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# Photofunctionalization of dental zirconia oxide: Surface modification to improve bio-integration preserving crystal stability

Marco Roy[a,*], Alfonso Pompella[b], Jerzy Kubacki[c,d], Adam Piosik[a], Bronisław Psiuk[e], Joanna Klimontko[c,d], Jacek Szade[c,d], Robert A. Roy[f], Wieslaw Hedzelek[a]

[a] Prosthodontic Department, Poznan University of Medical Science, Ul. Bukowska 70, 60-812 Poznan, Poland
[b] Dept. of Translational Research and New Technologies in Medicine and Surgery, University of Pisa Medical School, Via Roma 55, 56126 Pisa, Italy
[c] A. Chelkowski Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland
[d] Silesian Center for Education and Interdisciplinary Research, 75 Pulku Piechoty 1A, 41-500 Chorzów, Poland
[e] Refractory Materials Division,Institute of Ceramics and Building Materials, Toszecka 99, 44-100 Gliwice, Poland
[f] Private Practice, Pisa, Italy

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ABSTRACT

The use of zirconium oxide in dental implantology is rapidly increasing as it is regarded as being more aesthetical and biologically friendly than titanium oxide. The interaction of titanium oxide with cells and proteins has proven to be significantly affected by the inevitable atmospheric hydrocarbon contamination, defined as biological ageing. The latter has proven to be effectively reversed by UVC irradiation. Crystal structures of both Zr and Ti oxides are very similar, thus also $ZrO_2$ is prone to contamination by hydrocarbons. In the present study we have characterized the chemical-physical changes occurring to $ZrO_2$ after UVC irradiation. Firstly a reduction by 3-fold of carbon present on its surface. XRD analysis has indicated that UVC irradiation treatment does not affect the crystalline structure of $ZrO_2$, suggesting that it is possible to improve cell attachment on the surface without sacrificing the mechanical strength of the material. In addition a chemical model of interaction of cell surface proteins with the almost carbon free $ZrO_2$ surface obtainable after UVC irradiation is proposed, pointing to the important role likely played by integrins and RGD sequences originating in soluble proteins adsorbed at the cell/$ZrO_2$ interface. Hence in clinical practice UVC photofunctionalization could improve the soft tissue seal around dental implants functioning as a valid barrier between implant and peri-implant bone, thereby improving the long-term success of implants.



## 1. Introduction

The use of dental implants for the rehabilitation of partially or fully edentulous patients has been widely applied and with undeniable success. The long-term outcomes of dental implants is not dependent only on the intrinsic osseointegration process but also on the seal that the soft tissues create around the prosthetic abutment. The quality of the seal has an impact on the bacterial penetration and therefore can prevent bone loss and therefore have a gingiva which is in better shape [1]. Therefore, a lot of research has focused on surface modifications to improve the early response and strong attachment of cells to the implant-abutment surface. The results have shown a better fibroblast adhesion and proliferation upon surface modification [2,3]. Cell adhesion and the speed of the healing process is imperative to prevent/reduce bacterial colonization of the surface. However, surface modifications, such as sand-blasting and acid etching are associated with an increase in roughness and surface free energy creating not only a favorable environment for the cells but also for the presence of bacteria [4].

In the field of implant-prosthodontics titanium abutments are the gold standard, thanks to their high biocompatibility, strength and resistance to corrosion [5]. The major drawback for titanium is its limited aesthetic appearance due to its metallic-greyish color leading to the so called umbrella effect [6]. Especially noticed in patients with thin gingival biotype and with full ceramic crowns. These aesthetic concerns led to the development of $ZrO_2$ ceramic abutments which due to their good mechanical, biological and aesthetic properties and lack of electrolytic corrosion have been well received by the implant community [7–10]. The favorable biological properties of $ZrO_2$ are: no toxicity [11,12], nor mutagenecity

* Corresponding author.
*E-mail address:* metalmark@hotmail.it (M. Roy).

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[13,14] and lower inflammatory response as compared to titanium and polyethylene [15,16]. Moreover, bacteria colonization has been proven to be lower than that found for titanium surfaces [17]. Thus, less bone reabsorption around ceramic implant abutments is observed over the course of time. However, the biological properties of Titanium as known till today, are presently under investigation after the recent discovery and use of photofunctionalization; a method that exploits UVC irradiation to remove the hydrocarbon contamination deposited on titanium. As a result of the irradiation, the surface of the oxide becomes super-hydrophilic. In biological terms instead a virtually carbon free titanium surface has been reported to increase its bioactivity towards osteoblasts and enhance the overall process of osseointegration. In a previous publication we have shownthat the reason for this enhancement is in the interaction of amino acids, thus thanks to the interactions of proteins present on cell surfaces with titanium oxideafter UVC irradiation. That is, the energy of the UV rays is able to break the bonds between Titanium atoms and the O and/or N atoms of contaminant molecules. These sites on the surface become chemically active and become available for the attachment to the O,N,S atoms present on the proteins [18]. Even though $ZrO_2$ as described before has some advantages when compared to $TiO_2$ it cannot avoid the deposition of contaminant hydrocarbons on its surface already described for titanium as biological ageing. The aim of this study was to evaluate the effectiveness of UVC irradiation in removing hydrocarbons from the $ZrO_2$ surface and to analyze the chemical-physical aspects present. Thus, we are proposing a model for protein and in turn cell attachment to $ZrO_2$ after UVC induced decontamination. From a clinical practice point of view, the results could be of great interest as the soft tissues could form a more rapid and effective soft tissue seal around the implant functioning as a valid barrier between implant and peri-implant bone therefore improving the long-term success of implants.

