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Visible light induced photocatalytic inactivation of bacteria at modified titanium dioxide films on organic polymers

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Commercially available polypropylene foil was pre-treated with a low temperature oxygen plasma and covered with nanocrystalline titanium dioxide thin film by dip-coating technique. Afterwards the films were photosensitized by titanium(IV) surface charge transfer complexes formed upon impregnation with catechol. The photoactivity of such coatings up to 460 nm has been confirmed by photoelectrochemical measurements. Photoinactivation of *Escherichia coli* and *Staphylococcus aureus* was evaluated by glass adhesion test based on the ISO 27447:2009(E) standard in the presence of visible light. The coating showed a good antimicrobial activity induced by LED light (405 nm), in particular towards *Escherichia coli* ATCC 25922 strain. Adaptation of the ISO 27447:2009(E) standard developed to assess bacteria photoinactivation by photocatalytic coatings enables application of this procedure to compare the photoactivity under various irradiation conditions.

Introduction

In last decades a significant increase in using polymers in almost every field of human activity is observed. Low price and flexibility of use are the main reasons of this tendency. Polymers found also numerous applications in medicine, e.g. in production of various single use items, like syringes, catheters, vials, etc. The development of safer materials is extremely important when such products are considered. A polymer surface is exposed to the formation of biofilms, which is one of the etiological factors of nosocomial infections. According to the World Health Organization (WHO), nosocomial infections, defined as *infections acquired in hospital by a patient who was admitted for a reason other than that infection*, are one of the major problems of modern medicine.[1] They contribute to a mortality and morbidity thereby increasing health care costs. A new strategy in fight against nosocomial infections is to use photocatalytic coatings as antimicrobial agents. Among others TiO_2 shows a high activity in photodynamic inactivation of bacteria with the benefits of its physical and chemical stability, low toxicity, bio-compatibility and cheapness.[2] Unmodified titanium dioxide can be used as a photocatalyst only under UV light irradiation, what often implies the necessity of use of artificial sources of radiation. Charges (electrons and holes) photogenerated upon TiO_2 excitation can recombine or participate in redox reactions involving molecules adsorbed at the surface of photocatalyst. Redox potentials of the edges of conduction and valence bands determine the feasibility of oxidation and reduction processes.[3] The possibility of reactive oxygen species (ROS) photogeneration is fundamental when TiO_2 is considered to facilitate inactivation of microorganisms. ROS photogenerated at TiO_2 are responsible for bacteria inactivation, as reported by Matsunaga *et al*. in 1985.[4] Since then, photoinactivation has become a widely used technique for eliminating bacteria, fungi or viruses.[5]

Several methods of titanium dioxide photosensitization have been developed to achieve its visible light activity. The emphasis is put on methods encompassing non-metal and/or metal doping, dye sensitization and semiconductors coupling, while the surface modification with organic compounds is usually neglected due to a low photostability of such systems. According to Lewis theory a chemisorption of organic compounds at the titanium dioxide surface can be described as an acid-base reaction. Donor groups containing oxygen, nitrogen or sulphur are electron donors (Lewis bases) for the surface atoms Ti^{IV} (Lewis acid). Organic compounds containing hydroxyl or carboxyl groups coordinate to the titanium dioxide surface. Binding by -OH or -COOH groups guarantees formation of sustainable, often colourful complexes. The most efficient binding to TiO_2 surface is achieved by compounds containing two binding groups, due to several effects, like formation of a stable ring, the possibility of an additional stabilization by hydrogen bonds and the entropic effect associated with the formation of chelate complexes.[6] Derivatives of catechol, salicylic acid or phthalic acid seem to

be ideal ligands.[6a] A good photocatalytic activity of such materials upon both UV and visible light irradiation was reported by several authors.[7]

The aim of the present work was to investigate the photoinactivation of *Escherichia coli* and *Staphylococcus aureus* using photosensitized titanium dioxide coatings synthesized at polymeric surfaces, upon visible light irradiation.

