Photocatalytic, hydrophilic titanium dioxide prepared by direct current magnetron sputtering

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Hygienic surfaces are required for many industrial processes, for example production of food, cosmetics or pharmaceuticals, as well as in healthcare facilities. Often these surfaces are not sufficiently cleaned by conventional methods. Self-cleaning surfaces can improve hygienic safety by degradation of organic contaminants using photocatalysis.

The photocatalytic activity of Titanium dioxide (TiO_2) was first described by Fujishima and Honda[1]. Due to its band gap of 3.2 eV (in anatase crystal structure) TiO_2 absorbs only ultraviolet (UV) light of a wavelength below 390 nm. The electrons and holes generated this way can completely degrade organic surface contaminations[2] either by direct redox-reactions or by generation of highly reactive oxygen compounds like superoxide anions ($O_2^{-\bullet}$), hydroxyl radicals ($OH^{\bullet}$), hydrogen peroxide (H_2O_2) and peroxide radicals ($HO_2^{\bullet}$)[3].

TiO_2 surfaces can also exhibit photo-induced super-hydrophilicity[4]: Under illumination the contact angle with water decreases to zero. Hydrophilic surfaces are easy to clean because water can penetrate below dirt particles to remove them. Additionally it has been shown that hydrophilic surfaces improve bone ingrowth of medical implants[5]. Therefore TiO_2 can be an ideal surface for implants since it decreases the risk of contamination by photocatalysis and favours bone ingrowth by hydrophilicity.

We have developed a TiO_2 coating obtained by direct current magnetron sputtering of titanium targets in an argon-oxygen-atmosphere. The coating can be applied to a wide range of materials (metals, ceramics, glasses) of various shapes at a process temperature of 285 °C, and it forms a smooth, homogeneous, optically transparent layer. A typical coating time of four hours leads to a thickness of 0.4 µm. Furthermore the coating resists well to mechanical and chemical treatments.

Elastic recoil detection analysis (ERDA), using gold ions with 200 MeV of kinetic energy as probes, reveals a homogeneous composition of the coating over the whole coating thickness. Atomic fractions are 59 % oxygen, 38 % titanium, 3 % hydrogen and 1 % carbon (Figure 1).

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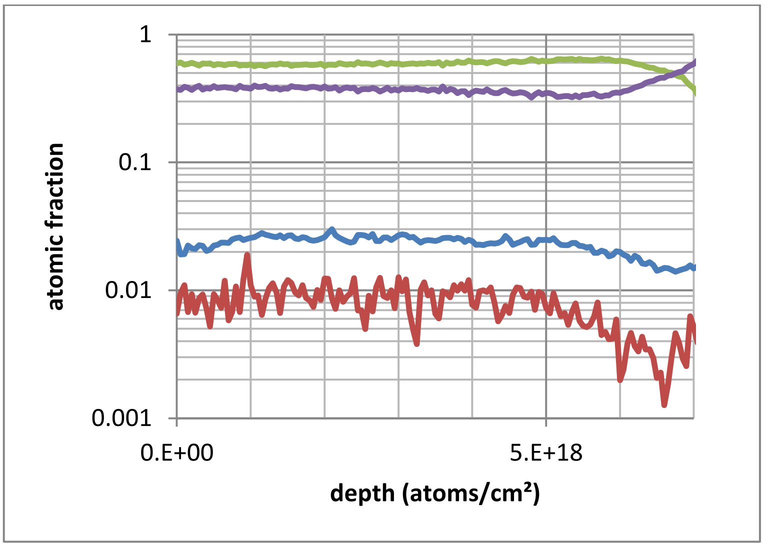

Figure 1: Atomic fraction of oxygen (green), titanium (violet), hydrogen (blue) and carbon (red) depending on depth in the coating obtained by ERDA. At a depth of $7 \cdot 10^{18}$ atoms/cm² the titanium substrate is reached.

