Bioactivation of Titanium Surfaces by Femtosecond laser Processing

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ABSTRACT

The primary objective of current orthopaedic biomaterials research is to design implants that can stimulate guided, controlled, and rapid healing. In the present study, we propose a novel method to tailor titanium surfaces by synthesizing 3D titanium oxide nanofibrous structures using femtosecond laser processing. The bioactivity of the Ti surface is evaluated by simulated body fluid (SBF). Our results show that the synthesized nanofibrous structures significantly promote the apatite ability of the titanium surfaces. The synthesized 3D nanofibrous structures could advance titanium interfacial properties to improve cell-implant surface interaction and develop new functional biomaterials.

Keywords: Titanium, Surface modification, Femtosecond laser, Nanofibrous structure, Bioactivity,

1 INTRODUCTION

One of the important factor recognized in the failure of orthopedic and dental implants has been inadequate tissue regeneration around them immediately after implantation owing to poor surface interaction between implants and the host tissue [1]. Thus in terms of tissue regeneration, the surface characteristics of the implant and its interaction with the surrounding tissue may indeed play a more critical role than the implant's bulk properties in defining the performance of the implants [2].

Titanium has been broadly employed for orthopedic and dental implants because of their biocompatibility, great mechanical properties, and light weight [3]. However, pure titanium is bioinert which exhibits poor bioactivity when implanted in a living body resulting in poor implant-tissue contact and fibrous encapsulation [4]. Thus, it's been of a great interest to enhance the bioactivity and the osseointegration ability of titanium implants and to impart the desire surface chemical and topographical properties by modifying their surface.

Several *in vivo* and *in vitro* studies indicate that surfaces with nanoscale features show additional biological effects by producing integration between oxide and apatite nano-crystals and also by improving the cell-material interaction [5]. Of the nanoscale structures, nanofibrous structures are especially suitable for surface modification compared to nanoparticles because of their continuous structure, variable pore size distribution, high surface to volume ratio and most importantly, morphological similarity to natural extra cellular matrix (ECM) [1]. In this respect, various surface modification methods such as mechanical methods, ion implantation, chemical treatment, sol-gel formation, plasma spray deposition, and laser surface processing have been introduced to improve the bioactivity of titanium implants by changing their surface chemical and topography.

All of these methods have their advantages and drawbacks in terms of achieving uniform topography and chemical composition as well as strong interfacial bonding. For instance, it was reported that the reproducibility of the sodium titanate hydrogel layer formation, after alkali treatment and succeeding hydroxyapetite precipitation is poor owing to differences in the titanium surface structure that depends on the titanium processing prior the alkali treatment [4]. Also, the risk of coating detachment and toxicity of related debris is high using sol-gel technique [6]. This present work proposes a novel method to modify titanium surfaces by synthesizing 3D titanium oxide nanofibrous structures using femtosecond laser processing. The bioactivity of the Ti surface has been evaluated using SBF. Implants' osseointegration rate is directly related to the efficiency of apatite formation on their surfaces. Hence, it's been hypothesized that a surface with high apatite-inducing ability could achieve rapid osseointegration.

2 EXPERIMENTAL DETAILS

2.1 Laser processing

Specimens of 10 × 10 × 2 mm have been cut from grade 2 (ASTM B265) pure Ti sheet using a diamond saw. The specimen have been then ground progressively using 180, 320, 400, and 600 grit silicate-carbon papers to remove macro-level surface defects and contaminants. Once ground they have been ultrasonically cleaned in distilled water and kept in a desiccator. The nanostructures have been synthesized by laser beam at laser power of 15 W and pulse repetitions of 8 MHz. The laser source implemented in this experiment is a 1040 nm wavelength direct-diode-pumped Yb-doped fiber amplified ultrafast system. The maximum output power of the laser was 16 W and the pulse repetition ranged from 200 kHz to 26 MHz. The laser parameters including laser repetition rate, pulse width and beam power are computer-monitored which allow a precise interaction with the performed experiments.

