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Sandblast-free double-etched titanium for dental implants application

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ABSTRACT

The residue of sand particles is an inevitable problem in sandblast and acid-etching (SLA) process. Reactive oxygen species (ROS) can significantly inhibit bacterial reproduction around the implants. Based on these two points, a sandblast-free double etching technique was proposed to obtain an antimicrobial titanium surface with hierarchical structures without inducing residual particles. Holes of 10–20 μm in diameter and pits of hundreds of nanometers were observed on etched surfaces by scanning electron microscopy (SEM). Meanwhile, ROS were also detected on etched surfaces by means of X-ray photoelectron spectroscopy (XPS). Namely that surfaces with hierarchical structures and antimicrobial performance without inducing residual particles were obtained. This novel double etched surface may be promising to dental implants.

1. Introduction

Sandblast and acid-etched (SLA) titanium surface gained great prevalence in dental implants over the past decades for its hierarchical structures [1–6]. On one hand, hierarchical structures can enhance the contact area of titanium, which favors the adhesion, proliferation and differentiation of osteoblasts, on the other hand, they also can improve the mechanical lock of implants and the bone, enhancing the initial fixation of the implants [3,7]. Although SLA titanium implants show wonderful osseointegration, considerable cell proliferation and high clinical success rate, problems such as poor wettability and the sand particles residual are still inevitable [2]. Recently, hydrophilic SLA titanium implants have been applied in clinic, but the problem of residual sand particles remain unsolved. One effective way to solve this problem is to develop a sandblast-free process. But the surface etched by a mixture of H_2SO_4 and HCl (same as SLA) without sandblast process shows poorer biomedical performances than SLA titanium [8,9]. Other researchers attempted to etch titanium disks using H_3PO_4, HF, H_2O_2 and even NaOH [9–11], and found that immersing titanium in NaOH for 24 h can obtain nanoporous structures. Although this is a sandblast-free technique, titanium shows a smooth surface without hierarchical structures in micro-scale. Research findings showed that micro/nano hierarchical structures could enhance the biological activity of titanium surface more compared with single micro or nano structures. Therefore, simple methods to avoid residual particles are still of great significance. As implants, antimicrobial property is also an essential criterion. Excellent antimicrobial performance can significantly prohibit the growth of bacterial around the implants, which promotes the initial stability and reduces the risk of complications like inflammation. Studies also showed that continuous oxygen can inhibit bacterial reproduction [7]. And many reactive oxygen species (ROS, $\cdot OH$, H_2O_2 and OH^-) could still exist on the etched surface of implants after being etched by H_2O_2. Considering the poor etching ability of single H_2O_2 to titanium, other coordination agents should be introduced to accelerate etching process, and NH_4OH may be a good candidate for it.

In this study, to obtain a hierarchical structure with ROS on it, TA2 titanium disks were firstly etched in a mixture of concentrated H_2O_2 and NH_4OH, and subsequently etched in a mixture of 60% H_2SO_4 and 11% HCl. Then we observed the surface morphology and chemical environment of this etched titanium. This study puts forward a novel sandblast-free double etched process for titanium modification, which can be promising to dental implants.

2. Experiment details

2.1. Corrosion process

Titanium disks with a diameter of 15 mm were cut from a TA2 titanium plate, and then mirror polished to the extent of $R_a \leq 0.5$ μm. All the samples were firstly ultrasonically cleaned in distilled water, absolute ethanol and ultrapure water for 10 min, respectively, and then pretreated in HF and HNO_3 mixture for 20 s.

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In the corrosion step, samples were ultrasonically immersed in a mixture of concentrated H_2O_2 and NH_4OH for 70 min (etched titanium) and subsequently corroded in 60% H_2SO_4 and 11% HCl mixture (1:1, v/v) at 70 °C for 15 min (double etched titanium). Samples were ultrasonically cleaned in ultrapure water for 10 min 3 times after each steps and finally dried in an oven (Thermo Scientific, HERATHERM Oven) at 60 °C for 3 h.

2.2. Materials characterization

Surface morphology was observed by Scanning electron microscopy (SEM, Nova NanoSEM 230). Surface chemistry was carried out using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) with Al Kα irradiation. The binding energies for each spectrum were calibrated based on the C1s spectra of 285.0 eV. Surface roughness was calculated by surface profiler (Dektak 150 surface profiler) with each testing line of 1000 μm.

3. Results and discussion

3.1. Surface morphology

Fig. 1 shows the morphologies of etched and double etched titanium disks. After being etched in concentrated H_2O_2 and NH_4OH mixture, porous surface with holes diameter of about 10–20 μm appeared (A), but the walls of these holes is relatively smooth at micro level except for some fluctuant textures (C). Different from etched titanium, double etched titanium disks possess more fine structures in a whole, and many typical SLA pits form on the whole surface (B and D), which can be expected to favor the differentiation of osteoblasts cultured on them [12]. Meanwhile, gills around the holes may favor the stretch of pseudopodia. Big holes with diameter of about 10–20 μm can serve as wonderful beds for osteoblasts due to the similar size of the holes and osteoblasts [4]. By the way, rough surface also favors the adhesion of the cells, and cell attachment and differentiation [13]. Meanwhile, better initial fixation of bone and implants can be considerably enhanced on this surface.

