

UV-irradiation-induced bioactivity on TiO₂ coatings with nanostructural surface

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Abstract

Titania (TiO₂) coatings with nanostructural surface prepared using plasma spraying technology were irradiated by ultraviolet light in simulated body fluids to improve their bioactivity. The *in vitro* bioactivity of the coatings was evaluated by investigating the formation of apatite on their surfaces in simulated body fluids. Bone-like apatite was observed to precipitate on the UV-irradiated TiO₂ coating with nanostructural surface after it was immersed in simulated body fluid for a certain period, but not on the as-sprayed and UV-irradiated TiO₂ coatings without nanostructural surface. The results indicate that the nano-TiO₂ surface can be activated by UV-irradiation to induce its bioactivity. The ability of apatite formation on the nano-TiO₂ surface was improved with the increase of UV-irradiation time. The *in vivo* results reveal that the as-prepared TiO₂ coating with nanostructural surface cannot induce the formation of new bones during the implantation period, but the UV-irradiated TiO₂ coating with nanostructural surface could do so during an implantation time longer than 2 months. Our results indicate that the osseointegration ability of the plasma-sprayed TiO₂ coating with nanostructural surface can be improved by UV irradiation.

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1. Introduction

It is well known that a native oxide film grows spontaneously on the surfaces of titanium and its alloys upon exposure to air and the oxide film is responsible for their passive properties. The excellent chemical inertness, corrosion resistance, repassivation ability and even biocompatibility of titanium and its alloys are thought to result from the chemical stability and structure of the titanium oxide film that is typically only a few nanometers thick. Therefore, the titanium oxide (titania, TiO₂) powders, ceramics, coatings and thin films were considered as biomedical materials

because of their biocompatibility, and much research on this was conducted [1–5]. However, the chemical stability of the TiO₂ was thought to result in its bioinertness in the human body, which limits its application to some extent. Some attempts have been made to obtain bioactive TiO₂ powders and films. Kasuga et al. [1] have demonstrated the formation of apatite on compacted TiO₂ powders by UV irradiation in simulated body fluids (SBF). The bioactive TiO₂ microspheres and sol-gel-derived titania films have also been reported in the literature [2–5]. However, the clinical application of TiO₂ powders and sol-gel-derived films is still plagued by their morphology and mechanical properties.

Plasma spraying is a popular deposition technique due to advantages such as rapid formation of coating, flexibility, a wide choice of materials, low cost, large and thick

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coating capability, and excellent adhesion to the substrate. Plasma-sprayed TiO₂ coatings are generally known to have excellent biocompatibility and corrosion resistance as well as high bonding to titanium alloys [7–9]. However, plasma-sprayed TiO₂ coatings are typically bioinert [10], and so the bonding between the TiO₂ medical implant and bone tissues is usually poor. Therefore, there is a need to improve the bioactivity of plasma-sprayed TiO₂ coatings to expand their clinical applications.

It has been shown that nano-sized surface topography can render biomedical implants with special and favorable properties in a biological environment. For instance, osteoblast proliferation was observed to be significantly higher on nanophase alumina, titania and hydroxyapatite (HA) in comparison to their conventional counterparts [6,11,12]. Balasundaram et al. [13] suggested that implants produced with conventional materials (or materials with constituent dimensions greater than 1 micrometer) could not invoke suitable cellular response to regenerate enough bone to allow them to be successful over a long period of time. In contrast, nanophase materials are viable alternative orthopedic implant materials because they mimic the dimensions of the constituents in natural bones.