2.2 In vitro bioactivity assay

The effect of Ti surface morphology on the apatite-inducing ability has been evaluated by soaking the specimens in SBF with ionic concentration nearly equal to the human blood plasma (see Table 1). A modified simulated body fluid (m-SBF) was prepared by dissolving the following reagents in sequence in distilled water: $NaCl$, $NaHCO_3$, Na_2CO_3, KCl, $K_2HPO_4.3H_2O$, $MgCl_2.6H_2O$, $CaCl_2$, and Na_2SO_4. The solution was buffered to pH 7.40 with HEPES and 1 M NaOH at 37 ℃ [7]. Each Ti specimen was then placed in a sterilized PE container with 30 ml SBF and kept in an incubator at 37 ℃ for 1 and 3 days. Finally, they were removed and rinsed with distilled water and dried in desiccators for characterisation.

Ion	Ion concentration (mM)	
	Blood Plasma	m-SBF
Na^+	142.0	142.0
K^+	5.0	5.0
Mg^{2+}	1.5	1.5
Ca^{2+}	2.5	2.5
Cl^-	103.0	103.0
HCO_3^-	27.0	10.0
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5
pH	7.2-7.4	7.4

Table1: Ion concentration of SBF in comparison with blood plasma

3 RESULT AND DISCUTION

Figure 1 shows SEM micrographs of nanofibrous layer synthesized on Ti surface at pulse repetition of 8 MHz. A close up view of the structures illustrates that they consisted of self-assembled closed-rings and bridges in which nanoparticles are merged together rather than loosely bonded, as shown in Figure 1C. The pores were interconnected with sizes of 900 nm. The nanoparticles are aggregated together in a semi-solid state rather than loosely agglomerated. Thus, the bond between the nanofibers and the Ti substrate is assumed to be strong.

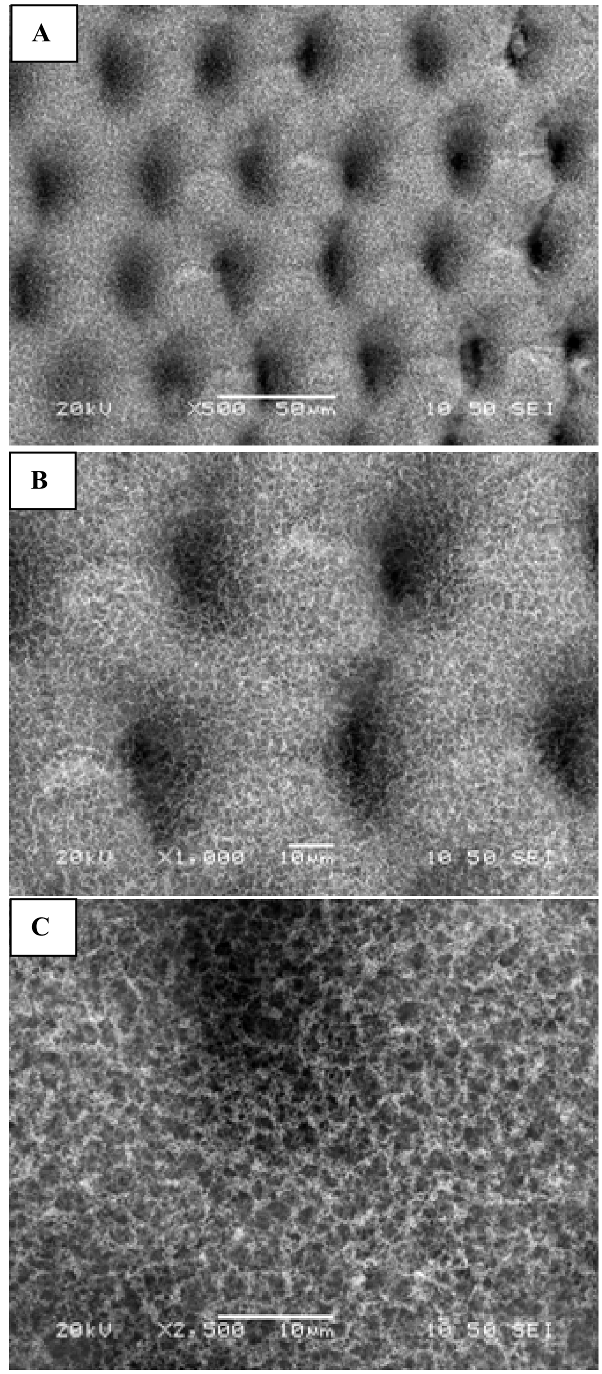

Figure 1: SEM micrographs of titanium oxide nanofiberous structures synthesized on a Ti substrate at laser power of 15W and repetition of 8 MHz at magnification of A) X500, B) X1000, and C) X2500.