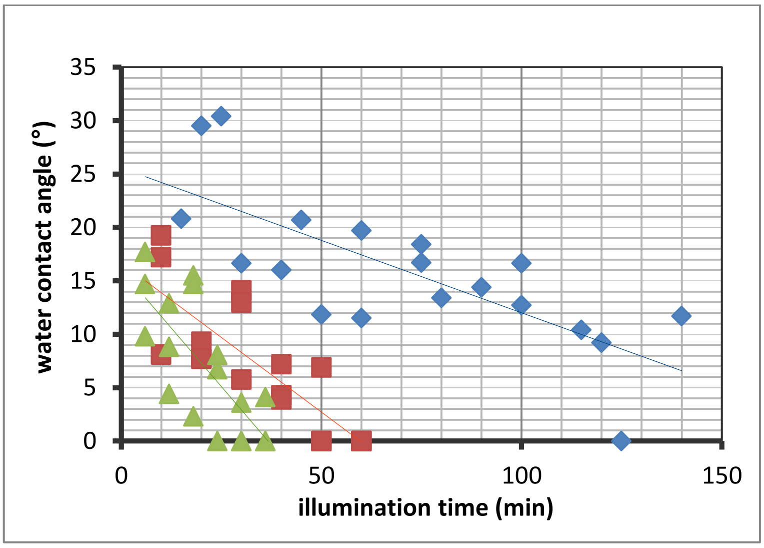

Figure 2: Water contact angle on TiO_2 coatings dependent on illumination time at wavelength 370 nm and intensity 5 W/m² (diamonds), 16 W/m² (squares) or 22 W/m² (triangles). For each intensity three independent experiments are combined in the graph. Lines are a guide to the eye.

The as prepared surface is super-hydrophilic with water contact angles below 3°. In ambient air the contact angle starts to increase after some hours of storage due to surface contamination. This effect can be reversed by UV irradiation. Under moderate UV-intensity corresponding to a Central-European summer day (16 W/m²) super-hydrophilicity is re-established within about an hour depending on the degree of surface contamination. This delay is shortened by illumination with higher intensity (Figure 2). For practical applications, for example on implant surfaces, it is important to preserve the hydrophilicity of the coating during storage. Therefore we have compared different storage conditions (Figure 3). When coated samples are stored in the dark at room temperature in physiologic saline solution, their surface remains super-hydrophilic for at least five months.

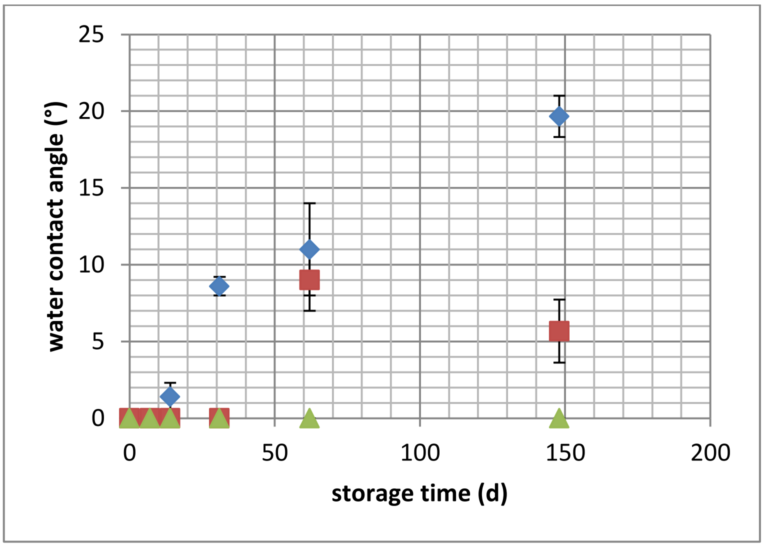

Figure 3: Water contact angle on TiO_2 coatings dependent on storage time in nitrogen gas (blue diamonds), distilled water (red squares) or physiologic saline (green triangles). Each point represents the mean value and standard deviation of three replicate samples.

