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Light-induced bioactive TiO_2 surface

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We have achieved bioactivity enhancement of nanostructured titania using ultraviolet (uv) light irradiation. The titania coating fabricated by nanoparticle plasma spraying consists of a nano-TiO_2 coating surface composed of primarily nanosized anatase. After irradiation by ultraviolet light in air for 24 h, the as-sprayed and UV-irradiated TiO_2 coatings were soaked in simulated body fluids (SBF) to investigate their bioactivity. The UV-illuminated TiO_2 coating induced bonelike apatite formation on the surface whereas no apatite could be detected on the as-sprayed TiO_2 coating. The formation of oxygen vacancies at the two-coordinated bridging sites by UV illumination is believed to result in the conversion of the corresponding Ti^{4+} sites to Ti^{3+} sites, which are favorable to the dissociation of water in the SBF and subsequent formation of Ti-OH and an apatite layer. Our results reveal that the surface bioactivity of titania coatings can be induced by UV illumination. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2162687]

The ability to induce bonelike apatite to form on artificial bone implants in the human body is vital to the successful bonding between the implants and bone tissues. It has been found that physical-chemical bonding between the implant and living bones could be achieved by the formation of a bonelike apatite in the body environment.[1,2] The formation of apatite on materials soaked in a simulated body fluid (SBF) is commonly used by biomedical researchers to evaluate the bioactivity and bone conductivity.[3]

Plasma-sprayed hydroxyapatite coatings are widely used clinically due to their excellent bioactivity (bone conductivity) and biocompatibility. However, clinical use of plasma-sprayed hydroxyapatite coatings is plagued by their low crystallinity and poor bonding strength to titanium alloys. The former gives rise to fast dissolution of the hydroxyapatite coating in contact with human body fluids subsequently shortening its lifetime,[4] whereas the latter results in delamination causing safety concerns.[5] Although some types of TiO_2 powders and gel-derived films can exhibit bioactivity,[6–9] plasma-sprayed TiO_2 coatings are always bioinert,[10] thereby hampering wider applications in bone implants. The introduction of surface bioactivity (bone conductivity) to plasma-sprayed TiO_2 coatings, which are generally recognized to have excellent biocompatibility and corrosion resistance as well as strong bonding to titanium alloys, makes them more superior than many current biomedical coatings. Here, we report a novel and simple method by means of ultraviolet (uv) light irradiation to convert TiO_2 coatings from being bioinert to bioactive. UV irradiation has been used to investigate the photocatalysis of titania powders and thin films.[11–13] An amphiphilic and superhydrophilic TiO_2 surface has been obtained by ultraviolet irradiation.[14–16] However, based on our literature search, the application of UV irradiation to improve the bioactivity or bone conductivity of plasma-sprayed titania coatings has not been investigated. In this letter, the formation and mechanism of apatite on the UV-illuminated TiO_2 coating are also discussed.

Commercial nanosized TiO_2 powders (P25, Degussa, Germany) with a size of about 30 nm were made into spherelike particles of 45–90 μm using a spray drying process. The nanosized TiO_2 powders are composed of about 80% anatase and 20% rutile phases. The particles were deposited onto Ti-6Al-4V substrates by atmospheric plasma spraying (APS) using a system made by Sulzer Metco, Switzerland, employing modified spraying parameters. Argon [40 standard liter per minute (slpm)] and hydrogen (12 slpm) were used as primary and auxiliary arc gas, respectively. The temperature in the core region of the plasma jet is relatively constant at approximately 12 000 K and dramatically decreases to about 3000 K towards the nozzle. The feeding rate of powders was about 10 g/min using argon (3.5 slpm) as the carrier gas. The arc current and voltage were 600 A and 70 V, respectively. Micro-Raman spectra were acquired in the backscattering mode using an unpolarized HeNe laser to investigate the surface structure. The excitation line wavelength was 632.8 nm and the laser power was 6.4 mW.

After ultrasonically cleaned in acetone and rinsed in deionized water, the TiO_2 coatings were irradiated by ultraviolet light in air for 24 h. A 125-W high-pressure mercury lamp was used as the UV light source. The primary wavelength of the UV light produced by the mercury lamp was 365 nm. Then, both the as-sprayed and UV-illuminated TiO_2 coatings were soaked in simulated body fluids (SBF) to evaluate their bioactivity. The SBF solution was buffered at pH 7.4 with trimethanol aminomethane-HCl and the ionic