SEM micrographs of the apatite-inducing ability of Ti nanofibrous layers for 1 day and 3 days of soaking in SBF are compared in Figure 2. The unprocessed Ti sample did not induce any apatite deposition after 3 days of soaking in SBF, whereas Ti showed high apatite-inducing ability even after 1 day of immersion in SBF. It can be observed that after 3 days of immersion, the precipitation layer became thick and scattered apatite globules with a diameter as big as 22 µm have been deposited on the Ti surface. This uniform apatite deposition on the nanofibrous structures indicates the very high reproducibility of apatite crystallization on the nanostructures.

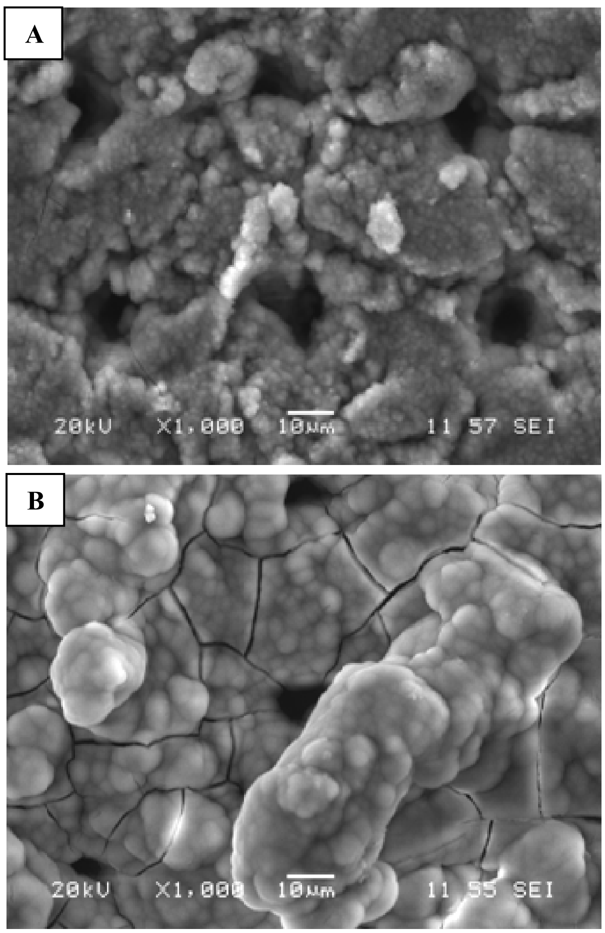

Figure 2: SEM micrographs of the morphology of surface modified by titanium oxide nanofiberous structures after soaking in SBF for A) 1day and B) 3days

Figure 3 compares XRD patterns of unprocessed Ti and Ti specimen modified with nanofibrous structures after soaking in SBF for 3 days. The wide peak at 2θ: 32.6° is attributed to the overlapping of (211), (112), (300), and (202) crystal planes of hydroxyapatite ($Ca_5H_2(PO_4)_3 \cdot OH$). hydroxyapatite (HA), which has a composition similar to the mineral phase of bone, is the most abundant inorganic material in the human body [8]. The Ti specimen was entirely composed of alpha-phase titanium (α-Ti), while the pattern of laser-processed surface indicates that it consisted of tetragonal TiO_2 (rutile and anatase). The sharp peaks in the patterns can be associated with the high crystallinity of the oxide phases. Titania exists in two main crystallographic forms, anatase and rutile [9]. The XRD peaks at 2θ: 25.28° (A101) and 2θ: 27.4 ° (R110) are often interpreted as the characteristic peaks of anatase and rutile phases, respectively [9].

