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Research Article

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Effect of UV Light Irradiation of Different Wavelengths on the Surface Wettability of Titanium Metal for Dental Implants

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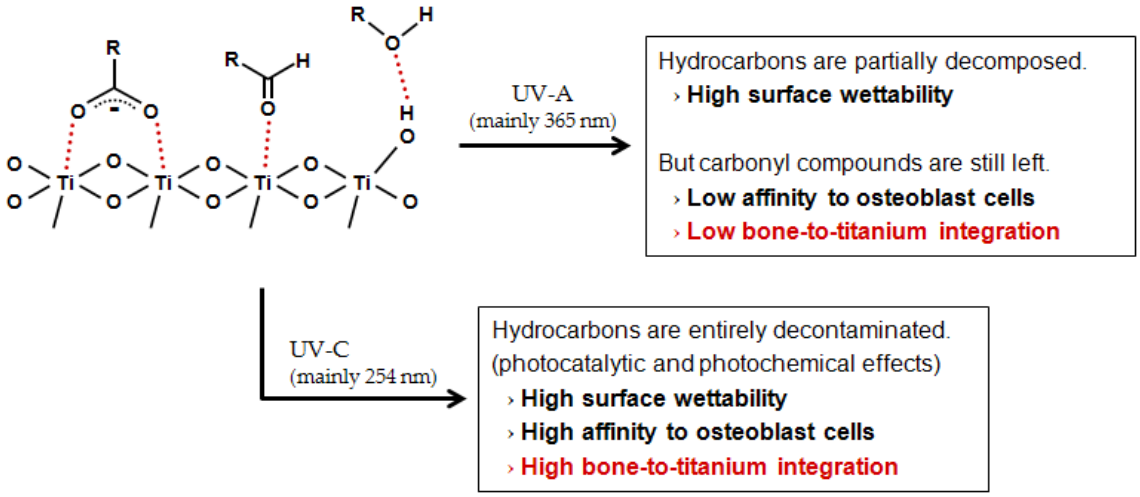
Abstract

In order to clarify the mechanism of strong osseointegration by UV light irradiation on titanium surface, we have discussed the correlation between the surface wettability and cleanliness at the molecular level. When the Ti disks (machined) were irradiated with UV-A (mainly 365 nm) or UV-C (mainly 254 nm) light, the contact angles of the water droplets smoothly decreased but leveled off at ca. 35° or 10°, respectively. This phenomenon could be explained by the low photocatalytic activity due to the thin TiO2 passive layer. On the other hand, the Ti disks (acid-etched) showed high wettability by both UV-A or UV-C light irradiation. From the results of XPS measurements, UV-A light irradiation of the Ti disks was found to decompose the C-C bonds in hydrocarbons but hardly decomposed the O-C=O bonds. In contrast, UV-C light irradiation of the Ti disks could effectively decompose both the C-C and O-C=O bonds in hydrocarbons by photocatalytic and photochemical effects. Sufficiently strong osseointegration of the disks (acid-etched) achieved by UV-C light irradiation could be explained by entirely decontamination of hydrocarbons from the titanium surfaces.

Graphical Abstract_XPS



High wettability of titanium surfaces can be achieved by partial decontamination of hydrocarbons. However, in order to obtain the strong enough osseointegration between bone tissues and titanium implants, hydrocarbons should be entirely decontaminated by UV-C light irradiation (mainly 254 nm).

Keywords: Osseointegration (bone to titanium attachment); Surface Wettability; Wavelengths of UV Light, TiO_2 Passive Layer on Titanium Metal; XPS Analyses

Introduction

Titanium metal is widely used for aircraft bodies, golf clubs, glasses, bicycles, and other structural components or systems because of its lightweight property and durability. Moreover, biochemically inert titanium is also used as biomaterials for fracture treatments or restorative treatments such as dental implants [1,2]. However, if a titanium implant does not attach or fuse well to the bone tissues, it may loosen and fall out in a short period. Thus, sufficiently strong osseointegration is desired for successful implant therapy. Ogawa et al. have reported that UV-C light irradiation (mainly 254 nm) on titanium dental implants, of which the surface was fully oxidized by sulfuric acid, dramatically enhanced osseointegration at least 8-fold as compared to conventional commercial dental implants [3-6]. They have also mentioned that osteoblast cells were efficiently cultivated (a cell-philic property) and thick bone tissues were tightly formed on the titanium implants irradiated with UV-C light.