Experimental

Preparation of coatings on polymer substrate

Transparent polypropylene films (Goodfellow UK, 0.1 mm thick, homopolymer) cleaned with pure water and ethanol (Sigma-Aldrich, 99.5% purity) were used as substrates. The low pressure low temperature plasma system (Diener Electronic Plasma Technology, Zepto) was applied to remove impurities and generate oxygen containing groups on the polymer surface. Flowing oxygen (99.5% purity, Air Products) at the pressure lower than 0.3 mbar was introduced to the chamber. The plasma generator was used at 100 W power and radio frequency of 40 Hz for a period of 30 seconds. Then titanium dioxide film was synthesized using a dip-coating method (Dip Coater, MTI Corporation). The speed of withdrawal of the sample from the aqueous, 1.5% (wt.) colloidal solution of nanocrystalline TiO_2 (Nanostructured & Amorphous Materials, Inc., particle size 5-30 nm, crystal structure of anatase, original concentration of 15%) was 1 cm min^{-1}. The coating process was done in air atmosphere. The films were dried in air at room temperature. Additionally, the films were impregnated with the organic modifier by immersion of the coated polymer for 5 min in an alcoholic solution of catechol (10 mmol dm^{-3}). Finally, impregnated films were washed with distilled water and dried in air at room temperature.

Thin films of TiO_2 and surface modified TiO_2 have been also prepared analogously on the ITO foil (resistivity: 60 Ω/sq).

UV–vis diffuse reflectance spectra of synthesized coatings were recorded using a Shimadzu UV-3600 spectrophotometer equipped with an integrating sphere attachment. The thickness and the surface topography of TiO_2 films were exanimated by scanning electron microscopy (SEM). The images were recorded with a TESCAN VEGA3 LMU apparatus operated at 15 kV.

Photoactivity

The photoactivity of TiO_2 and cat@TiO_2 was tested by photocurrent measurements. They have been done in the three-electrode cell using platinum wire and Ag/AgCl as counter and reference electrodes, respectively. The films of materials prepared on ITO foil were used as working electrodes. A quartz cuvette filled with KNO_3 solution in water as an electrolyte (0.1 mol dm^{-3}, pH = 6.0) was used as the electrochemical cell. Irradiation was done with monochromatic light in the range of 330-550 nm (every 10 nm) with XBO-150 xenon lamp equipped with a monochromator and a shutter (Instytut Fotonowy). The photogenerated current was measured for the potential range of –0.2-1 V *vs*. Ag/AgCl and the incident wavelength range of 330-550 nm using Autolab PGSTAT 302N electrochemical analyser. The solution was purged with argon before (5 min) and during the measurement.

Cultivation of the test bacteria

Two bacterial strains, representing Gram negative (G–) rod: *Escherichia coli* (ATCC 25922) and Gram positive (G+) coccus: *Staphylococcus aureus* (ATCC 25923), were used to evaluate antibacterial activity. *E. coli* was cultured overnight on McC medium (MacConkey Agar, Difco) for 24 h at 37°C, while *S. aureus* on TSA medium (Tryptic Soybean Agar, Difco) at the same conditions. Aliquots of these cultures were inoculated into the fresh fluid medium (Tryptic Soy Broth, Difco) and incubated under aerobic conditions at 37°C until the exponential growth phase was reached. The standard suspension of bacteria (approximately 10^5 CFU mL^{-1}) was obtained by serial diluting of these cultures.

Antimicrobial activity – adhesion glass method

Photoinactivation activity was evaluated by applying a glass adhesion test based on the ISO 27447:2009(E) standard.[8] Since the layer manufacturing process might contaminate the test surface, all TiO_2-coated foils were exposed to UV light for 5 min prior to the microbiological tests. 0.1 mL of the bacterial suspension (10^5 CFU mL^{-1}) was pipetted onto the test surface (30×30 mm^2) and covered with a cover glass (24×24 mm^2). Then the sample was placed in a square Petri dish (100×100×20 mm^3) equipped with a wet filter paper and a square metal plate as a support (Fig. 1). In this test the 405 nm 10 mW LED light (Instytut Fotonowy) with intensity of 1.0 mW cm^{-2} (measured at the sample level by Ophir NOVA II Radiometer, Laser Measurements Group) was applied. After irradiation, the samples on the cover glass were shaken out in 3 mL of saline solution, serially diluted and spread onto an appropriate agar media. In order to determine the number of viable cells (counted as colony-forming units per ml, CFU mL^{-1}) the samples were incubated at 37°C for 24 h and thereafter bacteria colonies were counted. Control tests on bacteria, involving neat and modified films kept in the dark and irradiated, were carried out for all experiments, applying adequate procedures.

