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An impact of the copper additive on photocatalytic and bactericidal properties of TiO_2 thin films

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The biological and photocatalytic activity of TiO_2 and TiO_2:Cu in relation to their structure, surface topography, wettability and optical properties of the thin films was investigated. Thin-film coatings were prepared by magnetron sputtering method in oxygen plasma with use of metallic targets (Ti and Ti–Cu). The results of structural studies revealed that addition of Cu into titania matrix (during the deposition process) resulted in obtaining of an amorphous film, while in case of undoped TiO_2, presence of nanocrystalline anatase (with crystallites size of 20 nm) was found. Moreover, an addition of cooper had also an effect on surface diversification and decrease of its hydrophilicity. The roughness of TiO_2:Cu film was 25 % lower (0.6 nm) as-compared to titania (0.8 nm). These modifications of TiO_2:Cu had an impact on the decrease of its photocatalytic activity, probably as a result of the active surface area decrease. Antibacterial and antifungal properties of the thin films against bacteria (*Enterococcus hirae, Staphylococcus aureus, Bacillus subtilis, Escherichia coli*) and yeast (*Candida albicans*) were also examined. For the purpose of this work the method dedicated for the evaluation of antimicrobial properties of thin films was developed. It was revealed that Cu-additive has a positive impact on neutralization of microorganisms.

Keywords: *TiO_2; thin film; microstructure; photocatalysis; bioactivity; optical properties*

1. Introduction

According to the European Centre for Disease Prevention and Control (ECDC), about three million infections are registered by the Health Service, with fatal consequences for over fifty thousand patients per year in Europe [1]. Another urgent problem is an increasing resistance of microorganisms to various antimicrobial agents and disinfectants [2]. For these reasons research into new methods for neutralizing microorganisms is essential [3]. One of the approaches is generating of antibacterial and antifungal thin coatings, which are applied onto a variety of substrates and devices to prevent the spread of microbes. Thin layer materials exhibiting antimicrobial activity are used in medicine, food production and in chemical and pharmaceutical industry [4–6].

Thin films can be functionalized by modification of the existing coating or by formation of entirely new layer with specific characteristics. Multifunctional bactericidal thin layers are characterized by transparency, hydrophobicity and resistance to scratching [7]. Nowadays, innovative antimicrobial coatings are produced based on titanium dioxide or titanium with addition of metal with proven antibacterial and antifungal activity [5–10]. Titanium dioxide is characterized by high chemical stability, good optical transparency and non-toxicity [2, 11–13]. It exhibits excellent photocatalytic properties in the presence of UV light. Due to absorption of a small amount of visible light, various modifications are applied to enhance the photocatalytic properties of the oxide [13, 14], e.g. by addition of carbon [15], nitrogen [16] or sulfur [17], which enables reduction of band gap, and therefore shift of the optical response to the visible range [13]. Photocatalytic properties of titanium dioxide are

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widely used in the process of elimination of toxic chemicals, such as bisphenol A, tetracycline, and sulfamethazile from wastewater [18–20].

TiO_2 forms a photosensitive thin coating of immunomodulatory and cytotoxic properties in the presence of UV light. Multiple reports of antifungal and antibacterial properties of TiO_2 in the presence of UV light, resulting from the photocatalytic activity of titanium dioxide have been published [2, 12–14]. The biocidal effect of titanium dioxide is generated by production of OH* and other reactive oxygen species (ROS) in the presence of UV radiation. The goal of such attack is cell membrane lipid peroxidation and a photooxidation of coenzyme A, both resulting in inhibition of cell respiration and cell death [2, 11]. It has been recently shown that *P. aeruginosa* cells exposed to TiO_2/UV undergo a critically fast inactivation of regulatory and signaling pathways, coenzyme-independent respiratory chains, and assimilation and transport of iron and phosphorus. TiO_2 affects the biosynthesis and degradation of iron-sulfur centers [10].

