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Photocatalytic effect of TiO_2-coated surfaces on the pathogenic microorganisms *E.coli* and *S.aureus*

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Abstract
The use of titanium dioxide as a strong photocatalytic substance can have a large effect in combating the spread of pathogens through heavily contaminated surfaces. For this purpose, various materials, such as metal, glass, and polymer were coated with rutile- and anatase-rich titanium dioxide by sol-gel method. The contact angle and photocatalytic activity of the coated surface were measured under UV irradiation. The anatase-rich titanium dioxide showed higher photocatalytic activity, which further increased with the coating thickness. The process temperature had an effect on the photocatalytic activity due to the temperature-dependent conversion of anatase to rutile crystal conformation. The coated surfaces had strongly reduced contact angles compared to the uncoated material. In particular, the anatase-rich surfaces resulted in superhydrophilic properties. Photocatalytically induced antibacterial activity against pathogenic microorganisms in liquid environments was demonstrated, especially for gram-negative *Escherichia coli* bacteria.

antimicrobial, surface coating, biomedical science

1. Motivation and Approach

In front of the current pandemic and the increasing threat of multi-resistant pathogens the interest in antimicrobially functionalized surfaces is growing. Since the use of surface disinfectants in public life requires human action, inherently antimicrobial surfaces are of particular importance. The use of titanium dioxide as a strongly photocatalytic substance can have a great effect in combating the spread of pathogens through heavily contaminated surfaces. Next to chemical vapour deposition, sputtering and electron-beam evaporation the sol-gel technique has emerged as one of the most promising techniques for TiO_2 surface coating. When UV light hits surfaces coated with titanium dioxide, highly oxidative reactive oxygen species are formed, which attack the cell membrane of adherent microorganisms and can lead to cell death. For this purpose different materials, such as metal, glass and polymer, were coated with titanium dioxide using the sol-gel method. Titanium dioxide can appear in three variants, wich are named rutile, brookite and anatase and differ in their crystal bulk structure and therefor in size and atoms per unit [1]. The detailed coating procedure and the used TiO_2 material can have a great effect on the wettability and photocatalytic activity resulting in antimicrobial effects of different strength. This effect is investigated in this work for relevant microbial pathogens.

2. Experimental detail

2.1. Coating

For the experiments, an adapted sol-gel method according to Malnieks et al. was used [2]. This was carried out with two different titanium dioxide starting materials. One solution was prepared with mainly anatase configuration TiO_2 P25, Evonik Industries AG, Essen, Germany and the other with mainly rutile configuration TiO_2 R210, Carl Roth GmbH + Co. KG, Karlsruhe, Germany. The ratio of the mixture was 1:10:4:0.5 of titanium dioxide, isopropanol, glacial acetic acid and desalinated water. The titanium dioxide was dissolved in isopropanol for $t = 1$ h at $\vartheta = 20$ °C under agitation. The glacial acetic acid was then added and stirred again for $t = 1$ h. Finally, the water was added and the solution was stirred for another $t = 0.5$ h. The pre-cleaned specimens of glass, PEEK and 1.2344 steel were coated with the sol 3-fold via dip coating whereby two procedures were used. In the 3x1 procedure, the samples were dried at $\vartheta_{dry} = 200$ °C for $t = 5$ min each time after dipping. In the 1x3 method, the specimen were directly dipped 3 times in succession and dried at $\vartheta_{dry} = 200$ °C for $t = 5$ min. Finally, the specimens of both methods except PEEK were calcined at $\vartheta_{cal} = 500$ °C for $t_{cal} = 1$ h.

2.2. Contact angle measurement

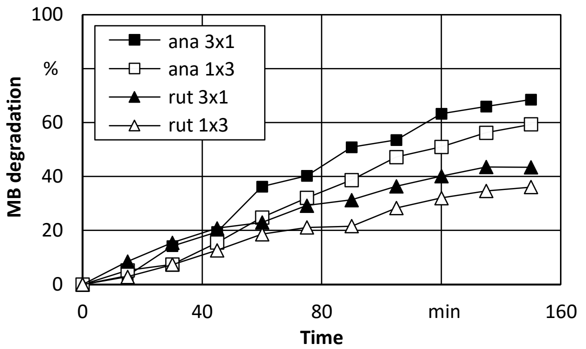
The contact angle measurement was performed on the Drop Shape Analyzer DSA 100B, Krüss GmbH, Hamburg, Germany. The lying drop method was used with a dropvolume $V_{dro} = 4$ µL, a measuring time $t_{mes} = 90$ s and a measuring interval $t_{int} = 1$ s at a temperature $\vartheta = 25$ °C. The coated surface was measured after 1 minute of UV irradiation and compared to the uncoated surface in **Table 1**. The higher activity is referred to as photoinduced superhydrophilicity which induces the photocatalytic removal of hydrophobic organic surface contaminants, thus increasing the wettability [3].