Each experiment was performed in quadruplicate and repeated at least twice. The mean, standard deviation and T-tests were calculated.

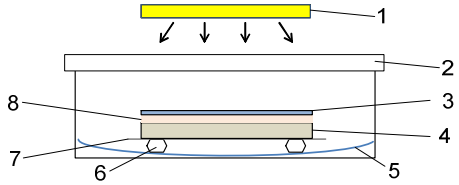

Figure 1. Schematic diagram of the irradiation set up. 1- light source, 2- plastic lid, 3- cover slide glass, 4- TiO_2-coated polymer, 5- wet filter paper, 6- metal nut, 7- metal plate, 8- bacterial suspension.

Results and discussion

Characterization of coatings

Nanocrystalline TiO_2 was successfully used for preparation of thin coatings on a polypropylene substrate (PP). Coatings obtained by the dip-coating technique were opaque and homogeneous. Coatings produced at the withdrawal rate of 1 cm min^{-1} yielded films of *ca*. 100-300 nm thickness, as estimated by SEM measurements.

The scanning electron micrographs of TiO_2 coatings of native (a, b) and damaged (c, d) samples are presented in Fig. 2. Micrographs c and d were taken for mechanically damaged film to enable the thickness measurements. The native films are smooth (micrograph a) with some narrow cracks of up to 150-300 nm width. These cracks are observed mainly close to the film edges and are characteristic for mineral coatings at flexible polymeric foils.

UV-vis diffuse reflectance spectra of the unmodified and modified TiO_2 coatings are shown in Fig. 3. The modified coating exhibits a clear absorption of visible light up to 550 nm. This results from the surface charge-transfer complexes formation.[6a]

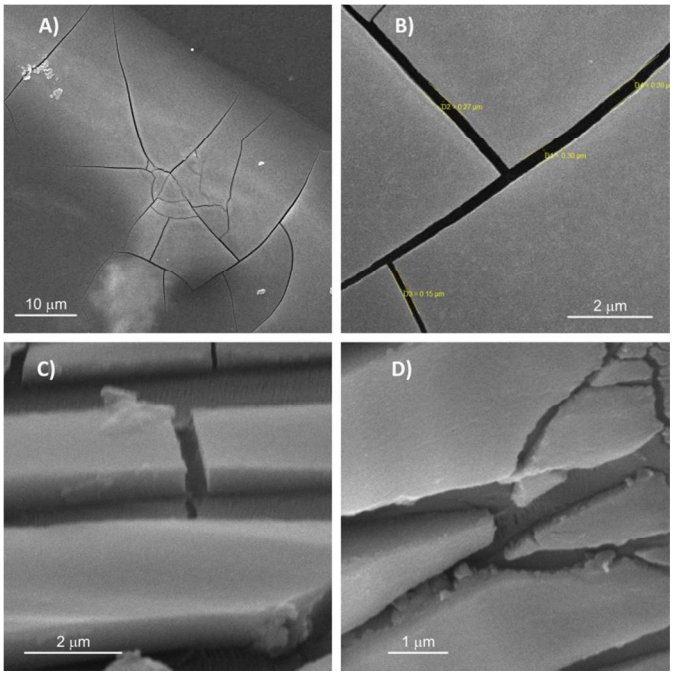

Figure 2. SEM micrographs of titanium dioxide coating on a polypropylene foil (a, b). The edge of TiO_2 film can be seen in (a), in the upper right corner. The mechanically damaged TiO_2 films (c, d) can be used for estimations of the film thickness.