Among 21 tested metals, the strongest antibacterial activity against *E. coli* and *S. aureus* exhibit copper and silver, followed by cobalt, nickel and aluminum [22]. Such data are not surprising. Since antiquity, silver or copper plates and cups were known as ensuring protection from diseases. In modern times, bactericidal and fungicidal coatings containing silver and copper are used in the production of medical equipment. According to many studies, copper is more promising as an antibacterial material compared to silver, mainly due to lower toxicity and higher cytocompatibility [8]. What's more, copper is metabolized in human body, while silver tends to deposit in human cells [23].

The thin-film coatings based on TiO_2 with an addition of metals, known from their high antimicrobial activity, are in demand in many areas of application. Today's challenge is to create a TiO_2 coating with addition of copper, silver or gold, that provides a combination of antibacterial and antifungal properties with an improved adhesion, strong mechanical properties and durability [24]. These parameters depend on the composition and thickness of thin layer applied to the substrate by specific methods. In this study we aimed to produce and compare TiO_2 and TiO_2:Cu doped films in terms of their photocatalytic and antimicrobial properties.

2. Experimental

Thin-film coatings were prepared by magnetron sputtering method [25]. During the deposition, metallic Ti and Ti–Cu targets were sputtered under oxygen plasma on Corning 7059 glass substrates. The analysis of material composition revealed that in TiO_2:Cu film there was 35 at.% of cooper additive. Structural properties of prepared films were determined based on the X-ray diffraction (XRD) measurements. For the experiments, Siemens 5005 powder diffractometer with CoKα X-ray (λ = 1.78897 Å) was used. The crystallite sizes were calculated using Scherrer's equation. The surface morphology of the films was investigated with the aid of a FESEM FEI Nova NanoSEM 230 scanning electron microscope (SEM) with 30 kV of acceleration voltage. Moreover, surface diversification was additionally examined by CCI Theta Lite optical profiler (Tylor Hobson). Also the wettability of manufactured coatings was investigated. For the measurements Theta Lite (Attension) stand was used. Photocatalytic properties of as-deposited films were determined based on phenol decomposition. The experiment was carried under UV-Vis light source in water cooled quartz-glass reactor. In 200 mL of the solution, the concentration of phenol was 10 ppm, while the sample size was 6 cm^2. Reactions were carried out under agitation with a magnetic stirrer (800 rpm) in order to provide homogenous concentration of the suspension in entire volume. To determine the change in phenol concentration, the samples containing its solutions were withdrawn from the reactor for 12 h, and analyzed by OceanOptics QE 65000 UV-Vis spectrophotometer coupled with Mikropack DH-2000-BAL deuterium-halogen light source. The concentration of the dye was calculated from the absorption peak at ca. 270 nm by means of a calibration curve.

Bactericidal and fungicidal properties of the coatings were studied in contact with bacteria strains: *Escherichia coli* PCM 144, *Staphylococcus aureus* PCM 2602, *Bacillus subtilis* PCM 2021, *Enterococcus hirae* PCM 2559 and fungus (yeast) *Candida albicans* PCM 2566. Thin films on glass substrates of 1 cm^2 in size were placed on a sterile 24-well test plate containing 1.5 mL of bacteria or fungi suspension of a known optical density. The bacteria were exposed to the films over 2 h, 4 h, 6 h and 24 h, and the suspension was collected in respective time periods. The survived microorganisms were counted by serial dilution method on agar plates after 24-hour incubation and expressed as colony forming units per mL (cfu/mL).

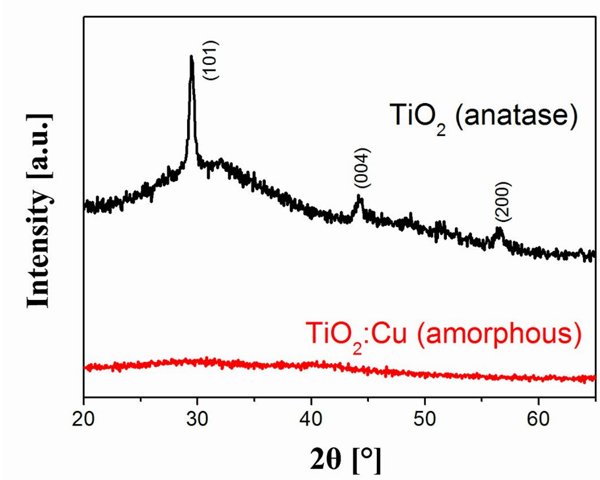

Fig. 1. XRD patterns of nanocrystalline TiO_2 and amorphous TiO_2:Cu thin films.

