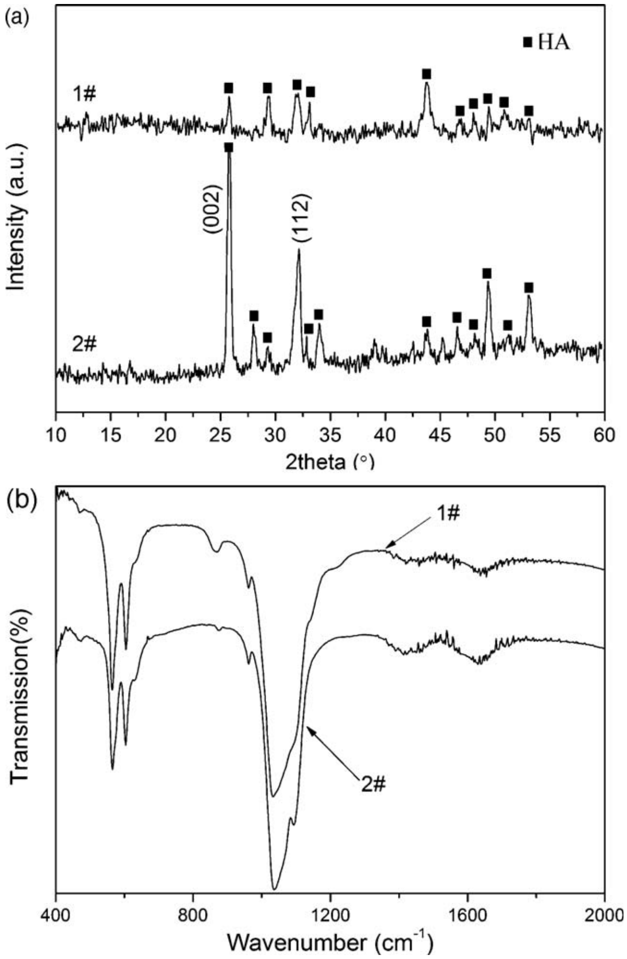

Fig. 2. XRD diagrams (a) and FTIR spectra (b) of the two specimens.

well). The samples were incubated for different periods (6, 12, 24, 48, and 72 h) at 37 °C under humidified atmosphere (5% CO_2). Colorimetric 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assays were performed to assess the cytotoxicity of cells treated as described above. All measurements were performed in triplicate, and at least three independent experiments were carried out.

3. Results and discussion

Fig. 1(a) shows the current density transient recorded during potentiostatic deposition at −1.8 V versus Ag/AgCl. The transient may be divided into three periods. Initially, charging of the double layer leads to a rapid current decay. Next, the current starts to increase either due to growth of independent

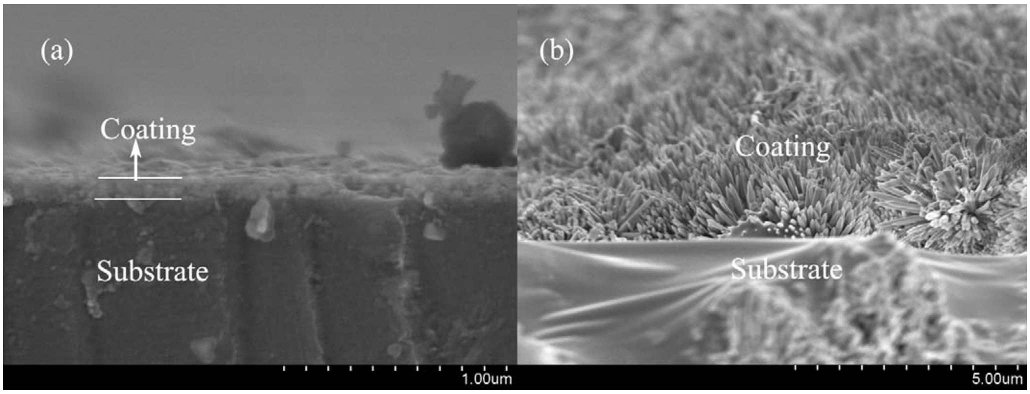

Fig. 3. The cross-section morphology of the 1# and 2# specimens.

Table 1
Two kinds of preparing processes were compared. 1# was the one designed in the present work. 2# was the commonly used one for preparing HA coating by electrodeposition as reported in references [2,6,12].