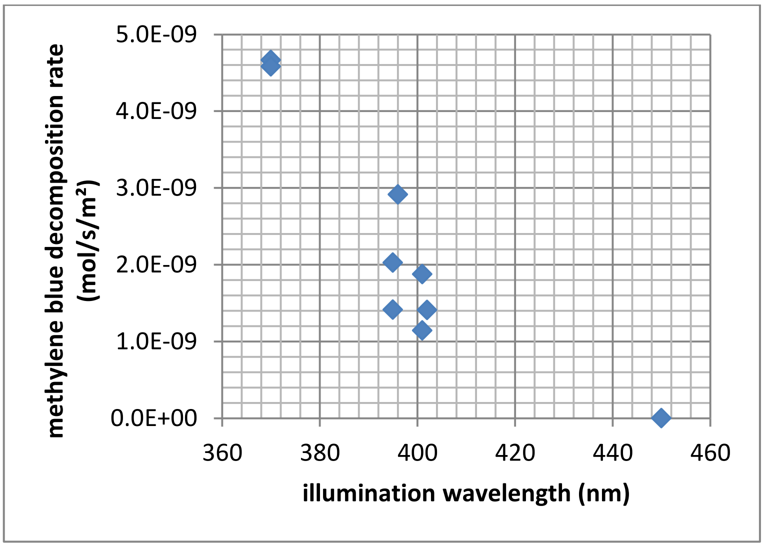

Figure 4: Methylene blue decomposition rate depending on illumination wavelength for comparable intensities (10 W/m² at 370 nm, about 10 W/m² at 400 nm, about 60 W/m² at 450 nm)

Photocatalytic activity of the coatings is shown by UV-light-induced photodegradation of methylene blue in an aqueous solution with an initial concentration of $2 \cdot 10^{-5}$ mol/L. Methylene blue is commonly used to examine the degradation of organic compounds due to its simple photometric quantification. For illumination at a wavelength of 370 nm and an intensity of 10 W/m² methylene blue is degraded at a rate per sample surface area of $5 \cdot 10^{-9}$ mol/(m² s) corresponding to an apparent quantum yield of $2 \cdot 10^{-4}$. There is also significant photocatalytic activity in case of illumination at a wavelength of 400 nm (Figure 4). Thus it is possible to exploit the photocatalytic activity using visible light of short wavelength, which is present for example in conventional indoor lighting.

The light-induced antimicrobial activity of the coatings is assessed under simulated daylight with small UV intensity (0.03 W/m²). This intensity can be found indoors within 2 m of a window during daytime[6]. *Kocuria rhizophila* is chosen as test organism, because it is a ubiquitous airborne cause of food spoilage and highly resistant against drying, radiation and high salt concentrations. Using an initial surface concentration of $(6.3 \pm 1.3) \cdot 10^4$ CFU/cm^2 the concentration of colony-forming units (CFU) was reduced by a factor of 300 compared to an uncoated surface within 24 h of illumination. Therefore even small UV intensities found indoors contribute to the decontamination of coated surfaces. Rapid sterilization of coated surfaces would be achieved using lamps of high UV intensity.

The hardness of the coatings obtained by the Vickers indentation method is 1000 HV 0.005/30. This corresponds to the highest values reported for natural TiO_2 crystals[7]. Due to its hardness and good adhesion to various substrates, the TiO_2 coating is suitable for surfaces exposed to severe mechanical treatments, for example during cleaning.

In summary we present a thin, transparent, chemically and mechanically stable TiO_2 coating with photocatalytic, anti-bacterial and super-hydrophilic properties. It can be applied for example to instruments and devices in food processing or healthcare facilities for easier disinfection and cleaning. The small UV fraction of daylight suffices to trigger the photoinduced effects at a low level. Higher activity can be obtained by exposure to direct sunlight or lamps of higher UV intensity. Most applications benefit from the unlimited repeatability of the photoinduced effects assuring a long functional lifetime of TiO_2 coatings. Yet TiO_2 coatings can also improve products as a single-use surface. For example medical implants can be rendered sterile and hydrophilic just before placement in the body to decrease the risk of infection and improve ingrowth.

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