3. Results and discussion

The studies of structural properties have revealed that the undoped titania thin film was nanocrystalline. Its structure was built from anatase crystallites of ca. 20 nm in size. Moreover, the value of its interplanar distance d was in a good agreement with the standard d_{PDF} [26]. No stress or relaxation occurred in the titania lattice. The TiO_2:Cu film was shown to be amorphous. This testified that incorporation of copper additive into titania during sputtering process counteracted the growth of anatase crystallites. In Fig. 1 and in Table 1 the results of XRD measurements are presented.

Table 1. Structural properties of TiO_2 and TiO_2:Cu thin films as-deposited on Corning 7059 glass substrate, based on XRD measurements.

Thin film	Type of structure	Plane	D [nm]	d [nm]	d_{PDF} [nm]
TiO_2	anatase	(1 0 1)	20	0.3519	0.3520 [26]
TiO_2:Cu	amorphous	–	–	–	–

D – average crystallite size

d – interplanar distance

d_{PDF} – standard interplanar distance

The influence of copper additive on the structure of titania films was also studied with the aid of scanning electron microscope. The images of the surface showed that both coatings were homogenous (Fig. 2). As it can be seen, only at higher magnification (200 000×) the difference in the morphologies can be observed. In case of TiO_2, fine grained structure occurs, what is in a good agreement with the studies performed by XRD method. For TiO_2:Cu, the situation is quite different because SEM image shows large grains, while the XRD studies revealed an amorphous nature of this film. In our opinion, crystallites of titanium oxide are surrounded by cooper oxides.

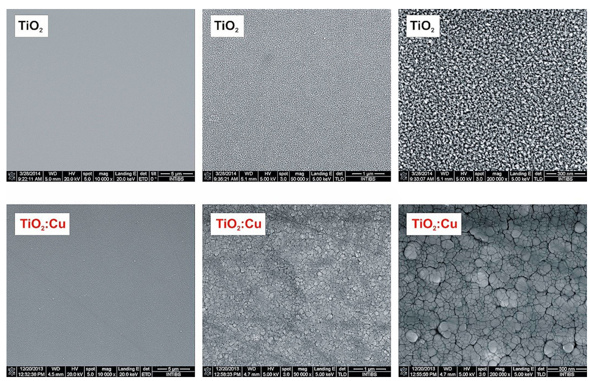

Fig. 2. SEM images of the surface of TiO_2 and TiO_2:Cu thin films.

In consequence, fairly disordered structure or a lack of long range order in TiO_2:Cu was observed. Such a morphology of the surface of thin films also affects directly their active surface area.

The analysis of the surface diversification performed with the aid of optical profiler revealed that the roughness of both films was less than 1 nm. In particular, the value of arithmetic mean deviation of the three-dimensional roughness profile (Sa) of amorphous TiO_2:Cu was 25 % lower (0.6 nm) than for the nanocrystalline TiO_2 (0.8 nm) (Fig. 3). This means that undoped titania had more diversified surface and its active area was larger as-compared to TiO_2:Cu.