Photocatalytic activity

To check the photoactivity of films, unmodified and sensitized thin layers of TiO_2 were produced at the surface of a conductive ITO foil (a mixture of indium and tin oxides). Cyclic voltammetry measurements revealed a peak related to oxidation of catechol, observed for the cat@TiO_2 material, but not for the unmodified titania film (Fig. 4). Oxidation of catechol at *ca*. 0.6 V *vs*. Ag/AgCl electrode is in agreement with previously reported measurements.[9]

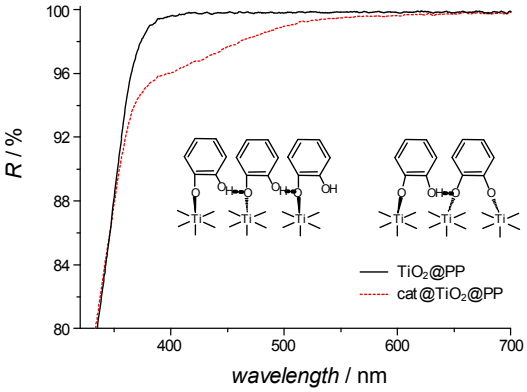

Figure 3. UV-vis diffuse reflectance spectra of films of neat titania (solid line) and titania modified with catechol (dotted line) deposited at polypropylene foils. The structures of Ti(IV)-catechol surface complexes are presented.[6a-c]

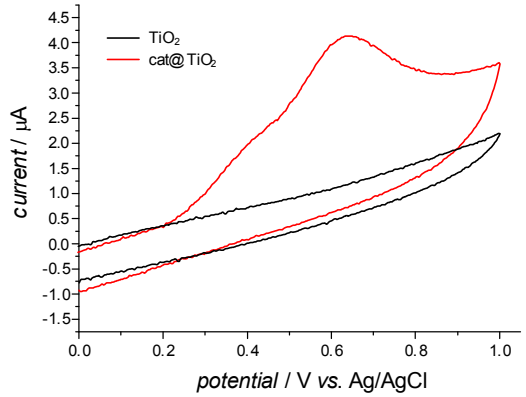

Figure 4. Cyclic voltammograms recorded for films of TiO_2 and cat@TiO_2 deposited at the surface of ITO foil.

Photocurrent measurements made for ITO electrodes with deposited materials were done for wide ranges of electrode potentials and wavelengths of incident light. Generation of anodic photocurrents was observed for the unmodified TiO_2 film when UV light (λ < 390-400 nm) was applied (Fig. 5a). At positive potentials anodic photocurrents were recorded also for the electrode covered with cat@TiO_2, however in this case the spectral range of activity was broadened up to *ca*. 520 nm (Fig. 5b). This proves the photosensitization of titania by surface charge transfer complexes of titanium(IV) with catechol as the ligand. The modified materials induce also cathodic photocurrents when the electrode is biased at negative potentials. This effect can be explained by the change of the Fermi level upon TiO_2 modification with catechol. It should be noticed that values of photocurrents induced by UV light,

measured for the modified material, are lower than those measured for unmodified titania. This difference originates from a less efficient electron-hole recombination when the excited state is reached via a direct excitation of TiO_2 when compared to the LMCT excitation of the surface complex.

