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Full Length Article

Construction of zinc-incorporated nano-network structures on a biomedical titanium surface to enhance bioactivity

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ABSTRACT

Surface topography had been identified as a crucial property that affects osseointegration; thus, topographical modification was the most frequently adopted technique in titanium-based implant research. In this study, ethyl cellulose was employed as an additive to construct a zinc-incorporated nano-network layer onto a titanium surface by the sequential treatments of spin-coating, high-temperature calcination, and alkali heat corrosion. SEM results showed that 20 mg/mL of ethyl cellulose was optimal to fabricate a relatively flat porous coating, and the ideal nano-network structures formed by only 4 h of corrosion. Other results of XPS and ICP further proved that zinc ions were successfully incorporated into the final samples (Ti-Zn0.1, Ti-Zn0.3, and Ti-Zn0.4). Moreover, the *in vitro* cellular (*e.g.*, CCK-8, ALP, mineralization) and bacterial assays presented that Ti-Zn0.3 substrates not only had the greatest proliferation and differentiation capacities for osteoblasts but also possessed relatively strong antibacterial abilities for both *Escherichia coli* and *Staphylococcus aureus*. This study provided a new way to rapidly construct the pro-osteogenesis and antibacterial nano-network structures on titanium surfaces for orthopedic application.

1. Introduction

Among various biomedical metals, titanium (Ti) and its alloys are widely used in clinical orthopedic and dental fields due to their excellent mechanical properties and favorable biocompatibility [1,2]. However, these native Ti implants have insufficient biological responses to bone tissue due to their bioinert surfaces, which might frequently result in implantation failures [3]. Besides the self-characteristics of bioinert materials, implant-related bacterial infections are also verified as the secondary factor to implantation failure. Therefore, how to promote osseointegration and simultaneously kill adhesion bacteria at the interface of bone and implant becomes a research focus in the orthopedic field.

Previous studies have proved that the surface properties of biomedical Ti implants usually played critical roles in their biological responses, such as chemical composition, topography, roughness, and surface energy [4–6]. Surface functionalization of an implant is demonstrated a promising alternative for improving osseointegration and/or reducing bacterial infection. In particular, surface nanotopology has received considerable attention, which can greatly upregulate cell functions (*e.g.*, adhesion, growth, differentiation) by interaction with cell-membrane receptor and/or functional proteins [7]. Among the common nanostructures, nano-network was often applied to improve osteogenic differentiation and osseointegration capacities, which is usually constructed by etching more than 24 h with a high concentration of alkali solution [8–10]. In this study, nano-network structures on Ti surface were prepared by using porous TiO_2 coatings. Ethyl cellulose, a common filler polymer, at a suitable concentration was used as a pore former to fabricate surface porous TiO_2 coatings. Moreover, the functional trace element zinc (Zn) was simultaneously incorporated into surface coatings to endow superior antibacterial and osteogenic properties to target implants.

Zn has been recognized as an essential trace element for the function or structure of more than 300 proteins and proved to be involved in many cellular processes (*e.g.*, DNA synthesis, enzyme activity, cell division) [11–13]. Many studies have proved that Zn can increase osteogenetic function in osteoblasts by improving cell proliferation, alkaline phosphatase activity, collagen synthesis, and protein synthesis [14,15]. In addition, zinc possesses excellent antibacterial ability by inhibiting multiple activities of bacteria [16,17]. Therefore, Zn attracts

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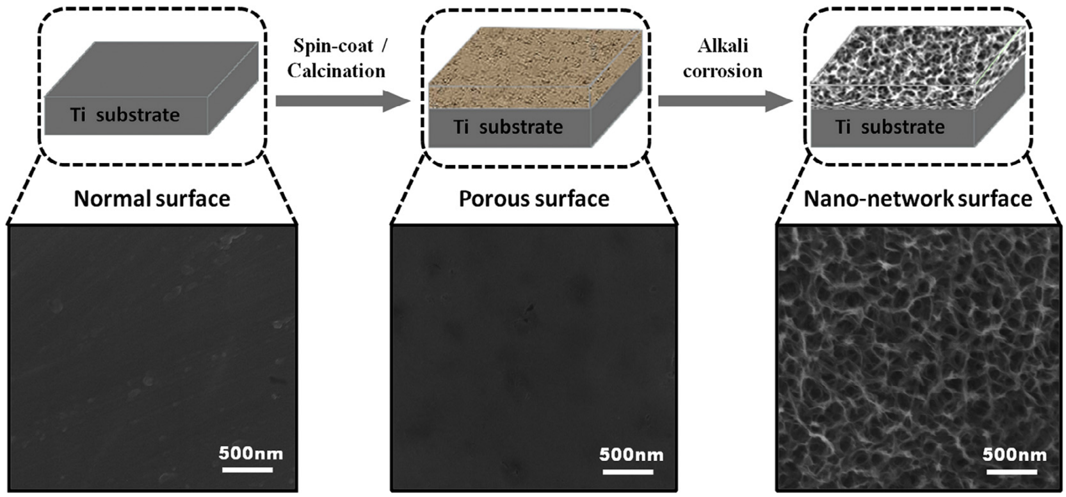

Fig. 1. Illustration of the fabrication of zinc-incorporated nano-network structures on native titanium surface.