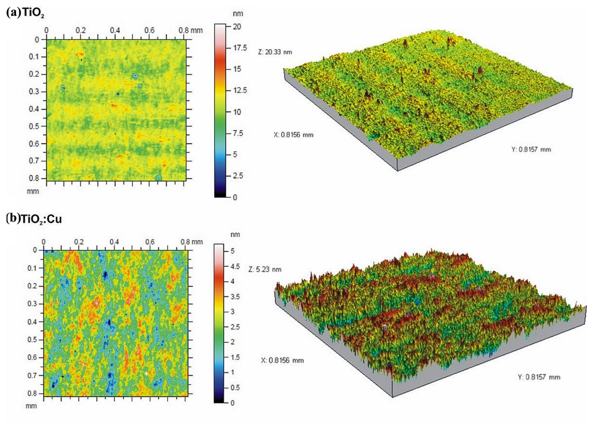

Fig. 3. Profiles of the surface topography of (a) TiO_2 and (b) TiO_2:Cu thin films, obtained from optical profiler.

Analysis of the wettability has also revealed different surface properties of TiO_2 and TiO_2:Cu thin films. Fig. 4 presents images of water drops on the surface of prepared films. Both coatings were hydrophilic, but addition of Cu during sputtering resulted in an increase of water contact angle up to 68°, while for undoped titania it was only 40°. Such change of the hydrophilicity was related to smaller surface area of amorphous TiO_2:Cu. This had an impact on the decrease in the number of free bonds on the films surface, which would be able to bind molecules of water.

Measurements of photocatalytic activity of TiO_2 and TiO_2:Cu have been carried out in the studies (Fig. 5). The results of phenol decomposition in presence of both prepared films have shown that Cu-additive provided a negative impact on titania activity. After 12 hours of UV-Vis irradiation about 10 % of phenol was decomposed when

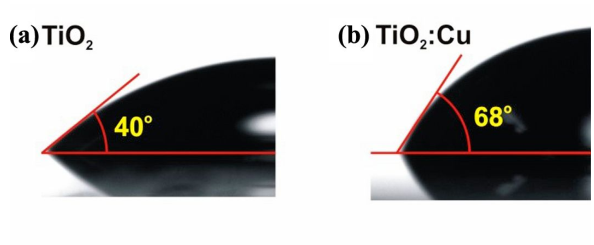

Fig. 4. Water contact angle of (a) TiO_2 and (b) TiO_2:Cu thin films.

there was a TiO_2 thin film in the reactor. In case of TiO_2:Cu, efficiency of this reaction was only about 7 %. Lower activity of titania with cooper additive as-compared to the undoped one is related to its smaller active surface area, which was confirmed by the results of surface topography studies.

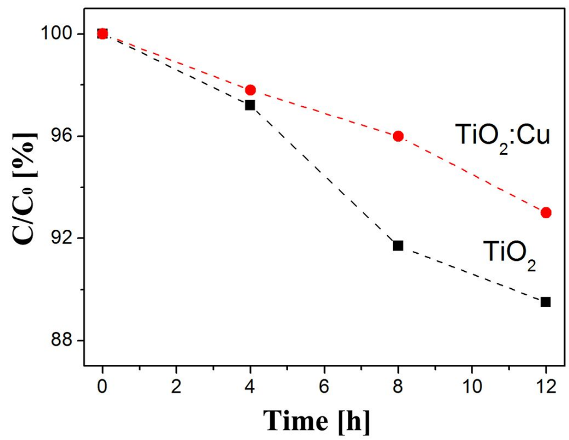

Fig. 5. Photocatalytic decomposition of phenol in presence of TiO_2 and TiO_2:Cu thin films.

Low activity level of TiO_2:Cu film was quite unexpected, because it should absorb more light in the visible region. It was confirmed by the lower level of transparency (Fig. 6), smaller than 10 % for TiO_2:Cu at $\lambda = 550$ nm, while for undoped titania it was about 80 %. Moreover, the shift of the optical absorption edge (λ_{cutoff}) from 320 nm to 505 nm also indicates that the coating with copper resulted in an increased level of absorption. Such effect is quite possible, but high load of copper ions on the surface of titania nanocrystals increased the efficiency of photo-generated charge recombination, which in turn might reduce the number of electrons and holes which could participate in reactions with oxygen, water or OH^- groups on the surface of the TiO_2:Cu film. In consequence, the photocatalytic activity of the titania film with copper additive is lower as-compared to the undoped one. Thin films based on titanium dioxide, due to its photocatalytic activity, possess bactericidal properties [21], however, to achieve biocidal effect the irradiation of TiO_2 surface with suitable energy is necessary. The goal is to obtain films that exhibit antimicrobial activity regardless of irradiation. Therefore, we have used copper – highly bactericidal material as an additive to TiO_2, providing a stable matrix, advantageous for many applications.