3.2. Surface chemical state

Fig. 2 shows the C1s (A) and O1s (B) narrow spectra of etched surface. Four basic peaks were fitted in Fig. 2A. The major peak at 285.0 eV represented the C-H or C-C component on the samples. The peak centered at 286.5 eV was identified as C-N bond; peak set at 287 eV for C=O; and peak at 289 eV for O-C=O. Carbonyl contamination is quite normal in XPS test, the total carbon content

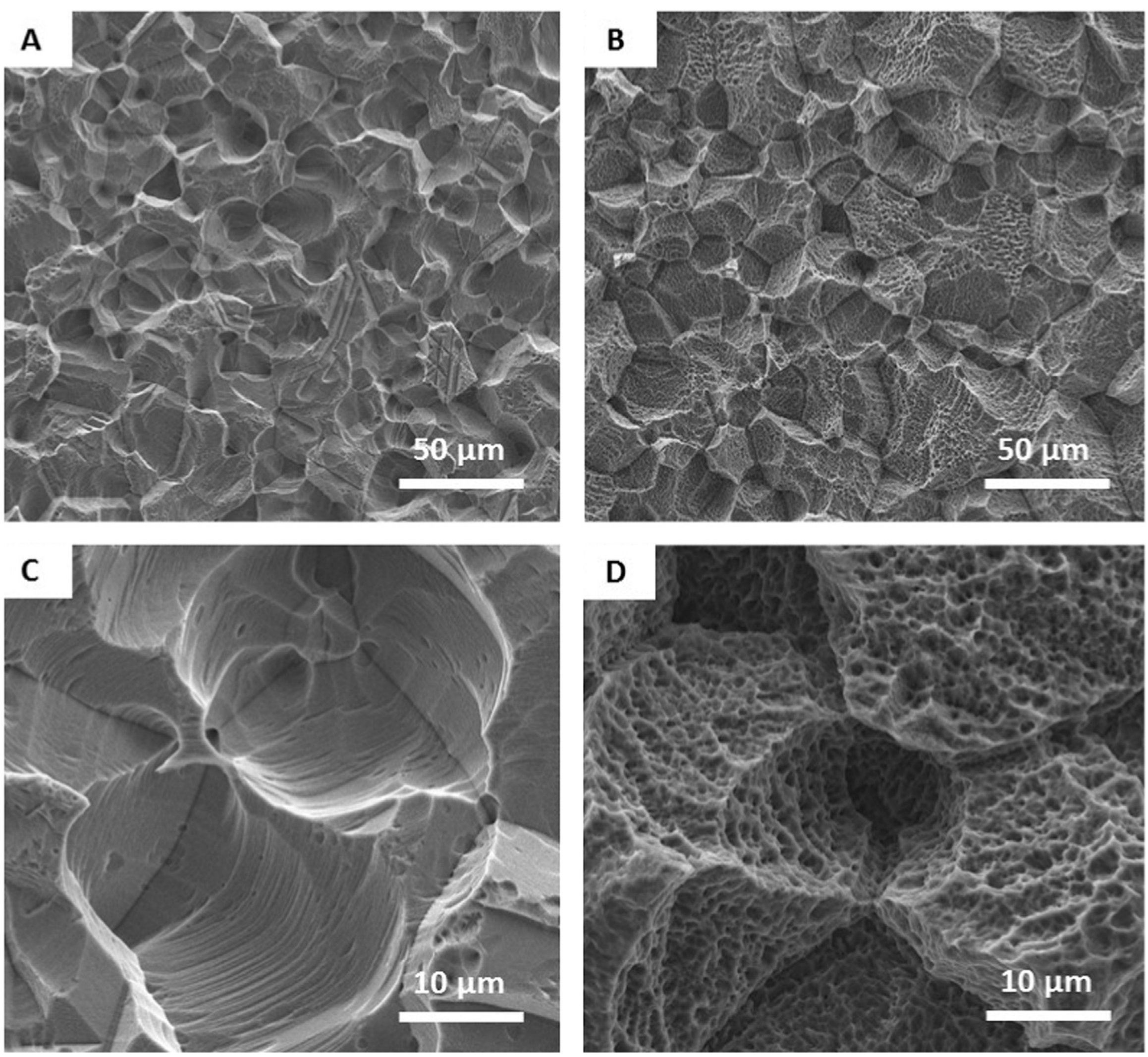

Fig. 1. Surface morphology of etched titanium (A and C) and double etched titanium (B and D).