Table 1: Contact angle measurement of the coated and uncoated materials for both coating procedures and TiO_2 variants

Material	θ_{pure}	TiO_2 anatas-rich		TiO_2 rutile-rich	
		θ_{3x1}	θ_{1x3}	θ_{3x1}	θ_{1x3}
Glass	55.2°±3.3	0°±0	0°±0	21.5°±1.5	11.4°±1.2
PEEK	78.5°±2.3	0°±0	0°±0	20.3°±2.9	15.1°±1.3
Metal	47.5°±4.1	0°±0	0°±0	24.2°±1.2	11.3°±3.6

3. Photocatalytic Activity

The photocatalytic activities of the coatings were evaluated by analysing photocatalytic degradation of methylene blue (MB) due to the appearance of reactive oxygen species under UV irradiation. The samples were placed in 100 ml MB solution with an initial concentration of 12.5 mg/l in accordance to DIN 52980:2008. Before irradiation, samples were stirred for 30 min in the dark to reach absorption–desorption equilibrium. A UV LAMP UVAHAND 200, DR. HÖNLE AG, GRÄFELFING, GERMANY with a power P = 180 W was used as light source. During irradiation, small volume samples were taken every 15 minutes to measure discoloration via absorbance at 620 nm on the FILTERMAX™ F5 MICROPLATE READER, MOLECULAR DEVICES LLC, SAN JOSE, USA.



Material	TiO_2 anatas-rich		TiO_2 rutile-rich	
Coating method	3x1	1x3	3x1	1x3
Degradation [%]/h	27.4	23.7	17.4	14.4

Figure 1. Photocatalytic activity of different TiO_2-samples obtained by the 3×1 and 1x3 method on glass via methylene blue degradation

The results in **Figure 1** show a 10-20 % higher photocatalytic activity for the anatase-rich TiO_2 material P25 as already discovered by Luttrell et al [4]. Furthermore the 3x1-method results in 5-10 % higher photocatalytic effects than 1x3-method. This is probably due to the curing of each of the three layers and thus an overall higher layer thickness than the 1x3 method. In this method, the three layers were not cured individually at ϑ_{dry} = 200 °C and partially dissolved back into the sol during the next dipping step. According to Luttrell et al. the photocatalytic activity in anatase conformation is mainly dependent on the layer thickness [4].

4. Antimicrobial Activity

The antimicrobial effect was investigated for the anatase-rich TiO_2 material due to the higher photocatalytic values. All coated materials were incubated with common nosocomial pathogens *S. aureus* and *E. coli* for t_{inc} = 24 h at ϑ_{inc} = 37 °C. Before incubation the experimental setup was UV irradiated for t_{UV} = 10 min to activate the coating. After incubation the microorganisms were stained with fluorescent dye to distinguish between live and dead cells. The results in **Figure 2** shows significant antimicrobial activity for the polymer test specimens. This can be explained by the absence of a calcination step at ϑ = 500 °C. At ϑ > 400 °C, the ratio of anatase to rutile may change with increasing temperature in favor of the less active rutile conformation [5]. The higher toxicity for *E. coli* can be explained by the thinner cell wall of gram-negative bacteria, which has a lower protective function against oxidative reactive oxygen species compared to gram-positive bacteria [6].

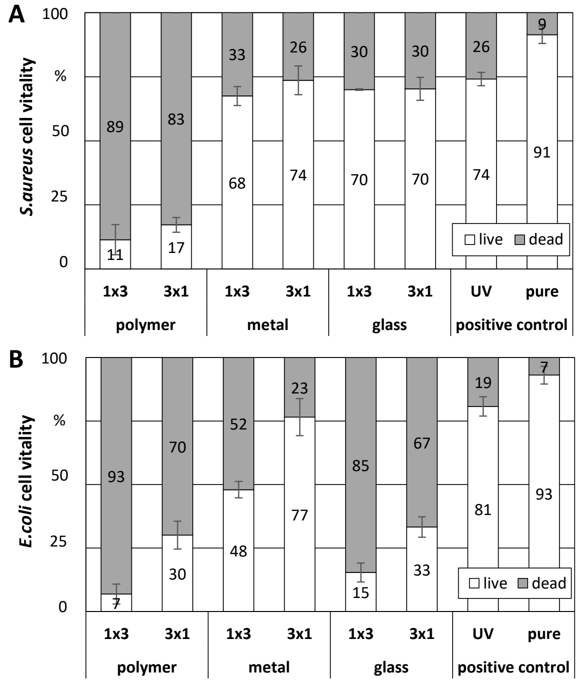


Figure 2. Antimicrobial activity of different TiO_2-samples obtained by 3×1 and 1x3 method via live-dead fluorescent staining of *S. aureus* cells (A) and *E. coli* cells (B) after UV irradiation

5. Conclusion

Using titanium dioxide as a strong photocatalytic substance can have a great effect in combating the spread of pathogens through highly contaminated surfaces. The application of the photocatalytically most active anatase-rich TiO_2 results in superhydrophilic surfaces and an antibacterial effect, especially against gram-negative microorganisms. The processing temperature has to be considered in order to avoid a loss in photocatalytic activity due to the temperature dependant conversion from anatase to rutile crystal conformation. The results show a great antibacterial potential for liquid environments. As biofilm formation is a major problem in such environments the photocatalytic effect on complex bacterial structures has to be investigated in the future. The economic large-scale implementation of appropriately coated surfaces requires further research.

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