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High-current anodization: A novel strategy to functionalize titanium-based biomaterials

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ABSTRACT

Although titanium (Ti) - based materials have been widely used in orthopedic field, their infections and instability remain serious complications. To overcome these shortcomings, we modify the surface of Ti by a high-current anodization (HCA) in $AgNO_3$ electrolyte. Our results show that highly ordered nanopores within micropits on Ti surface can be easily fabricated over a wide range of $AgNO_3$ concentrations. In this structure, AgO nanoparticles (NPs) are embedded in partially crystallized (anatase) TiO_2 substrates. Potent antibacterial ability of the HCA treated samples has been demonstrated. Meanwhile, improved cytocomaptibility is also observed after addition of Na_3PO_4 and $Ca(NO_3)_2$ into the electrolyte. The micro-roughness of the HCA treated sample surfaces may contribute to their mechanical interlocking ability with adjacent bone, while the nanopores may enhance osteoblast functions and serve as carriers of various drugs. Moreover, the technique we reported here is also applicable to other electrolytes (such as $Cu(NO_3)_2$, $CuCl_2$, $Zn(NO_3)_2$, and so on) thus widens its applications.

1. Introduction

Titanium (Ti) - based materials are suitable for orthopedic implants because of their good mechanical properties, corrosion resistance, and biocompatibility [1], but bacterial infection and mechanical loosening are serious post-operation complications. The surface characteristics of biomaterials regulate cell response and biofunctionality and hence, surface modification has been widely adopted because the surface of materials can be selectively functionalized to cater to different requirements while preserving the favorable bulk attributes of the materials. Surface modification methods include physical ones such as blasting, thermal spraying, physical vapor deposition, and plasma immersion ion implantation & deposition as well as chemical techniques such as sol-gel coatings, anodization, and chemical vapor deposition [2–5].

Electrochemical anodization is a common surface modification method for Ti-based materials and especially suitable for biomedical implants with a complicated shape [6,7]. During anodization, Ti acts as the anode and is exposed to an electrolyte at an applied voltage. When the voltage is less than 100 V, an amorphous and compact oxide layer is usually fabricated, whereas a higher voltage tends to produce spark discharge because of the local breakdown leading to the formation of an irregular porous oxide layer [5]. The latter is commonly referred to as micro-arc oxidation (MAO). MAO oxide layers have been extensively studied due to the enhanced apatite formation and osteointegration abilities, mechanical interlocking property with adjacent bone, good corrosion resistance, and bonding strength with the substrate [8–10]. However, the morphology of MAO coatings is on the micrometer scale and there is increasing evidence that a nano surface topography may be more effective in enhancing osteoblast functions compared to micro ones [4,11]. Since Zwilling and co-authors synthesized nano-porous/tubular oxide layers on Ti6Al4 V alloy by anodization in a fluoride containing electrolyte at very low voltage (5–10 V) in 1999 [12], the formation mechanism, new preparation methods, and potential applications have been extensively explored [13–15]. In the biomedical field, it has been demonstrated that TiO_2 nano-pores/tubes (NP/Ts) with the proper microstructures and dimensions can promote osteoblast spreading and proliferation, enhance alkaline phosphatase (ALP) activity, collagen secretion, and extracellular matrix mineralization [16–18], and many *in vitro* results have been corroborated by some *in vivo* experiments [19,20]. Another merit of NP/Ts is that they may serve as carriers in local delivery of drugs on demand [21–25]. However, their release behavior is usually uncontrollable

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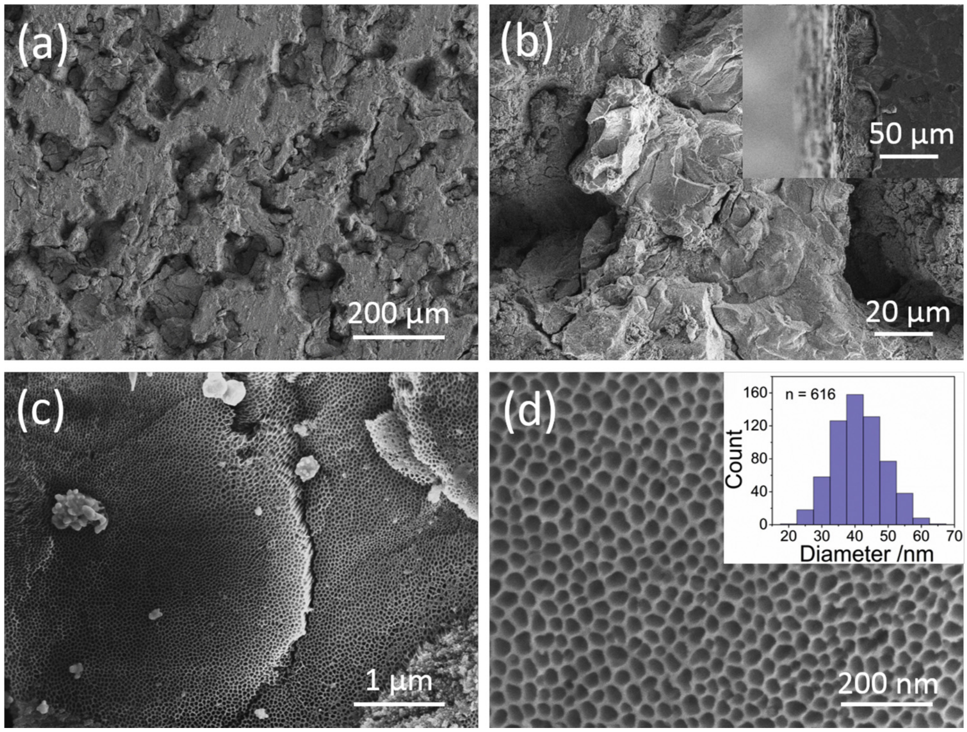