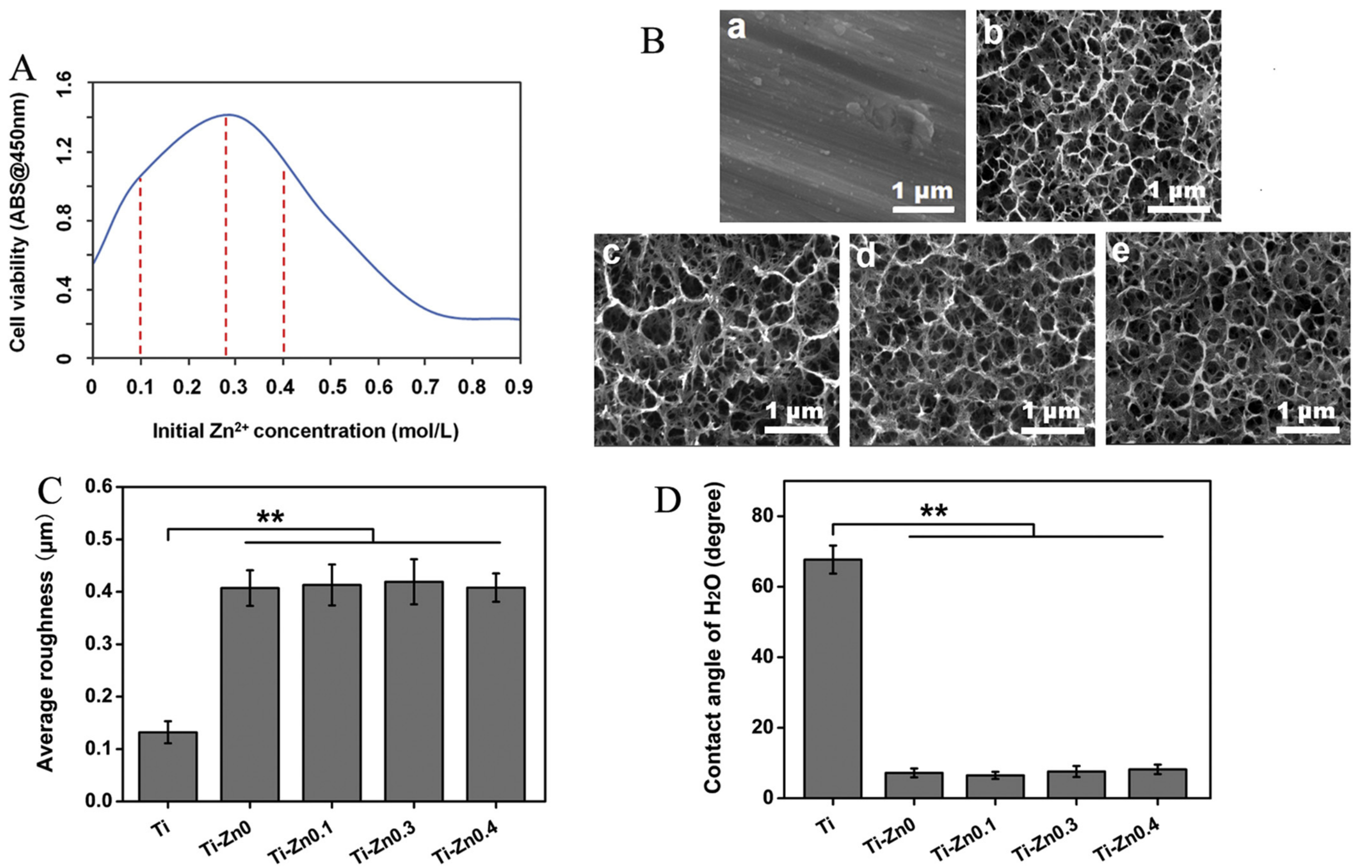

Fig. 2. (A) Cell viabilities of osteoblasts grown onto different substrates containing various concentrations (0–0.9 mol/L) of zinc after culture for 4 days; and (B) SEM images of different substrates: Ti (a), Ti-Zn0 (b), Ti-Zn0.1 (c), Ti-Zn0.3 (d), and Ti-Zn0.4 (e); (C) surface roughness and (D) water contact angles of different samples (n = 6).

the attention of many researchers and has been applied in various kinds of biomaterials [14,15]. In previous works, Wu embedded ZnO hybrid nanostructures or quantum dots in a hydrogel or titania nanotubes, and by *in vitro* antibacterial experiments, it was shown that the ZnO system can provide long-term bacterial infection-prevention and accelerated wound healing [18,19].

Accordingly, Zn-incorporated nano-network structures were constructed on a native Ti surface by sol-gel and alkali heat treatments. The aims of this study were as follows: (1) to fabricate a series of Zn-incorporated nano-network structures using ethyl cellulose and (2) to characterize the osteogenic and antibacterial abilities of different substrates and screen the optimal Zn-incorporated implant.

2. Materials and methods

2.1. Materials

Native titanium (diameter: 15 mm; thickness: 3 mm) was provided by Northwest Institute for Nonferrous Metal Research, China. Ethyl cellulose (EC) and $ZnCl_2$ were purchased from Aladdin Industrial Co.