

Ultraviolet A and Ultraviolet C Light-Induced Reduction of Surface Hydrocarbons on Titanium Implants

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Abstract

Keywords

- ▶ photofunctionalization
- ▶ sandblasted acid etched
- ▶ ultraviolet A irradiation
- ▶ ultraviolet C irradiation
- ▶ X-ray photoelectron spectroscopy

Objective The carbon, titanium, and oxygen levels on titanium implant surfaces with or without ultraviolet (UV) pretreatment were evaluated at different wavelengths through X-ray photoelectron spectroscopy (XPS).

Materials and Methods This interventional experimental study was conducted on nine Dio UFII implants with hybrid sandblasted and acid-etched (SLA) surface treatments, divided equally into three groups. Control group A samples were not given UV irradiation, while groups B and C samples were given UVA (382 nm, 25 mWcm²) and UVC (260 nm, 15 mWcm²) irradiation, respectively. The atomic ratio of carbon, titanium, and oxygen was compared through XPS.

Results Mean carbon-to-titanium ratio and C1 peaks considerably increased in Group A compared to those in experimental Groups B and C. The intensity of Ti2p and O1s peaks was more pronounced for group C compared to that for groups A and B.

Conclusions Although the decrease in surface hydrocarbons was the same in both UV-treated groups, the peak intensity of oxygen increased in the UVC-treated group. Thus, it can be concluded that compared with UVA irradiation, UVC irradiation has the potential to induce more hydrophilicity on SLA-coated implants.

Introduction

Commercially available implants are inevitably contaminated with hydrocarbons in their packaging,¹ with an average percentage ranging from 17.9% to 76.5%.² Increase in carbon content decreases the hydrophilicity, thus increasing the chances of implant failure.^{3,4} Pretreatment of dental implants either with ultraviolet (UV) irradiation

(photofunctionalization) or with nonthermal plasma treatment⁵ effectively removes the carboxylic groups, thus resulting in superhydrophilic surface.^{6,7} However, UV radiation showed superiority, particularly on titanium implants.^{6,8} Thus, in the present study, higher and lower wavelengths, UVA and UVC radiations, respectively, were employed on titanium implants as it is difficult to evaluate the optimum wavelength for photofunctionalization.

Materials and Methods

An interventional experimental study was conducted at the Science and Engineering Research Centre Engineering Campus, Universiti Sains Malaysia (USM), on hybrid SLA-coated Dio UFII dental implants. A total of nine implants, each 10 mm long and 4.0 mm in diameter, were acquired for X-ray photoelectron spectroscopy (XPS) analysis. The Human Research Ethics Committee USM approved the study protocol. A purposive (nonprobability) sampling technique was adopted. Three replicate samples were required to analyze the objectives.

Ultraviolet Irradiation

Nine SLA-coated Dio UFII hybrid implants of identical dimensions were randomly divided into three groups with three samples in each group. Group A was the control group, whereas groups B and C samples were photofunctionalized for 10 min with UVA (382 nm, 25 mW/cm²) and UVC (260 nm, 15 mW/cm²), respectively, by placing them in a UVACUBE 100 (Honle, Germany). Since UVA has the potential to penetrate through glass and clouds to change chemical bonds, while UVC does not,⁹ implants were removed from glass or plastic containers before UV irradiation to ensure exposure to all wavelengths.

X-Ray Photoelectron Spectroscopy Analysis

After irradiation, the titanium implant surface was evaluated using XPS. The atomic carbon/titanium (C/Ti) ratio of titanium implants was compared among the study groups. Representative XPS profiles of carbon, titanium, and oxygen contents on titanium implant surfaces were analyzed.¹⁰

The XPS wide and narrow scan spectra were acquired using AXIS Ultra Delay-Line Detector (DLD), Kratos, equipped with an Al K α X-ray source (1486.6 eV) at 10 mA and 15 kV, analyzing a 300 μ m \times 700 μ m area under a 4.8 EX10-9 Torr Ultrahigh vacuum environment inside a sample analysis chamber. Using the multichannel plate and DLD with a takeoff angle of 90° and an acceptance angle of 30°, the analyses were performed in the hybrid lens mode with the slot aperture, and the analyzer was operated in fixed analyzer transmission mode with the pass energy of the hemispherical

analyzer set at 160 eV for the survey/wide scan and 20 eV for the high-resolution scans/narrow scans. All the scans were required under charge neutralization conditions using a low-energy electron gun within the field magnetic lens.