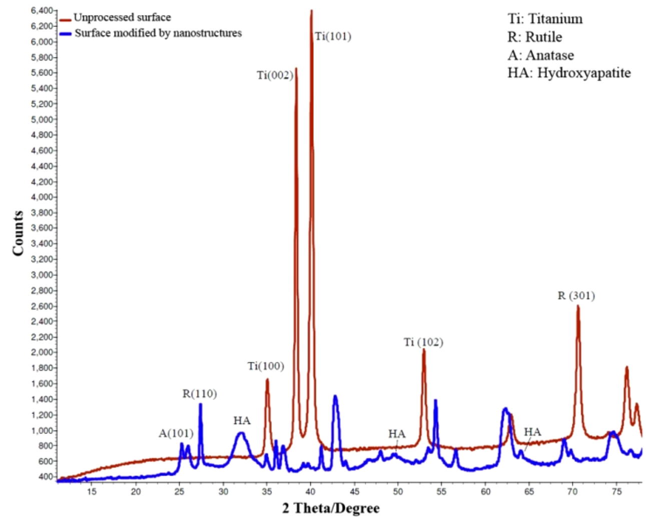

Figure 3: XRE patterns of unprocessed Ti and Ti specimen modified with nanofibrous structures after soaking in SBF for 3days.

The results of this study demonstrate that the modification of titanium surfaces with synthesized nanofibrous structures greatly improve the wettability which consequently increases the apatite-inducing ability of the titanium surfaces. Also the results suggest that due to the high temperatures used and the presence of atmospheric oxygen, nanofibers become oxidized and covered by a titanium oxide layer. This layer consisted of TiO_2 (rutile and anatase) and cubic TiO (hongquiite). Several studies have demonstrated that both rutile and anatase enhance the apatite-inducing ability, which improves bioactivity and osteointegeration of Ti implant surfaces surfaces [10].

4 CONCLUSION

This study describes a novel method to synthesize 3D titanium oxide nanofibrous structures on titanium surfaces by high repetition femtosecond laser under ambient conditions. The tailored surface induced a thick, dense apatite layer within 3 days of soaking in SBF.Our results have indicated that the surface morphology as well as surface physiochemical properties (surface reactivity and wettability) of the nanofibrous layers significantly influenced the apatite-inducing capability of the Ti surfaces.

The XRD analyses have shown that laser ablation of the Ti surface led to formation of rutile and anatase phases that improved the bioactivity of the Ti surfaces. The proposed method suggests a promising step toward modifying the surface of titanium implants to support new bone formation and achieve rapid bone healing.

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REFERENCES

[1] E. M. Christenson, et al., "Nanobiomaterial applications in orthopedics," Journal of Orthopaedic Research, 25 (1), 11 – 22, 2007.

[2] U. Sampathkumaran, M. R. De Guire, R. Wang, "Hydroxyapatite Coatings on Titanium," Advanced Engineerin Materials, 3, (6), 401-405, 2001.

[3] M. Long, H.J. Rack, "Titanium alloys in total joint replacement—a materials science perspective," Biomaterials, 19, 1621–39, 1998.

[4] L. Jonasova, F.A. Muller, A. Helebrant, J. Strnad, P. Greil, "Biomimetic apatite formation on chemically treated titanium," Biomaterials, 25, 1187–1194, 2004.

[5] A. Palmquist, O. M. Omar, M. Esposito, J. Lausmaa, P. Thomsen, "Titanium oral implants: surface characteristics, interface biology and clinical outcome," J R Soc Interface 7, S515–S527, 2010.

[6] G. Mendonça, D. B.S. Mendonça, F. J.L. Araga˜o, L. F. Cooper, "Advancing dental implant surface technology – From micron- to nanotopography," Biomaterials, 29, 3822–3835, 2008.

[7] A. Oyane, K. Onuma, A. Ito, H.M. Kim, T. Kokubo , T. Nakamura, "Formation and growth of clusters in conventional and new kinds of simulated body fluids," J Biomed Mater Res,64A:339–48, 2003.

[8] L.T. de Jonge, S.C.G. Leeuwenburgh, J.G.C. Wolke and J.A. Jansen, "Organic–inorganic surface modifications for titanium implant surfaces," Pharm Res, 25 (10), 2357–2369, 2008.

[9] L.Q. Jing, B.F. Xin, F.L. Yuan, L.P. Xue, B.Q. Wang and H.G. Fu, "Effects of surface oxygen vacancies on photophysical and photochemical processes of Zn-doped TiO_2 nanoparticles and their relationships," J Phys Chem B, 110 (36), 17860–17865, 2006.

[10] X.X. Wang, S. Hayakawa, K. Tsuru and A. Osaka, "Bioactive titania gel layers formed by chemical treatment of Ti substrate with a H_2O_2/HCl solution," Biomaterials, 23 (5), 1353–1357, 2002.