In this study, the correlation between the wettability and cleanliness levels of titanium surfaces have been discussed from the viewpoint of surface science. It is known that TiO_2 shows photo catalytic reactivity to decompose various organic compounds into CO_2 and H_2O under UV light irradiation. However, we have reported that carboxylic acids interacting with the Ti^{4+} sites of TiO_2 surfaces are very slowly decomposed as compared to alcohols under UV-A light irradiation (mainly 365 nm). Therefore, the effects of the UV light wavelengths on the decontamination of titanium surfaces have been evaluated in detail by XPS analyses.

Experimental

Sample preparation [3, 4]

Two different types of titanium disks (diameter: 20 mm, thickness: 1.5 mm) were prepared as model surfaces of titanium dental implants. One was mechanically polished by a lathe and denoted as Ti disk (machined), clearly showing a metallic luster. The other was treated with a H_2SO_4 solution (67 %) at 393 K for 75 sec and denoted as Ti disk (acid-etched). The surface of the Ti disk (acid-etched) was a gray color due to the formation of the TiO_2 layers.

Characterization

The Ti disk samples were characterized by X-ray diffraction (XRD-6100, Shimadzu, Japan), FE-SEM observation (SU8010, Hitachi, Japan) and X-ray photoelectron spectroscopy (ESCA3200, Shimadzu, Japan). Before the SEM observation, the samples were cleaned by ultrasonic treatment in acetone. XPS measurements were performed under high vacuum conditions (6×10^{-7} Pa) after fixed periods of UV light irradiation. Surface wettability of the Ti disks was evaluated using a water contact angle meter (CA-X, Kyowa Interface Science, Japan) in a clean room of Osaka Prefecture University under controlled conditions (class 10, 273 K, 46% humidity). The Ti disks were irradiated with UV light for fixed periods and water of ca. 1 μL was dropped onto the surface with a micro syringe. The contact angles of water droplets were measured at 4 - 5 points of each sample to obtain the average values.

UV light Irradiation

UV-A region light (λ = 315 - 380 nm) was irradiated onto the Ti disks under ambient conditions with a high-pressure Hg lamp (Toshiba, SHL-100UVQ-2, 100 W). The UV light intensity measured by a UV radiometer (Topcon, UVR-2) was ca. 0.5 mW/cm^2 (λ = 360±20 nm) and ca. 0.03 mW/cm^2 (250±20 nm) at an irradiation distance of 23 cm. UV-C region light (λ = 200 - 280 nm) was similarly irradiated onto the Ti disks under ambient conditions using a bacterial lamp (low-pressure Hg lamp) (Toshiba, GL-15, 15 W). The UV light intensity was ca. 0.1 mW/cm^2 (λ = 360±20 nm) and ca. 5.0 mW/cm^2 (250±20 nm) at an irradiation distance of 5 cm.

Results and Discussion

(Figure 1) shows the Ti2p XPS spectra of the Ti disk (machined) and Ti disk (acid-etched) samples. For the Ti disk (machined), the $Ti2p_{3/2}$ peak due to a Ti^{4+} state was observed at 458.4 eV but no peaks due to reduced Ti^{3+} or Ti0 states were observed [2,7,8]. These results clearly indicate that a stoichiometric TiO_2 passive layer exists even on the Ti disk (machined) having a metallic luster. Similarly, the gray-colored Ti disk (acid-etched) showed a $Ti2p_{3/2}$ peak due to a Ti^{4+} state at 458.0 eV, suggesting that the TiO_2 layer was relatively thicker of at least 10 - 50 nm than the Ti disk (machined). In order to discuss the different surface morphologies of the Ti disks, SEM observation was performed.