The spectra were analyzed using Vision software (AXIS Ultra DLD, Kratos), which included vision manager and vision processing. The linear method was used for background subtraction and curve fitting. Binding energy was referenced to an adventitious carbon at 284.6 eV.

Statistical Analysis

SPSS version 20.0 (SPSS, Inc, Chicago, Illinois) was used for the data entry and analysis. The mean difference in the concentration of carbon, titanium, nitrogen, and oxygen, as well as the difference in C/Ti ratio among the three groups, was determined through one-way analysis of variance. The post hoc Tukey's test was used for multiple comparisons. $P < 0.05$ was considered statistically significant and $P > 0.05$ statistically nonsignificant.

Results

The average percentage of carbon for group A was highest at approximately 51.11 ± 12.4 , compared to groups B (25.8 ± 0.27) and C (26.37 ± 0.84 ; $P < 0.01$) (►Table 1). When compared group-wise, the difference between groups B and C was insignificant (►Table 2 and ►Fig. 1).

Average titanium and oxygen percentages were significantly lower in group A and higher in groups B and C ($P < 0.01$) (►Table 1); there was no significant difference between Groups B and C (►Tables 1, 2 and ►Fig. 1). Nitrogen percentages were similar among all groups (►Table 1).

Mean C/Ti ratios (►Table 1) were significantly higher in group A than in UV-treated groups ($P < 0.05$), with no significant difference among groups B and C (►Table 2 and ►Fig. 1).

XPS spectra showed Ti2p, O1s, and C1s peaks for titanium surfaces in each group (►Figs. 2–4). In C1s XPS spectra (►Fig. 3), the predominant peak attributed to hydrocarbon (C-C, C-H) at 284.7 eV and the other three peaks (at 286.531, 288.241, and 288.954 eV, representing C-O, C=O, and O-C=O, respectively) were significantly reduced after UVA and UVC treatment (►Fig. 3).

Table 1 Average levels of concentration for various components and ratio and comparison among the three groups (one-way analysis of variance)

	Group, mean \pm SD			P (ANOVA)
	Control	UVA	UVC	
Carbon	51.11 (12.40)	25.80 (0.27)	26.37 (0.84)	0.008 [†]
Titanium	14.35 (4.06)	22.29 (0.50)	21.81 (0.55)	0.011*
Nitrogen	1.15 (0.23)	0.82 (0.26)	0.81 (0.40)	0.353
Oxygen	33.39 (8.70)	51.33 (0.11)	51.02 (0.68)	0.007 [†]
Carbon/titanium ratio	3.90 (1.81)	1.16 (0.03)	1.21 (0.07)	0.029*

Abbreviations: ANOVA, analysis of variance; SD, standard deviation; UVA, ultraviolet A; UVC, ultraviolet C.

*The mean difference is significant at the 0.05 level.

[†]The mean difference is significant at the 0.01 level.

Data are expressed as mean and SD ($n=3$).