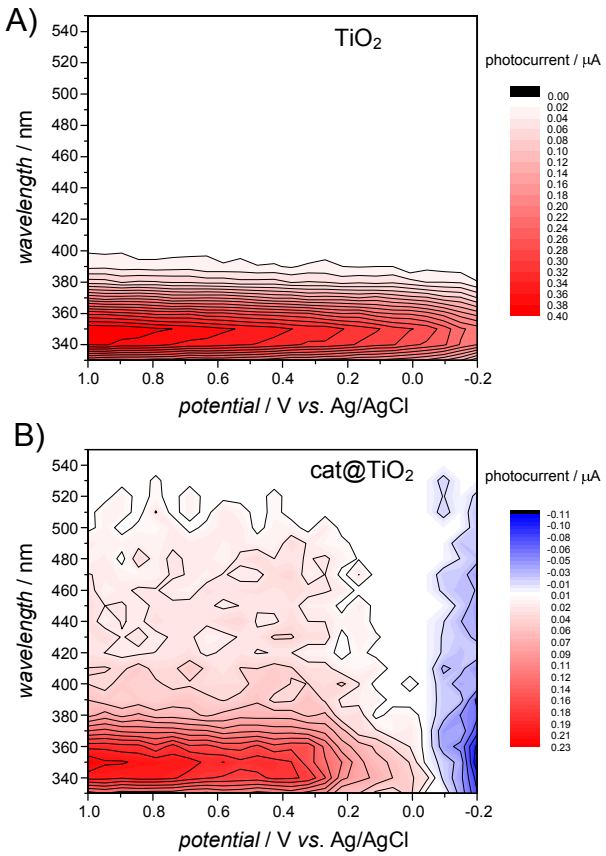

Figure 5. Photocurrent measurements for thin layers of materials deposited at ITO foil recorded for incident light in the range of 330-550 nm at potentials –0.2 to 1.0 V: a) TiO_2, b) cat@TiO_2.

Photocatalytic antibacterial activity – adaptation of ISO standard

Due to a wide variety of methods used to test antibacterial activity of photocatalytic coatings, the ISO 27447:2009(E) standard was chosen.[8] However, this procedure is mainly designed for photocatalytic coatings deposited on inorganic supports, irradiated with UV light. Therefore, due to differences in the support (polymers) used for the synthesis of TiO_2 coatings and the irradiation light source (visible light), the procedure was adopted to our requirements. The differences between the modified and ISO procedures, with the description of the experimental set-up, are listed in Table 1 (compare also Fig. 1).

Table 1. Comparison of the major changes in the parameters of ISO 27447:2009(E) procedure with the glass adhesion method used in this study.

Parameter	ISO 27447:2009(E)	Adopted glass adhesion test
Bacteria cultivation	Nutrient agar	McC medium (*E. coli*), TSA (*S. aureus*)
Sample size	50 × 50 ± 2 mm^2	30 × 30 ± 2 mm^2
Sample size covered by an adhesive glass	400-1600 mm^2	576 mm^2
Volume of test bacterial suspension	0.15 mL	0.10 mL
Light source	Fluorescent BLB lamp 300-400 nm	405 nm LED
Light intensity	0.001-0.25 mW cm^{-2}	1.0 mW cm^{-2}

After 4 hours irradiation with visible light (LED source, λ_{max} = 405 nm) the modified titanium dioxide films were found to be most efficient in bacteria inactivation at the starting concentration of 10^5-10^6 CFU mL^{-1}. Due to the fact that bacteria absorb light of the wavelength lower than 340 nm, the applied light could be absorbed efficiently only by the Ti(IV)-catechol surface complex.[10] The irradiation conditions enabled neither a direct titanium excitation, nor a direct bacteria inactivation. Therefore, no photoinactivation effect was observed under visible light irradiation of neat TiO_2 coatings (Fig. 6).

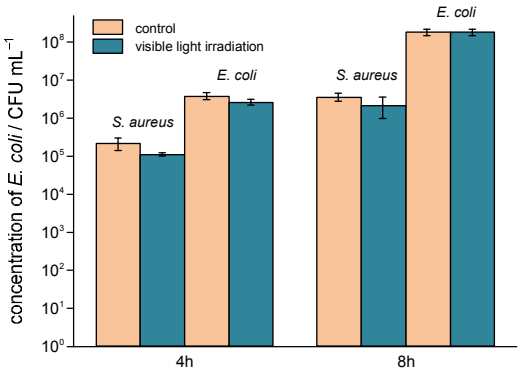

Figure 6. The concentration of *S. aureus* and *E. coli* after 4 and 8 hours of visible light irradiation (405 nm, 1.0 mW cm^{-2}) for unmodified TiO_2 coatings.

However, after 8 h of irradiation in the presence of cat@TiO_2 the concentration of *E. coli* decreased by the factor 10^3, from the initial bacteria concentration of *ca.* 10^6 CFU mL^{-1} (Fig. 7). None toxic effect of the modified coating (cat@TiO_2) in tests carried out in the dark was observed. These results are consistent with the reported lack of toxicity of catechol itself towards *E. coli*.[9]

In the case of Gram(+) coccus, bacterium *S. aureus*, the photoinactivation curve (Fig. 8) is similar to that for *E. coli*. The ratio between the initial and final concentrations of viable bacteria was again close to 10^3.