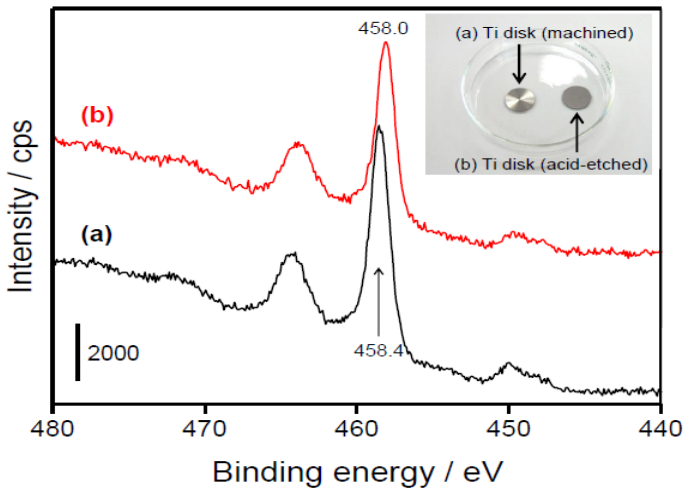


Figure 1: Ti2p XPS spectra of: (a) Ti disk (machined) and (b) Ti disk (acid-etched). Inset: photographs of the Ti disks.

Support Information_XPS

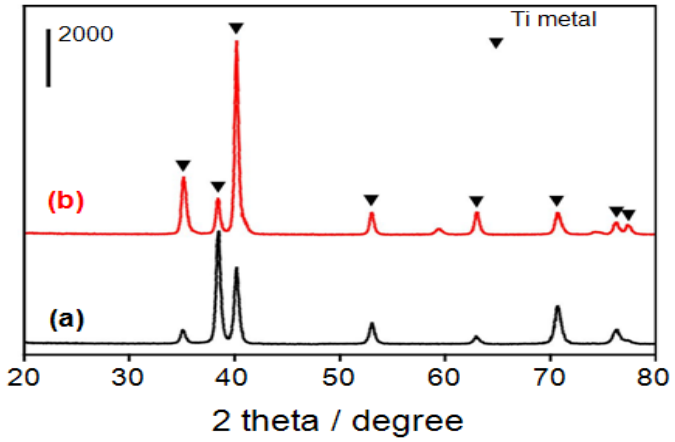


Figure 1: S1 XRD patterns of (a) Ti disk (machined) and (b) Ti disk (acid etched)

(Figure 2) shows the SEM images of the surface morphologies of the Ti disks were discussed by SEM images. Ti disk (machined) and Ti disk (acid-etched) samples. Although the Ti disk (machined) with a metallic luster showed radial grooves due to a mechanical polish treatment, the surface was relatively smooth in a micron size order. In contrast, the Ti disk (acid-etched) with a gray color showed a rough surface with ca. 20 - 30 μm-sized grains. However, from the XRD patterns shown in (Figure 1) S1, all diffraction peaks were assigned to titanium metal and no diffraction peaks due to anatase or rutile phases were observed. This means the stoichiometric TiO_2 passive layer on the Ti disks exists as an amorphous phase.

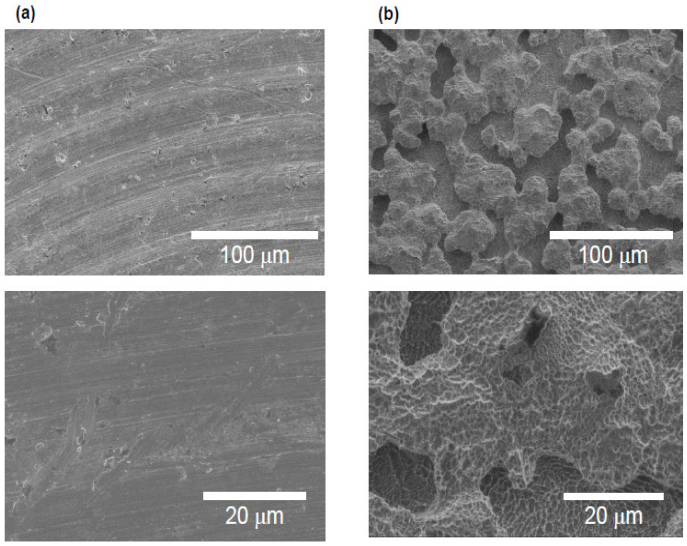


Figure 2: SEM images of: (a) Ti disk (machined) and (b) Ti disk (acid-etched).