Table 2 Group-wise comparison for components using Tukey's test

Dependent variable	Group (I)	Group (J)	Mean difference (I-J)	SE	p
Carbon	Control	UVA	25.31*	5.86	0.012
		UVC	24.74*	5.86	0.013
	UVA	UVC	-0.57	5.86	0.995
Titanium	Control	UVA	-7.94*	1.95	0.015
		UVC	-7.46*	1.95	0.020
	UVA	UVC	0.48	1.95	0.967
Oxygen	Control	UVA	-17.94*	4.11	0.011
		UVC	-17.63*	4.11	0.012
	UVA	UVC	0.31	4.11	0.997
Carbon/titanium ratio	Control	UVA	2.75*	0.85	0.042
		UVC	2.69*	0.85	0.045
	UVA	UVC	-0.05	0.85	0.998

Abbreviations: SD: standard deviation, SE: standard error, UVA: ultraviolet A, UVC: ultraviolet C.

*The mean difference is significant at the 0.05 level.

The data are expressed as mean and SD (n=3).

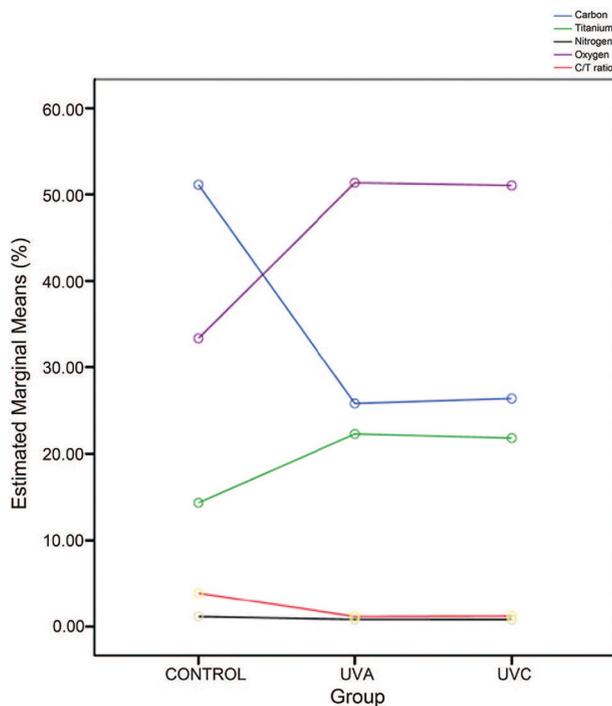


Fig. 1 Line graph presents average percentage for each component and carbon/titanium ratio for the three groups. The data are expressed as mean \pm standard deviation (n = 3).

For Ti2p spectra (\rightarrow Fig. 2), the titanium peaks were slightly more intense for group C at 458.5 eV compared with those for groups A and B.

For O1s spectra (\rightarrow Fig. 4), the first peak (predominant peak at 529.94 eV) was assigned to O1s in TiO₂ (O=2), whereas the second peak was assigned for O1s in C-O and C=O at 531.262 eV, while the third peak at 531.837 eV indicated the O1s in titanium hydroxide (Ti-OH) and O-C=O. All the three O1s peaks in XPS spectra showed an increasing trend of O1s after UVA and UVC treatment. The significant increase

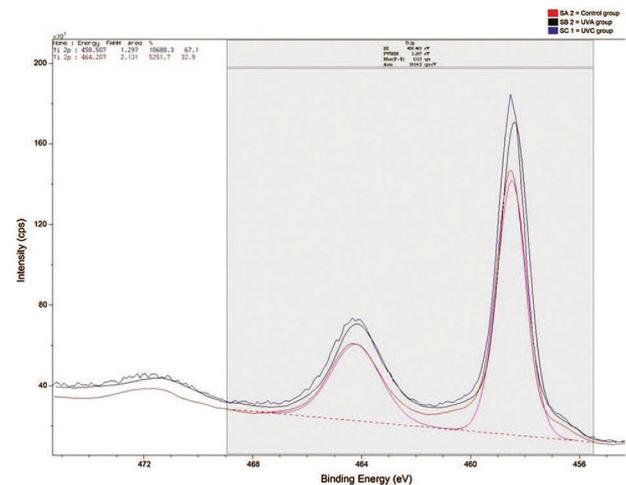


Fig. 2 X-ray photoelectron spectroscopy high-resolution spectra of the titanium surfaces of all the three groups showing Ti2p profile.

in peak intensity at 531.837 eV was more pronounced for Group C than for Groups A and B.