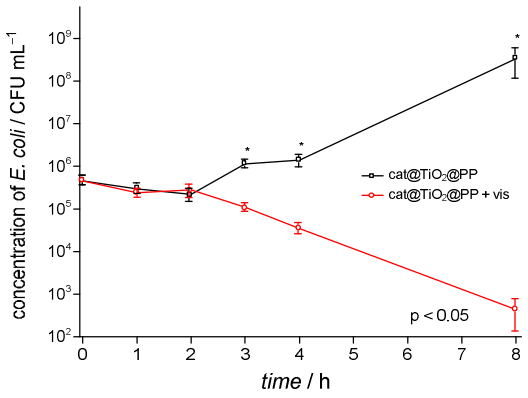

Figure 7. Concentration of *E. coli* under visible light irradiation (405 nm, 1.0 mW cm^{-2}) measured for TiO_2 coatings modified with catechol (dark – □, light – ○).

The mechanism of photoinactivation process can be evaluated through the shape analysis of curves presented in Figs. 7 and 8. For both bacteria strains, in the first phase, two hours long incubation step is observed. This phase is characterised by balancing the amounts of generated ROS with their elimination by bacteria's self-defence mechanisms, involving superoxide dismutase (SOD) and catalase. These enzymes protect cells from the oxidative stress according to the following mechanism:

$$2O_2^- + 2H^+ \xrightarrow{SOD} O_2 + 2H_2O_2$$

$$2H_2O_2 \xrightarrow[catalase]{catalase} O_2 + 2H_2O$$

The increasing concentration of ROS initiates oxidation of the cell wall and membrane components, contributing to bacteria death.[11] The photocatalytic activity of cat@TiO_2 film towards *S. aureus* inactivation appeared slightly lower when compared with the activity against *E. coli*. The analysis of Figs. 7 and 8 points at the essential influence of visible light on bacteria photoinactivation.

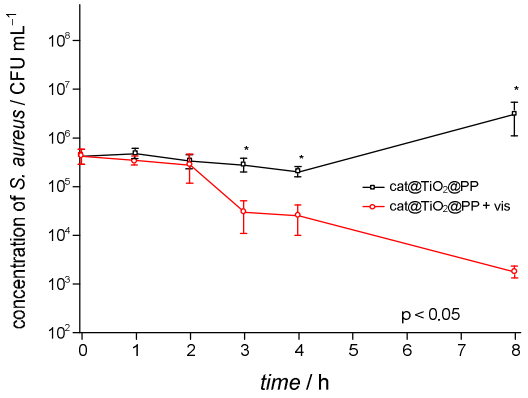

Figure 8. Concentration of *S. aureus* under visible light irradiation (405 nm, 1.0 mW cm^{-2}) measured for TiO_2 coatings modified with catechol (dark – □, light – ○).

Conclusions

We have demonstrated that catechol-photosensitized TiO_2 films, produced at polymeric foils, can be used as potential anti-microbial coatings. The test bacteria *Escherichia coli* and *Staphylococcus aureus* were inactivated by the photocatalyst (cat@TiO_2). The ratio of population reduction decreased by *ca.* three orders of magnitude after 8 h of visible light (405 nm) irradiation. Applied irradiation conditions did not induce bacteria inactivation in the presence of non-sensitized TiO_2 films. Furthermore, the applied adaptation of the ISO 27447:2009(E) standard procedure can be used in future for evaluating the antibacterial activity of films and coatings under various irradiation conditions (*e.g.* under visible light irradiation).

The synthesized photocatalytic coatings may provide a new strategy of reducing the risk of nosocomial infections by applying them on plastic items used in medicine.

