Antibacterial UHMWPE surfaces through pulsed laser ablation of titanium targets

D. Delle Side, V. Nassisi, E. Giuffreda, L. Velardi , [1] [2] P. Alifano, A. Talà and S. M. Tredici [3]

[1]Dipartimento di Matematica e Fisica "*Ennio De Giorgi*", Università del Salento, Italy

[2]Istituto Nazionale di Fisica Nucleare sez. di Lecce, Italy

[3]Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Lecce, Italy

During the last years, the occurrence of severe threats to public health raised the attention on the conditions under which pathogens spread across the population. For example, in the cases of the Avian Influenza[1] or of the Severe Acute Respiratory Syndrome[2], it has been shown that infections are likely in healthcare workers, although correct antiseptic strategies would ensure good safety levels. In general, several reports pointed out that infectious agents are nested in common use objects such as shopping carts handlebar[3], computer keyboards[4], clinical surfaces[5], faucet handles[4], door handles[6]. Although a proper treatment with antiseptic detergents would greatly reduce risks, there are situations in which such a strategy is inapplicable, for example in the case of the shopping carts. Consequently, clearly emerges the necessity of permanent antimicrobial coatings that could overcome the limitations of the usual cleaning processes.

Since 1985, the year in which Matsunaga and colleagues[7] reported for the first time its antimicrobial activity, there has been a great interest in the application of titanium dioxide for sanitization purposes. The antimicrobial effect of TiO_2 arises from its great photocatalytic activity under UV light exposure. Despite of the fascinating properties of TiO_2, the requirement of the biohazardous UV light to stimulate its photocatalytic activity severely limits its application in living environments. For this reason, a great scientific effort has been devoted to the development of methods that could enable TiO_2 photocatalysis in the visible range. Currently, impurity doping is the most common technique for expanding the spectral response of pure titania photocatalysts[10]. Moreover, several reports clearly indicate that non-stoichiometric titanium oxides are reactive under visible light exposure, with excellent photocatalytic properties[11,12]. These findings suggest the possibility of a new technique for an easy synthetization of non-stoichiometric titanium oxides films based on the implantation of the ions obtained through laser ablation on impurities adsorbing materials.

In general, materials contain on their surfaces oxygen-rich compounds (CO or H_2O are clear examples). Using energetic Ti ions that impinge on the surface of such materials, it is possible to break the bonds that tie oxygen with the other elements. In such a way we consequently obtain the chance to stimulate the formation of non-stoichiometric titanium oxides on that substrate, as it is customary in ion implantation[13].

In this work we present the first proof-of-concept of this technique, using Ultra High Molecular Weight Polyethylene (UHMWPE) as substrate. It is indeed known that in this polymer at least 11% of surface contaminants elements is represented by oxygen[14]. This fact makes UHMWPE a good candidate for this experiment. Moreover, in order to reach our goal, it is essential that the energetic ion beams used for the bombardment process have a broad energy spread. In this way, the ions with higher energy will break the bonds, while the lower energy ones could create new bonds with the free oxygen. For this reason we choose a setup in which large energy spread ion beams obtained by laser ablation are accelerated to bombard the samples surface.

In order to obtain insights on the effect of the technique under development, we performed some measurements to understand the status of the UHMWPE surfaces before and after treatment. AFM analysis showed that the root mean square surface roughness of the treated UHMWPE increased from 23.2 to 94.6nm, the average height from 172 to 637nm and the average roughness from 18.4 to 73.7nm. Moreover, the elemental composition maps obtained through an EDS analysis has shown that in many cases titanium and oxygen are found together in the same sites of the treated surfaces. Together with the measurements focused at the surface changes, we performed also a qualitative investigation of the visible-light response of the treated material with

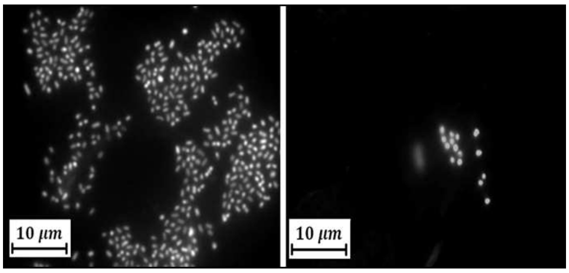

Figure 1. Representative fluorescence microscopy images of a blank (left) and treated samples (right). The treated sample was the one exposed for 7 days in the air atmosphere.

respect to the blank one trhough UV-Vis spectroscopy, measuring the absorbance of the samples.

Finally, we performed a bacterial surface adhesion test on a blank and 3 different treated samples, which differed for the exposure time on the normal air atmosphere after treatment (respectively: 2, 4 and 7 days). The resulting fluorescence microscope images are shown in Fig. 1. Quantitative analysis, performed by counting the bacterial cells observed in 50 microscopic fields randomly selected, revealed that the mean values of percentages of adherence to the substrate with respect to the blank were $50 \pm 14\%$ (2 days), $32 \pm 11\%$ (4 days) and $10 \pm 5\%$ (7 days).

The surface analysis clearly showed that the treated polymer underwent to significant morphology modifications. Important is the fact that EDS revealed that Ti and O are often together on the treated samples, giving an indication of the oxide formation. The UV-Vis spectra showed that the modified polymer has a slight, although sensible, increase of the absorbance in the visible range, indicating that the treatment went into the right direction.

Antimicrobial tests are really interesting, since gave surprising results on the efficacy of the resulting coatings. Moreover, it has been clearly shown that the effectiveness increases with the time of the exposure to free air. This is probably due to titanium natural tendency to develop an oxide layer on its surface. This circumstance is important, since ensures that the efficacy of the treatment is not compromised while the surface is in normal atmosphere.

Concluding, we showed in these experiments that bombarding an oxygen rich surface with a broad energy spread dose of Ti ions the formation of a (non-stoichiometric) titanium oxide film with high antimicrobial activity in the visible range is induced. This technique seems to be promising and could simplify the commonly used treatment modality. Despite of this, these results are just preliminary and deserve more attention, in particular to obtain more insights on the nature of the titanium oxide formed on the substrates and on the experimental parameters affecting the results.

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