(Figure 3) shows the time courses of the contact angles of water droplets on the Ti disks under UV-A light irradiation (λ = 315 - 380 nm) with a high-pressure Hg lamp. When the Ti disk (machined) was irradiated with UV-A light, the contact angles of water droplets decreased but leveled off at 30 - 35°. Although the UV-A light intensity was increased up to 4 times (irradiation distance was shortened from 23 cm to 11 cm), the water contact angles on the Ti disk (machined) hardly changed because of a relatively smooth surface morphology. In contrast, when the Ti disk (acid-etched) was irradiated with UV-A light irradiation from a 23cm distance (condition 1 [0 - 48 h]: ca. 0.5 mW/cm^2 at λ = 360±20 nm and ca. 0.03 mW/cm^2 at 250±20 nm), the contact angles of water droplets quickly decreased to 0° in 30 min because of a rough surface morphology. These results suggested that the surface wettability of the Ti disks was closely related to the surface morphologies.

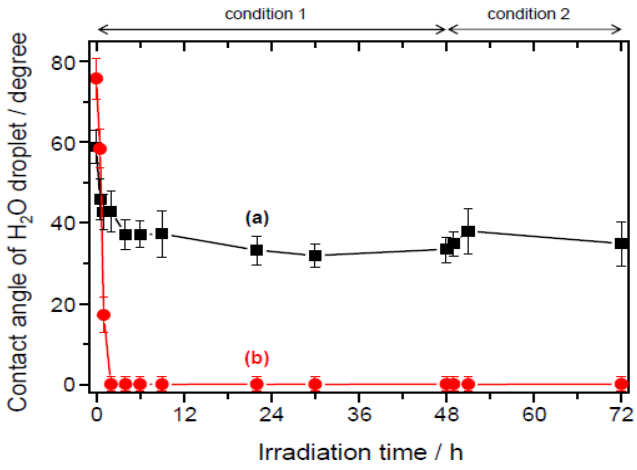


Figure 3: Time courses for changes in the contact angles of water droplets on the Ti disks under UV-A light irradiation using a high-pressure Hg lamp.

- **Condition 1:** distance: 23 cm (0 - 48 hours), λ = 360±20 nm: ca. 0.5 mW/cm^2, 250±20nm: ca. 0.03 mW/cm^2.
- **Condition 2:** distance: 11 cm (48 - 72 hours), λ = 360±20 nm: ca. 2.0 mW/cm^2, 250±20nm: ca. 0.07 mW/cm^2.

In order to discuss the correlation between surface wettability and the amounts of hydrocarbons on the Ti disks under UV-A light irradiation (λ = 315 - 380 nm), XPS measurements were carried out. (Figure 4) shows the C1s XPS spectra of the Ti disk surfaces under UV-A light irradiation. The main band at ca. 285 eV and sub and at ca. 289 eV can be assigned to the C-C and O-C=O bonds of the hydrocarbons, respectively [9-11]. It was clearly shown that the band due to the C-C bond efficiently decreased but the O-C=O bond hardly decreased by UV-A light irradiation. As reported in previously, carboxylic acids or aldehydes were very slowly decomposed by the TiO_2 photo catalysts with UV-A light irradiation since carboxylic compounds strongly interact with the Ti^{4+} sites of TiO_2 surfaces [12,13]. These results clearly indicate that high wettability on the Ti disks with a TiO_2 passive layer can be achieved only by partially decontaminating the hydrocarbons on its surface by UV-A light irradiation [14,15]. However, Ogawa et al. have mentioned sufficiently strong interaction between bone tissue and the titanium surface as well as high cell-philic properties were not obtained by UV-A light irradiation from a high-pressure Hg lamp [3-6]. These results clearly suggest that the carboxylic compounds and/or carboxylate ions left on the titanium surfaces inhibit the efficient cultivation of osteobrast cells as well as the formation of bone tissue.

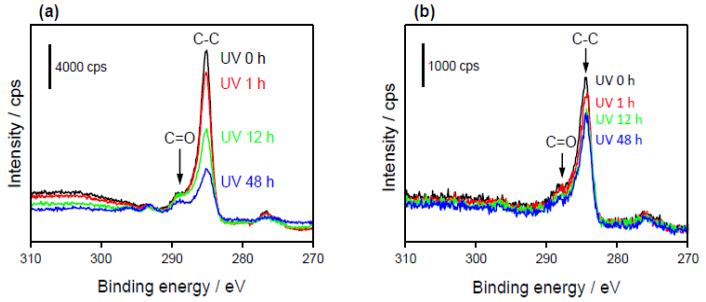


Figure 4: C1s XPS spectra of: (a) Ti disk (machined) and (b) Ti disk (acid-etched) under UV-A light irradiation (distance: 23 cm, λ = 360±20 nm: ca. 0.5 mW/cm^2, 250±20 nm: ca. 0.03 mW/cm^2) using a high-pressure Hg lamp.