In our previous work [14], we showed that a TiO₂ coating with nano-structured surface could be produced using plasma spraying. The surface of the TiO₂ coating produced with nano-particles (denoted as “nano-TiO₂ coating”) comprises particles about 50 nm in size, whereas the surface of the TiO₂ coating produced with submicro-particles (denoted as “micro-TiO₂ coating”) is composed of particles about 100 nm in size, as shown in Fig. 1. After post-treatment using hydrogen plasma immersion ion implantation (PIII), the nano-TiO₂ coating exhibits excellent bioactivity. The hydrogen plasma-implanted nano-TiO₂ coating can induce the formation of carbonate-containing hydroxyapatite on the surface after immersion in a simulated body fluid (SBF). In contrast, the as-sprayed nano- and micro-TiO₂ coatings as well as hydrogen-implanted micro-TiO₂ coating cannot do so after immersion for the same period of time. The results indicate that the bioactivity of plasma-sprayed

TiO₂ coatings depends on a nano-structured surface composed of enough small particles in addition to hydrogen incorporation which yields surface Ti–OH functional groups to facilitate the formation of carbonate-containing hydroxyapatite. Although the bioactivity of plasma-sprayed nano-TiO₂ coating can be improved by hydrogen-PIII, there may be other methods that can yield similar results.

An amphiphilic and super-hydrophilic TiO₂ surface can be obtained by ultraviolet irradiation [15,16], which should be beneficial to the bioactivity of TiO₂ surface. We subsequently investigated the use of ultraviolet (UV) light irradiation in air to convert plasma-sprayed TiO₂ coatings from being bioinert to bioactive [17]. In the work reported here, we investigate systematically the effects of UV irradiation in SBF on the bioactivity of plasma-sprayed nano-TiO₂ coating by means of both in vitro and in vivo evaluation.

2. Experimental details

2.1. Preparation of coatings

Nano-TiO₂ powders (P25, Degussa, Germany) with size of approximately 30 nm and submicro-TiO₂ powders (Wuhan Institute of Materials Protection, China) with size of approximately 0.3 μm were used as feedstock materials. The two types of powders were agglomerated by spray drying before plasma spraying. The anatases content was about 85% in the nanopowders and 5% in conventional powders. Commercial titanium alloy (Ti6Al4V) blocks with dimensions of 10 mm × 10 mm × 2 mm were employed as substrates. Prior to plasma spraying, all the substrates were sandblasted with brown corundum. The coatings were deposited on an atmospheric plasma spraying system equipped with a Sulzer Metco F4-MB plasma gun mounted on an ABB S3 robot. The plasma spraying parameters are as follows: argon (40 slpm) and hydrogen (12 slpm) as the primary and auxiliary arc gas, respectively. The feeding rate of powders was about 10 g min⁻¹ using argon (3.5 slpm) as the carrier gas. The arc current and

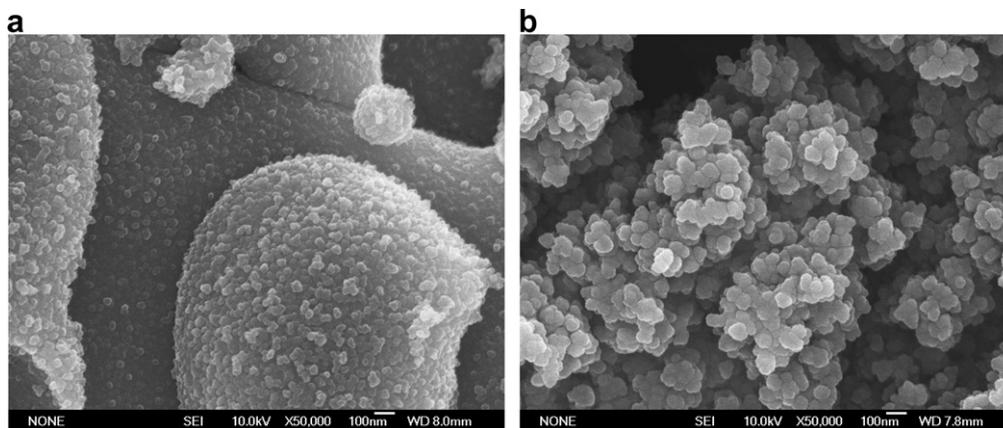


Fig. 1. High-magnification surface SEM views of as-sprayed TiO₂ surfaces: (a) nano-TiO₂ coating and (b) micro-TiO₂ coating.

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