Fig. 1. (a) and (b) Low-magnification and (c) and (d) High-magnification SEM images of the HCA treated sample. The inset in (b) shows the cross-sectional morphology of the sample. The inset in (d) shows the histogram of pore diameter distribution. The sample is anodized in 0.5 g/L $AgNO_3$ and other electrochemical parameters can be found in "Experimental" section.

and cytotoxicity may result. To accomplish good bioactivity, annealing of TiO_2 NP/Ts is usually required. In addition, NP/Ts have poor adhesion because of the presence of fluoride-rich layers [13] and so their biosafety and stability are questionable.

In the present work, we prepared oxide layers combining the advantages of MAO layers and nano-porous/tubular structures on Ti by a novel one-step high-current anodization (HCA) in $AgNO_3$ electrolyte. Almost all of their merits are integrated and their drawbacks are avoided on the HCA treated samples. Their antibacterial ability and cytocompatibility were investigated. In addition, the extensibility of the technique and the formation mechanism of the structure were also studied.

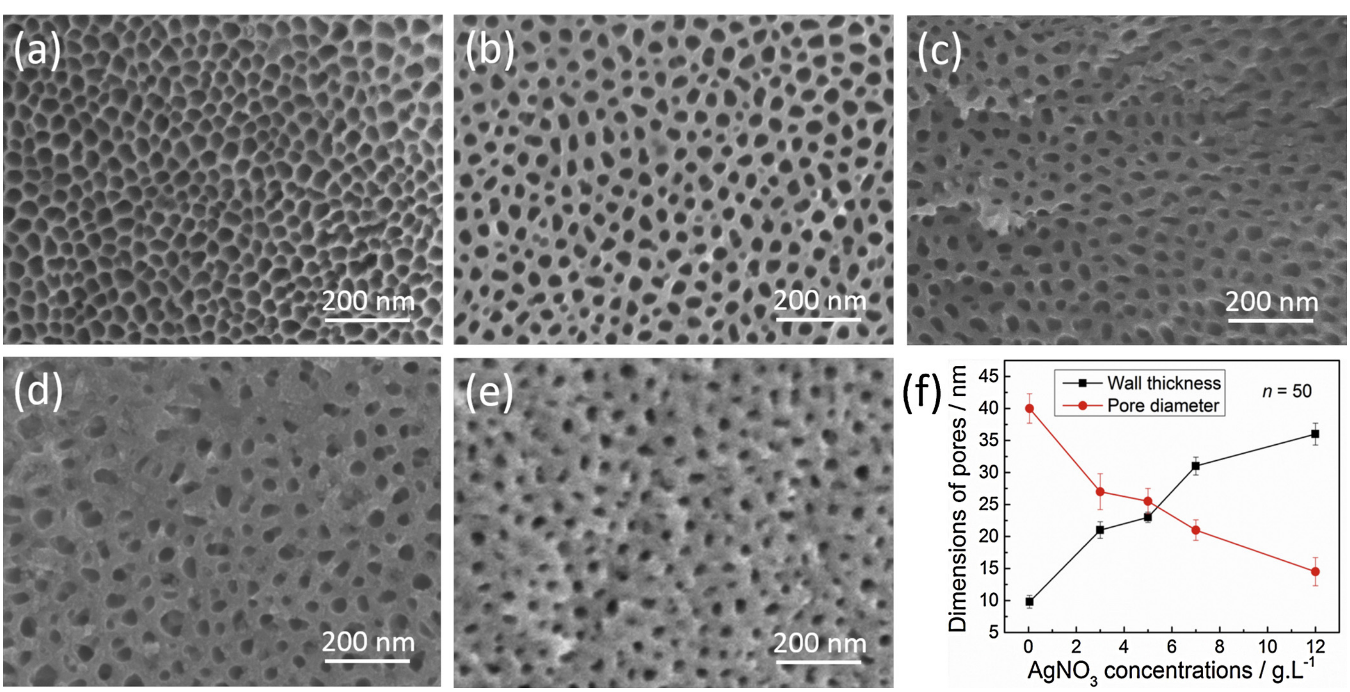

Fig. 2. Surface SEM images of the samples anodized in aqueous solutions containing different $AgNO_3$ concentrations: (a) 0.5 g/L, (b) 3.0 g/L, (c) 5.0 g/L, (d) 7.0 g/L, (e) 12.0 g/L. Other electrochemical parameters can be found in "Experimental" section. (f) Variation of the pore diameters and thickness of the anodized samples as a function of $AgNO_3$ concentrations.