Next, we have investigated the changes in surface wettability of the Ti disks under UV-C light irradiation (λ = 200 - 280 nm) with a bacterial lamp (Figure 5).

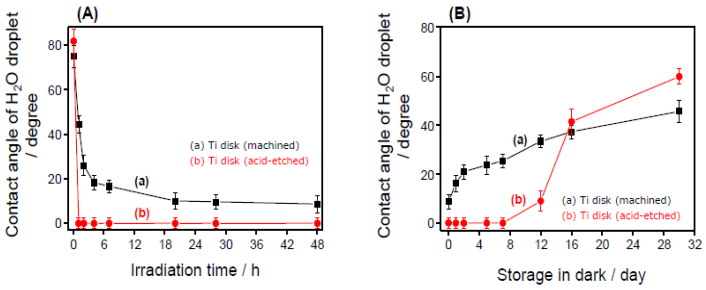


Figure 5: Time courses for changes in the contact angles of water droplets on the Ti disks (A) under UV-C light irradiation (distance: 5 cm, λ = 360±20 nm: ca. 0.1 mW/cm^2, 250±20 nm: ca. 5.0 mW/cm^2) using a 15 W bacterial lamp (low-pressure Hg lamp) and (B) under dark conditions. (a) Ti disks (machined) and (b) Ti disk (acid-etched)

Shows the time courses of the contact angles of water droplets on the Ti disks (A) under UV-C light irradiation and (B) under dark conditions. When the Ti disk (acid-etched) was irradiated with UV-C light, the contact angles of water droplets immediately decreased to 0° in 30 min. Interestingly, when the Ti disk (acid-etched) was placed in the dark, high wettability (water contact angle of 0°) was maintained for 7 days. In contrast, when the Ti disk (machined) was irradiated with UV-C light in the same manner, the contact angles of water droplets decreased but leveled off at ca. 10°. As compared to the results in (Figure 3-(a)), UV-C light irradiation (mainly 254 nm) was clearly more effective in obtaining high surface wettability of the Ti disks than UV-A light irradiation (mainly 365 nm). When the Ti disk (machined) was

placed in the dark after UV light irradiation, the contact angles of water droplets immediately increased

In order to clarify the effect of UV-C light irradiation (λ = 200 - 280 nm) on the surface wettability of the Ti disks, hydrocarbons adsorbed on the Ti disks were evaluated by XPS measurements (Figure 6).

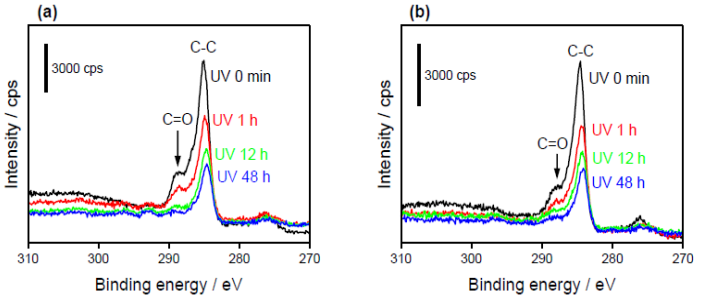


Figure 6: C1s XPS spectra of: (a) Ti disk (machined) and (b) Ti disk (acid-etched) under UV-C light irradiation (distance: 5 cm, λ = 360±20 nm: ca. 0.05 mW/cm^2, 250±20 nm: ca. 5.0 mW/cm^2) using a bacterial lamp (low-pressure Hg lamp).