Discussion

This study proved that high carbon levels are generally detected on commercial implant surfaces, indicating that exposing implants to UV radiation remove the surface hydrocarbons, thereby exposing the OH and oxygen radicals, resulting in a superhydrophilic surface, which attracts water molecules, proteins, and bone-forming cells.⁸ Therefore, hydrophilicity is indeed dependent on the carbon and oxygen ratios, with greater the carbon content, lesser the hydrophilicity, and vice versa. Previously, it has been reported that UVA and UVC irradiations of acid-etched implants for approximately 48 h at 0.1 and 2 mW/cm², respectively, continuously decreased the atomic percentage of carbon from 50% to <20% in both

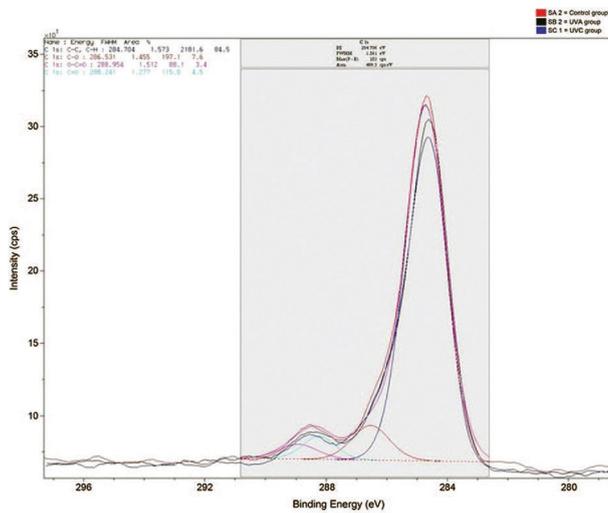


Fig. 3 X-ray photoelectron spectroscopy high-resolution spectra of the titanium surfaces of all the three groups showing C1 profile.

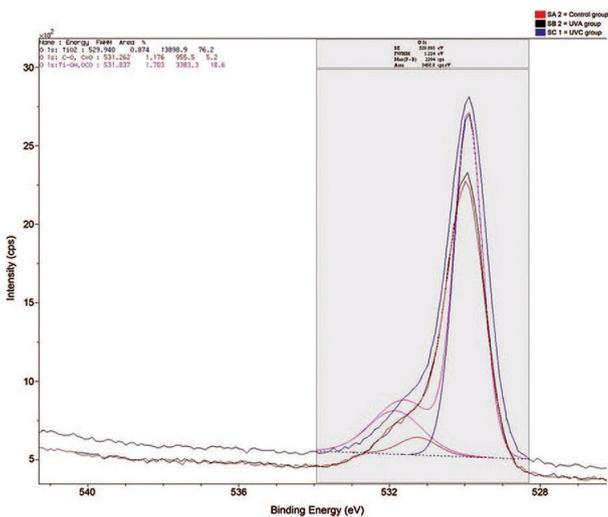


Fig. 4 X-ray photoelectron spectroscopy high-resolution spectra of the titanium surfaces of all the three groups showing O1 profile.

groups.¹¹ A previous study showed that decreasing the percentage of carbon to <20% in acid-etched implants caused maximum cellular proliferation and hydrophilicity on the surface.¹⁰ In this study, SLA implants were photofunctionalized for just 10 min with UVA (382 nm, 25 mW/cm²) and UVC (260 nm, 15 mW/cm²) irradiations. The important positive factor is that after irradiating the implants for a short period and at higher intensity, the carbon percentage decreased to approximately 25% in both experimental groups. Thus, a slight increase in the exposure time may decrease the carbon content to <20% and further reduce C/Ti ratios, which are much more feasible for dental chair-side procedures compared with treating the implants for 48 h as performed previously.^{11,12}