## 2. Materials and methods

### 2.1. $ZrO_2$ samples and UVC light irradiation

Yttrium tetragonally stabilized zirconium oxide disks 10 mm in diameter and 2 mm thickness were prepared from commercially available zirconia blocks Lava plus (Lava™ Plus,3 M ESPE). The disks surface was polished with a wet abrasive powder grade 240 (63–50 μm) and this was followed by being sintered in a dedicated dental ceramic furnace (Lava™ Furnace 3 M ESPE). The process described is in line with the protocol used during the fabrication of zirconia dental abutments. The $ZrO_2$ disks were divided into 2 groups, UVC-irradiated and untreated. The UVC-irradiated group underwent a 12 min UVC irradiation treatment by using a Ushio TheraBeam® SuperOsseo device.

### 2.2. Structural and surface analysis

To determine the crystalline phases of the $ZrO_2$ discs and to analyze if surface irradiation could induce any change in the crystal phase before and after UVC photofunctionalization, the X-ray diffraction experiments (XRD) were carried out. A high-resolution Panalytical Empyrean diffractometer was used with Cu $K_\alpha$ radiation (λ = 1.5418 Å, 40 kV, 30 mA) equipped with a PIXcel detector.

Data was collected in the 5°–140° 2θ range with 0.0131° steps. The phase analysis was performed by the "X'Pert High Score Plus" computer program and with the data from ICDD PDF-4 database. The lattice parameters were determined from diffraction lines using the Chekcell v.4 program.

By Using the Toraya et al. method [19], it was possible to calculate the tetragonal/monoclinic volume fraction ratio $V_m$ as:

$$V_m = \frac{1.311x}{1 + 0.311x} \quad (1)$$

where,

$$x = \frac{I_m(\bar{1}11) + I_m(111)}{I_m(\bar{1}11) + I_m(111) + I_t(101)} \quad (2)$$

$I_m(hkl)$ and $I_t(hkl)$ are the integrated intensities of the monoclinic and tetragonal peaks, respectively. The tetragonal fraction ($V_t$) is given by:

$$V_t = 1 - V_m \quad (3)$$

The surface topography and morphology of the $ZrO_2$ discs was analyzed by scanning electron microscope (SEM) Mira III from Tescan coupled with electron X-ray dispersive spectroscope (EDS) Aztek Automated from Oxford Instruments. Topographical features of the $ZrO_2$ untreated sample was studied on the sample covered by a 5 nm Cr layer. The chemical analysis of the composition and distribution of the particular elements of both UVC – irradiated and untreated discs was performed on the samples without the conducting layer. The chemical composition of the surface layer was analyzed by X-ray Photoelectron Spectroscopy (XPS) method on PHI5700/660 Physical Electronics spectrometer, focusing our investigation on the changes in concentration of C1s (carbon), Zr3d (zirconia) and O1s (oxygen).

The atomic concentration of elements present on the samples before and after irradiation was determined from the field under the peak according to the method used with MULTIPAK software. In order to analyse the shape of the core lines, the fitting procedure was applied to C1s, Zr3d and O1s electronic state by Simpeak 2.1 software. Since the depth of analysis for both EDS and XPS techniques is different by about one order of magnitude (for EDS method equals 1–3 μm while for XPS 2–3 nm) we also performed a comparison of the obtained results for both techniques.

The changes in wettability between the UV-irradiated and untreated zirconia disks was analyzed by contact angle measurement. The water contact angle measurements were performed using a CAM101 goniometer with an accuracy of ±0,01°. The contact angles were determined in air using the static sessile drop method. Thirty images of water droplet ~15 μL placed on the surface were recorded during 30 s. Based on obtained images the average CA values were calculated. The final contact angle values were taken as the average of three measurements at different parts of surfaces. The measurements were repeated 3 times for each sample (n = 3) calculating the angle created by 1 μL $H_20$ and its surface.

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## 3. Results

### 3.1. The morphology and structural analysis

The XRD results of the zirconia samples are presented in Fig. 1. Fig. 1a shows the X-ray diffraction pattern in a range of 2θ angle from 20 to 100°. It clearly shows strong peaks which could be attributed to the tetragonal ($P4_2/nmc$) phase of $ZrO_2$ and considerably weaker lines of the monoclinic ($P2_1/c$) phase.Moreover, detailed analysis of the experimental profiles presented in the enlarged region in Fig. 1a, included decomposition of the*hkl* (211) and (103) lines, show also the presence of a cubic phase (Fm-3m) of $ZrO_2$. A small amount of $Y_2O_3$ was also noticed on the diffraction pattern.