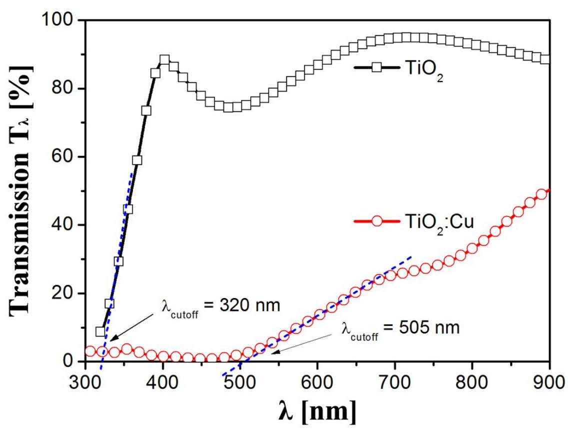

Fig. 6. Transmission characteristics of TiO_2 and TiO_2:Cu thin films as-deposited on Corning 7059 glass substrates.

In this work the effect of Cu-additive on antimicrobial properties of titania thin films was investigated. The experiments were carried out with the use of *Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus*, *Enterococcus hirae* and *Candida albicans* (Fig. 7). It was found that addition of copper into titania structure during sputtering process resulted in increasing its antimicrobial activity for all tested bacteria.

4. Conclusions

The results of the investigation have shown that addition of copper into titania matrix during a deposition process resulted in obtaining

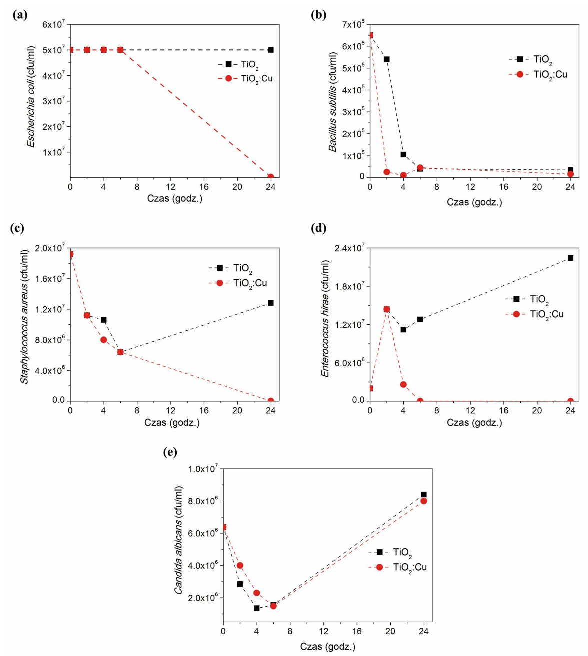

Fig. 7. Antimicrobial activity of TiO_2 and TiO_2:Cu thin films against: (a) *Escherichia coli*, (b) *Bacillus subtilis*, (c) *Staphylococcus aureus*, (d) *Enterococcus hirae*, (e) *Candida albicans*.

an amorphous film, while undoped titania had nanocrystalline anatase structure, built from crystallites of 20 nm in size. Addition of copper had also an effect on the change of surface diversification. The roughness of TiO_2:Cu film was 25 % lower (0.6 nm) as-compared to titania (0.8 nm). This had also an effect on an increase of water contact angle (from 40° to 68°). In consequence of these modifications, also the photocatalytic activity of TiO_2:Cu was lower, which probably was caused by the decrease of active surface area. In conclusion, thanks to addition of Cu, the prepared coatings revealed antimicrobial activity also in darkness providing an advantageous effect on neutralization of microorganisms.

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