Acknowledgements

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Notes and references

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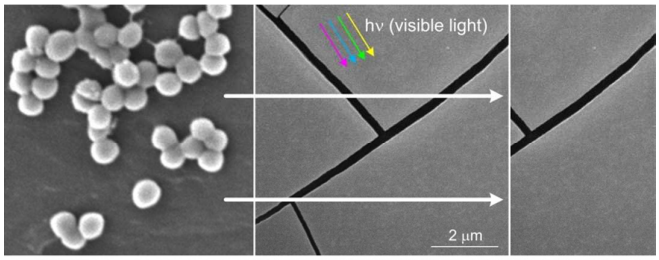
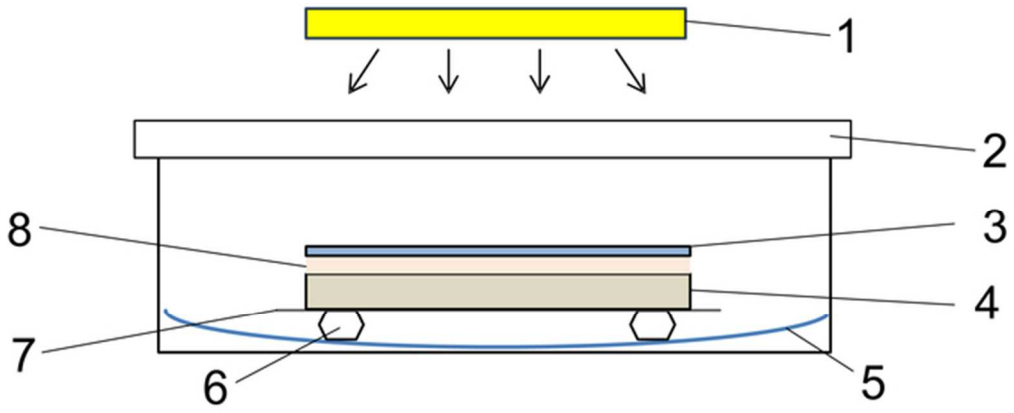
Graphical abstract

Visible light induced photocatalytic inactivation of bacteria at modified titanium dioxide films on organic polymers

Rafał Sadowski, Magdalena Strus, Marta Buchalska, Piotr B. Heczko and Wojciech Macyk

A transparent polypropylene foil pre-treated with a low temperature plasma and covered with sensitized, nanocrystalline TiO_2 thin film, appears a useful, self-sterilizing material active upon visible light irradiation.





56x23mm (300 x 300 DPI)