Although both UVA and UVC irradiations can remove surface hydrocarbons, UVC is considered superior because it can improve hydrophilicity, protein absorption, and cell function.^{10,13} Remarkably, the effect on hydrocarbon levels on microarc oxidized (MAO) titanium disks after irradiating

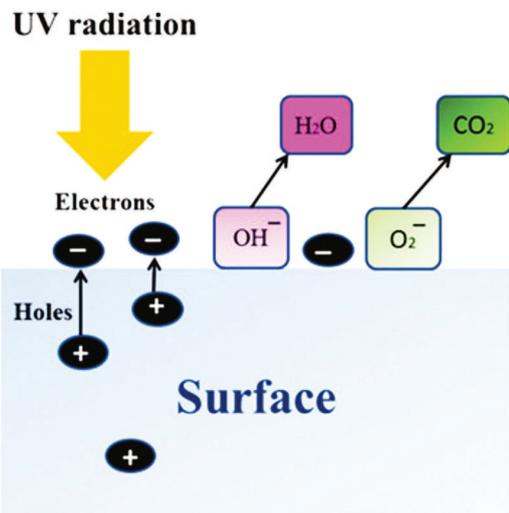


Fig. 5 The brief illustration of photocatalytic activity on surface.

15 W UVA and UVC lamps for 24 h¹³ was almost the same as that observed in this study; alternatively, carbon atomic percentages decreased to a similar level in both UV-treated groups even after 10 min of irradiation.

Meanwhile, Ti-OH peaks in the O1s spectra showed an increasing trend in both irradiated groups (►Fig. 4). Although Ti-OH levels were almost similar in both UV-treated groups, the peak oxygen intensity at 529.89 eV increased for UVC-treated implants compared with that for UVA-treated implants. This difference in oxygen peaks proves that UVA and UVC irradiations employ different mechanisms for the removal of hydrocarbons. UVA irradiation removes surface hydrocarbons through photocatalysis, whereas UVC irradiation directly decomposes hydrocarbons through photolysis, generating more Ti-OH.^{14,15} During photocatalysis, UVA irradiation causes excitation of electrons, resulting in the release of various OH radicals and anionic oxygen species or superoxide radical anions. These reactive species further induce the photocatalytic decomposition of organic hydrocarbon molecules to the end products water and CO₂ (►Fig. 5).⁵ In photolysis, UVC irradiation converts Ti⁴⁺ ions to Ti³⁺ ions generating oxygen vacancies that react with absorbed water and form Ti-OH on the titanium surface.¹³ In this study, this phenomenon can be linked to a higher oxygen peak and a slightly more intense Ti2p peak in the UVC-treated group, probably due to photolysis. Lower titanium and oxygen peaks of group B showed inefficient oxygen, titanium, and OH radical production, concluding that UVA light causes photocatalytic hydrocarbon removal due to lower light intensity.

These findings from SLA-coated implants are similar to those of a prior study conducted using MAO-coated implants,¹⁶ proving that UVC photofunctionalization potentially induces greater surface energy and hydrophilicity on different implant surfaces. However, since the main focus was to evaluate the changes in carbon, titanium, and oxygen contents on titanium surfaces, further studies must be done to evaluate the cellular attachment changes after UVA and UVC treatment on SLA-coated implants. Using this standardized technique of photofunctionalization, the

state of hydrocarbons and biological response of various implants with different surface coatings can be analyzed and compared.

Conclusion

In this study, SLA-etched surface titanium implants were exposed for 10 min using a standardized UVA and UVC irradiation through the UVACUBE 100. Although the decrease in surface hydrocarbons was the same in both of the UV-treated groups, the peak intensity of oxygen was increased in the UVC-treated group. Thus, we conclude that, compared with UVA irradiation, UVC irradiation has the potential to induce more hydrophilicity on SLA-coated implants.

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None.

Conflicts of Interest

None.

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