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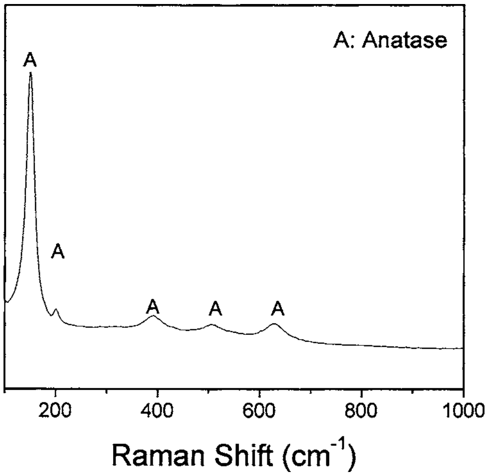

FIG. 1. Raman spectra obtained from the as-sprayed TiO_2 coating.

concentrations in the solution are nearly equal to those in human blood plasma.[3] The surfaces of the TiO_2 coatings before and after SBF immersion were assessed using cold field-emission scanning electron microscopy (SEM) (JEOL JSM-6700F).

The Raman spectra (100–1000 cm^{-1}) obtained from the as-sprayed TiO_2 coating are shown in Fig. 1. The peaks around 152, 200, 390, 510, and 630 cm^{-1} corresponding to nanosized anatase are observed in the as-sprayed coating. The high magnification surface views of the as-sprayed TiO_2 coating depicted in Fig. 2 also indicate that the surface of the as-sprayed TiO_2 coating comprises nanosized anatase grains smaller than 30 nm on the surface. However, X-ray diffraction (XRD) results obtained in our previous work indicated that the coating had primarily the rutile structure with a small amount of anatase and TiO_{2-x} suboxide, most of which is Ti_3O_5 (Ref. 17). The phase difference between the outermost layer and the interior of the coating results from the difference in the thermal history. The cooling rate for the formation of the outer layer is faster than that of the interior of the coatings because of the continuous heat provided by the plasma and subsequent melt. Therefore, the metastable phase, such as anatase, can be retained at room temperature.

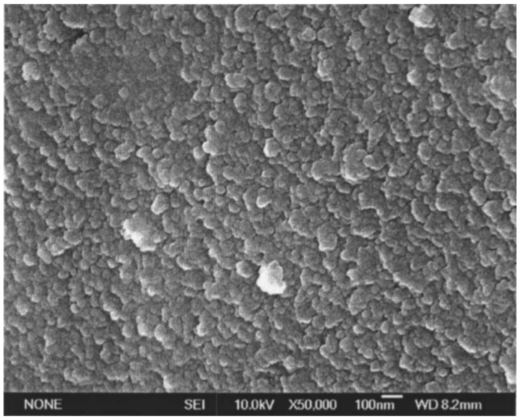

FIG. 2. High magnification SEM surface views of the as-sprayed TiO_2 coating.

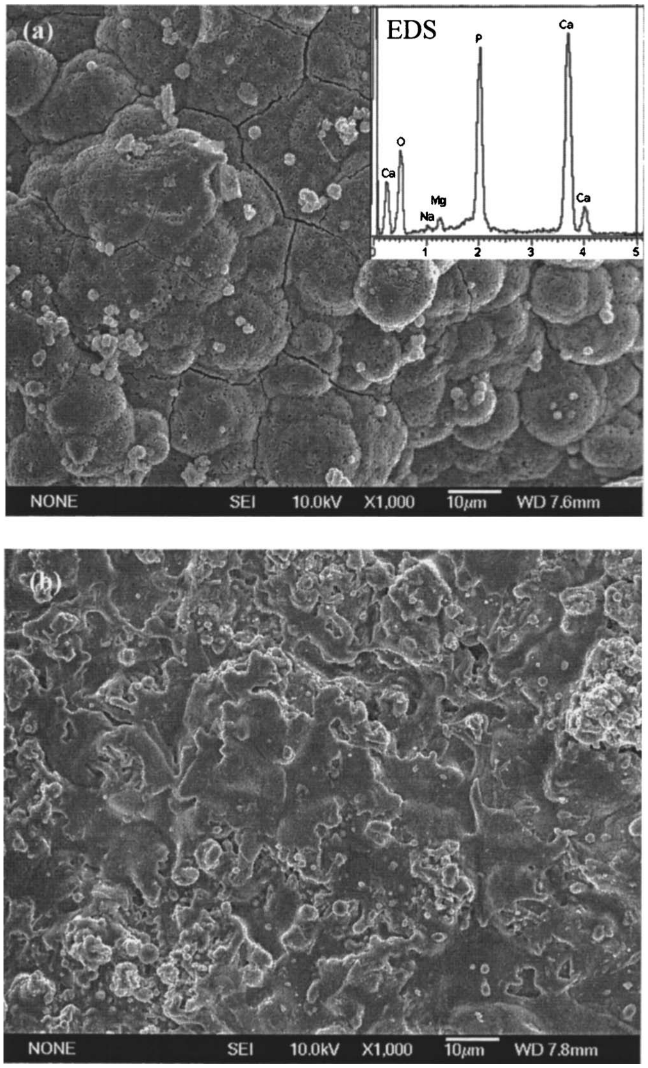

FIG. 3. Surface views of TiO_2 coatings soaked in SBF for four weeks: (a) UV illuminated and (b) as sprayed.