No.	Electrolyte	Deposition time	Post-treatment
1#	0.042 M $Ca(NO_3)_2{\cdot}4H_2O$ + 0.025 M $NH_4H_2PO_4$	5 s	1 M NaOH for 30 min
2# [2,6,12]	0.6 mM $Ca(NO_3)_2{\cdot}4H_2O$ + 0.36 mM $NH_4H_2PO_4$ + 0.1 M $NaNO_3$	60 min	Without

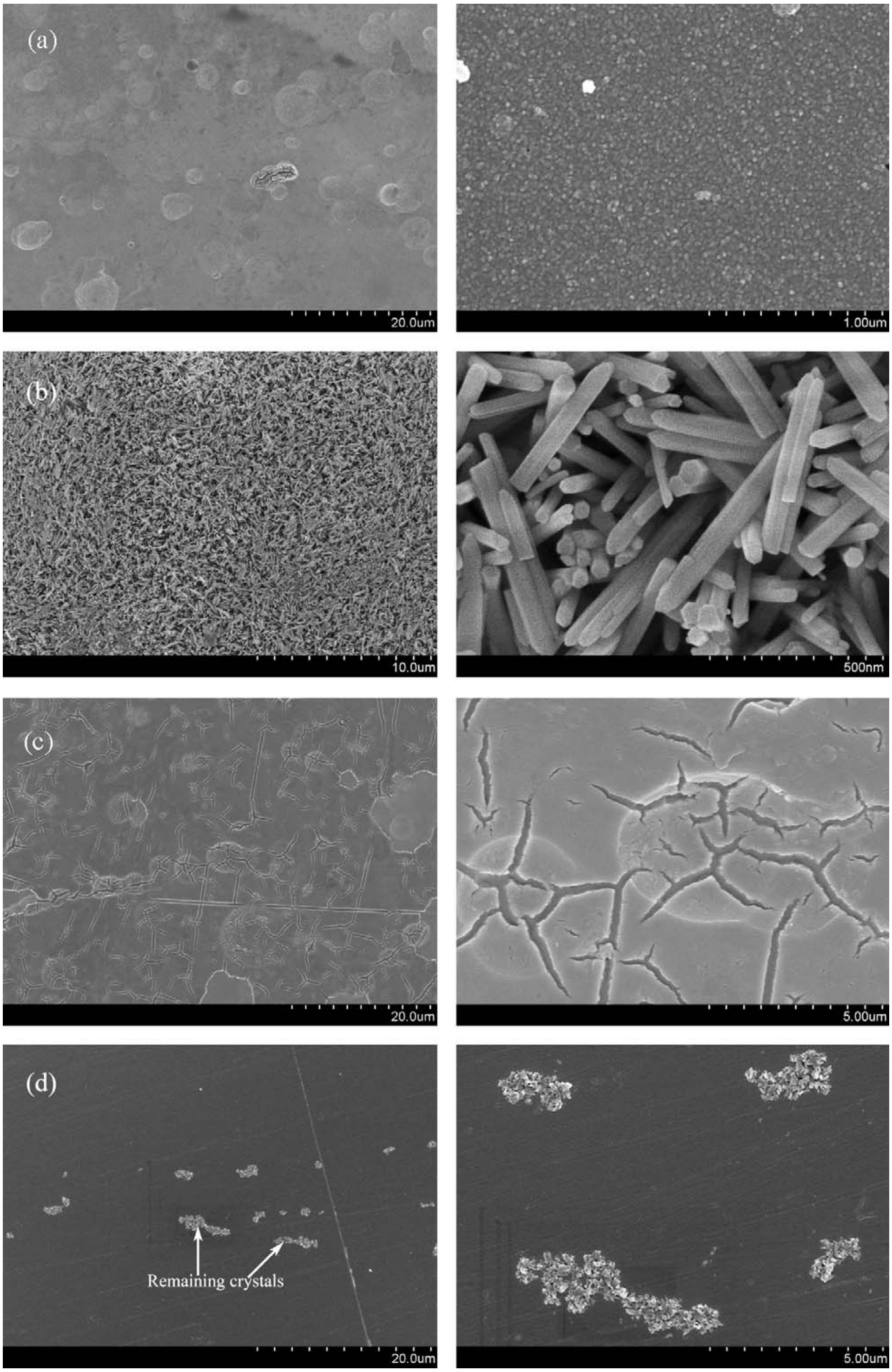

Fig. 4. Surface morphology of the as-prepared two specimens ((a) 1#, (b) 2#) and after 3 min ultrasonication ((c) 1#, (d) 2#).