Shows the C1s XPS spectra of the Ti disks under UV-C light irradiation. When the Ti disks were irradiated with UV-C light from a bacterial lamp, both bands due to C-C (285 eV) and O-C=O (289 eV) effectively decreased. As mentioned in (Figure 4), since carboxylic compounds on the Ti disks are hardly decomposed by UV-A light irradiation, the efficient decontamination of carboxylic compounds by UV-C light irradiation is assumed to be a photochemical effect. In fact, USHIO Co. Ltd. (a developer of light sources in Japan) has reported that quartz surfaces showed high surface wettability by vacuum-UV light irradiation from a Xe_2 excimer lamp in the presence of O_2 or O_3 [16]. They have also mentioned that changes in wettability of quartz surfaces are closely related to a decrease in the intensity of the C1s XPS spectra. Since a quartz surface does not show any photo catalytic reactivity, the high surface wettability obtained by V-UV light irradiation can be explained by the efficient decontamination of hydrocarbons. Ogawa et al. have actually mentioned sufficiently strong interaction between bone tissue and titanium implants could be obtained by UV-C light irradiation from a bacterial lamp [3-6]. These results attest to the strong osseointegration between bone tissue and titanium dental implants which can be achieved by entirely decontaminating hydrocarbons by UV-C light irradiation.

Finally, as shown in (Figure 7), we have confirmed the correlation between the surface wettability and the intensity of the C1s XPS spectra. When the Ti disk, which showed high wettability by UV-C light irradiation, was placed in dark conditions for 3 days, the contact angle of water droplets was still 0°. At this time, the main band due to the C-C bond at 285 eV slightly increased but the sub and due to the O-C=O bond at 289 eV hardly increased.

When the Ti disks were placed in the dark for a long period (1 - 4 weeks), the surface wettability recovered to its initial state and the intensity of the C1s XPS spectra, especially due to the O-C=O bond, gradually increased. From such experimental evidence, high surface wettability could, in fact, be achieved by removing some fraction of the hydrocarbons on the Ti disks by UV-A light irradiation (λ = 315 - 380 nm). However, the entire decontamination of hydrocarbons on the TiO_2 surface by UV-C light irradiation could sustain high wettability for long periods even under dark conditions.

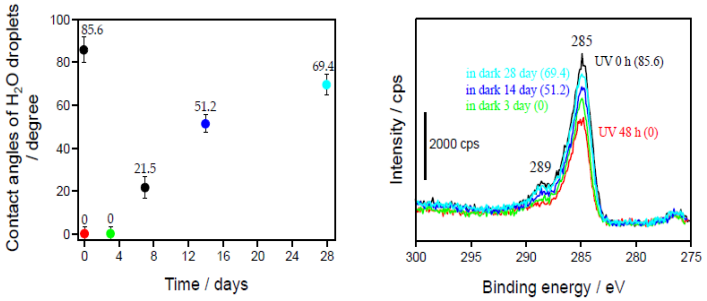


Figure 7: Contact angles of water droplets on the Ti disk (acid-etched) under dark conditions and the corresponding C1s XPS spectra.

Conclusions

The effect of UV light irradiation of different wavelengths on titanium surfaces used in dental therapy were investigated at the molecular level from the viewpoint of the correlation between increased surface wettability and cleanliness for improved osseointegration. A stoichiometric TiO_2 passive layer with an amorphous phase existed even on the Ti disk (machined) having a metallic luster. On the other hand, a thicker TiO_2 layer was confirmed to exist on the surface of the Ti disk (acid-etched) resulting in a gray color.

Although there is a difference in degree, UV-A light (λ = 315 - 380 nm) irradiation could improve the surface wettability of the Ti disks. However, although UV-A light irradiation could efficiently decompose the C-C bonds in hydrocarbons, it hardly decomposed the O-C=O bonds in carboxylic compounds. That is, the highly wettable titanium surface with a TiO_2 passive layer can, in fact, be achieved by decontaminating even some fraction of the hydrocarbons. In contrast, UV-C light irradiation (λ = 200 - 280 nm) could more efficiently improve surface wettability of the Ti disks as compared to UV-A light irradiation. Moreover, UV-C light irradiation on the Ti disks effectively decomposed the C-C and O-C=O bonds in hydrocarbons by both photo catalytic and photochemical effects. The Ti disks (acid-etched) on which most of the carboxylic compounds were decomposed by UV-C light irradiation showed high surface wettability for a period as long as one week. Studies are underway to further elucidate

the photo catalytic mechanisms involved in order to strengthen osseointegration.

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