After UV irradiation and immersion in SBF for four weeks, a newly formed layer resembling dried mud is formed on the surface of TiO_2 coating [Fig. 3(a)]. The energy dispersive x-ray spectroscopy (EDS) spectrum [shown at the top right corner of Fig. 3(a)] corresponding to the newly formed layer indicates that the compound contains calcium and phosphorus. The Na and Mg signals in the EDS spectra originate from the SBF solution. The XRD and Fourier transform infrared (FTIR) analyses (not shown here) indicate that the surface compound is carbonate-containing hydroxyapatite (bonelike apatite). In our control experiment involving the as-sprayed coating without UV illumination, no new surface precipitates can be detected after soaking in SBF for four weeks, as shown in Fig. 3(b).

Our results indicate that only the surface of the TiO_2 coating irradiated by ultraviolet possesses good apatite formability. It is widely accepted that the atomic coordinations on the TiO_2 surface differ from those in the bulk since the atom arrangements are truncated on the surface. The perfect surface is built up from five-coordinated Ti atoms and two-coordinated O atoms, which are more energetically reactive than the six-coordinated Ti and three-coordinated O atoms in the bulk. By UV illumination, oxygen vacancies are most likely created at the two-coordinated bridging sites, resulting in the conversion of the corresponding Ti^{4+} sites to Ti^{3+} sites.[18] Ti^{3+} sites are favorable for dissociating water which is absorbed in atmosphere.[19–21] This results in an abundance of Ti-OH groups to form at the bridging oxygen sites on the surface of titania coating. The reactions can be listed as follows:

$$2\mathrm{Ti(IV)} + \mathrm{O_O} + h\upsilon \rightarrow 2\mathrm{Ti(III)} + \mathrm{V_O} + 1/2\mathrm{O_2},$$

$$\mathrm{Ti(III)} + \mathrm{H_2O} \rightarrow \mathrm{Ti(IV)} - \mathrm{OH} + 1/2\mathrm{H_2}.$$

It has been suggested that OH groups on ceramic surfaces are effective in inducing the formation of an apatite layer. For instance, gel-derived TiO_2 has been shown to induce surface apatite formation, but single-crystal anatase and titania synthesized by hydrothermal methods cannot.[22] The difference is believed to be due to the Ti-OH functional groups forming a negatively charged surface on the titania gel. We also believe that to be the reason for the surface bioactivity of the UV-illuminated TiO_2 coating and the lack of it on the as-sprayed TiO_2 coatings. Ti-OH reacts with the hydroxyl ion in the SBF to produce a negatively charged surface with the functional group Ti-O^- as follows:

$$\mathrm{Ti} - \mathrm{OH} + \mathrm{OH^-} \rightarrow \mathrm{Ti} - \mathrm{O^-} + \mathrm{H_2O}.$$

Due to the formation of the negatively charged surface, the calcium ions in the SBF solution are attracted to the negatively charged surface of the titania coating. This is followed by the arrival of HPO_4^{2-} resulting in a hydrated precursor cluster consisting of calcium hydrogen phosphate. After the precursor clusters are formed, they spontaneously grow by consuming calcium and phosphate ions from the surrounding body fluids. The calcium phosphate phase that accumulates on the surface of the UV-illuminated titania coatings is initially amorphous (*a*-CaP). It later crystallizes to a carbonate-containing hydroxyapatite (bonelike apatite) structure by incorporating carbonate anions from the solution with the *a*-CaP phase.

In order to investigate the stability of the irradiated materials, the UV-illuminated coating was stored in the dark for one week and then soaked in SBF for four weeks. The results show that apatite can also be induced to precipitate on the coating surface. The Ti-OH groups formed on the titania surface after UV irradiation can be retained for a period of time and some surface stability is indicated.

In summary, bioactivity can be induced by UV illumination on plasma-sprayed TiO_2 coatings prepared from nanosized powders. After immersed in SBF for four weeks, apatite can precipitate on the surface of irradiated TiO_2 coating, whereas no apatite is formed on the control. The bioactivity of the TiO_2 coating surface is not lost after it is stored for one week. The formation of oxygen vacancies at the two-coordinated bridging sites by UV illumination is believed to result in the conversion of the corresponding Ti^{4+} sites to Ti^{3+} sites, which are favorable to the dissociation of water to form Ti-OH on the titania coating surface and subsequent formation of an apatite layer in SBF.

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