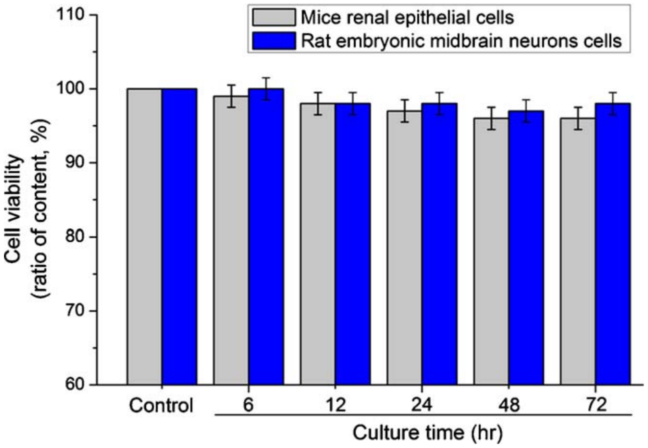

Fig. 5. Cytotoxicity experiment of the specimens prepared by 1# process. Data are the average of three independent experiments performed in triplicate. $p < 0.05$ compared with the corresponding controls.

nuclei or due to growth of dependent nuclei with a simultaneous increase in the number of nuclei. During the third period, the current peak is followed by a decrease because diffusion fields develop around each cluster and interact, and eventually result in a transition to planar diffusion-limited growth [6]. It can be seen that the 1# specimen reached maximum current density after 4.2 s during the electrodeposition, indicating that the two-dimensional nucleation process ended at that time. The 2# specimen, on the other hand, reached maximum current density after 600 s of deposition.

Thin-film X-ray diffraction patterns of the 1# and 2# specimens are shown in Fig. 2(a). The peaks from both coatings match well with the HA pattern. The higher intensity of the (0 0 2) plane of 2# specimen compared to the standard HA pattern is indicative of a preferred apatite crystal growth direction along the *c* axis on the substrate. The two specimens were also analyzed by FTIR, as shown in Fig. 2(b). The bands attributed to PO_4^{3-} absorptions at $\nu = 580$, 600, 960, and 1030 cm^{-1} confirm the presence of HA. This is in agreement with the XRD studies.

Fig. 3 shows the cross-section morphologies of the 1# and 2# specimens. The coating thickness of 1# specimen was around 100 nm (Fig. 3(a)), while the 2# specimen had a coating thickness of 1.5–3.5 μm and was composed of rod-like HA crystals (Fig. 3(b)). It is well known that the adhesion strength of the HA coating on the titanium surface is very important for clinical application. The nominal adhesion strength measured by the adhesive and detaching method will be affected by the porosity of the coating and the type of adhesive used. Here, the porosity and thickness of the 1# coating differed sharply from those of the 2# coating (Fig. 3). Thus, the nominal adhesion strength measured by the adhesive and detaching method is unsuitable for evaluation. Therefore, the ultrasonication method was applied in the present work to evaluate coating adhesion. After applying the same oscillation power for the same duration, the amount of crystals remaining on the substrate gave a good indication of the adhesivity of the coatings.

SEM images of the 1# and 2# specimens before and after ultrasonication (Fig. 4) show that a uniform and dense layer composed of numerous Ca–P nanoparticles covered the surface of the 1# Ti substrate before oscillation (Fig. 4(a)). The 2# Ti specimen (Fig. 4(b)) was also covered with an HA layer after 60 min. The layer consisted of rod-like HA crystals with a well-defined hexagonal cross-section. After 3 min of ultrasonication of the 1# specimen, HA particles still remained on the substrate, maintaining a good surface coverage (Fig. 4(c)). However, on the 2# specimen, most of the HA crystals deposited on the smooth substrate had been peeled off, making most of the substrate surface visible (Fig. 4(d)). The experimental results showed that the 1# specimen had better adhesivity than the 2# specimen.

Fig. 5 shows the cytotoxicity of the 1# specimen evaluated by means of an MTT viability assay. We did not find any significant time-dependent decrease in cellular viability after 72 h incubation, indicating that the 1# specimen was non-toxic. Further in vivo experiments are underway in our laboratory.

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