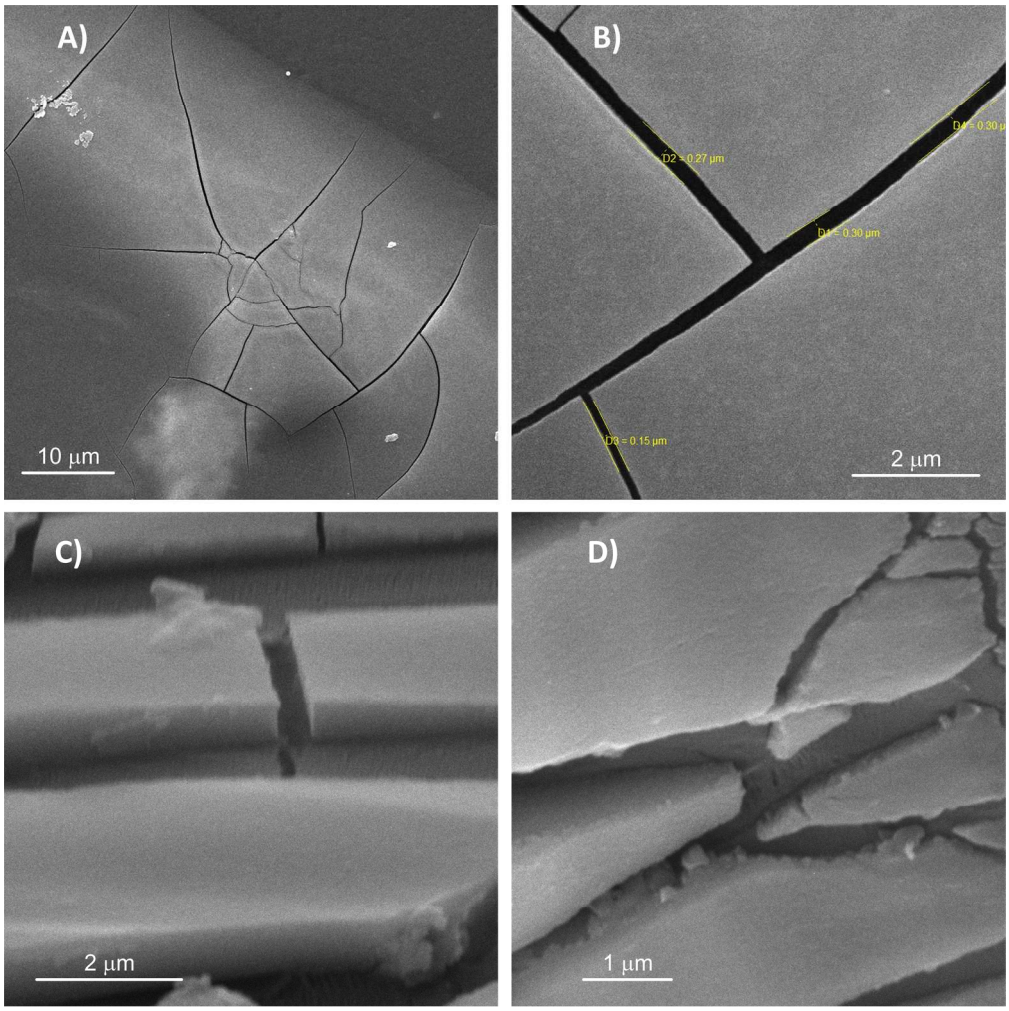


Figure 2
187x187mm (300 x 300 DPI)

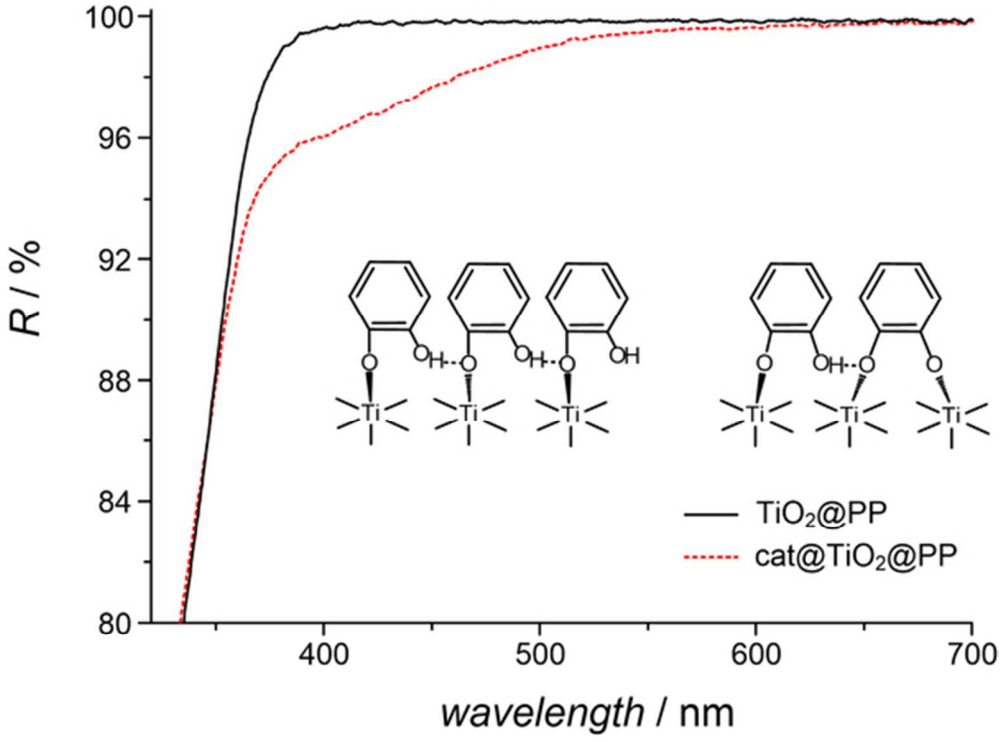


Figure 3
51x38mm (300 x 300 DPI)

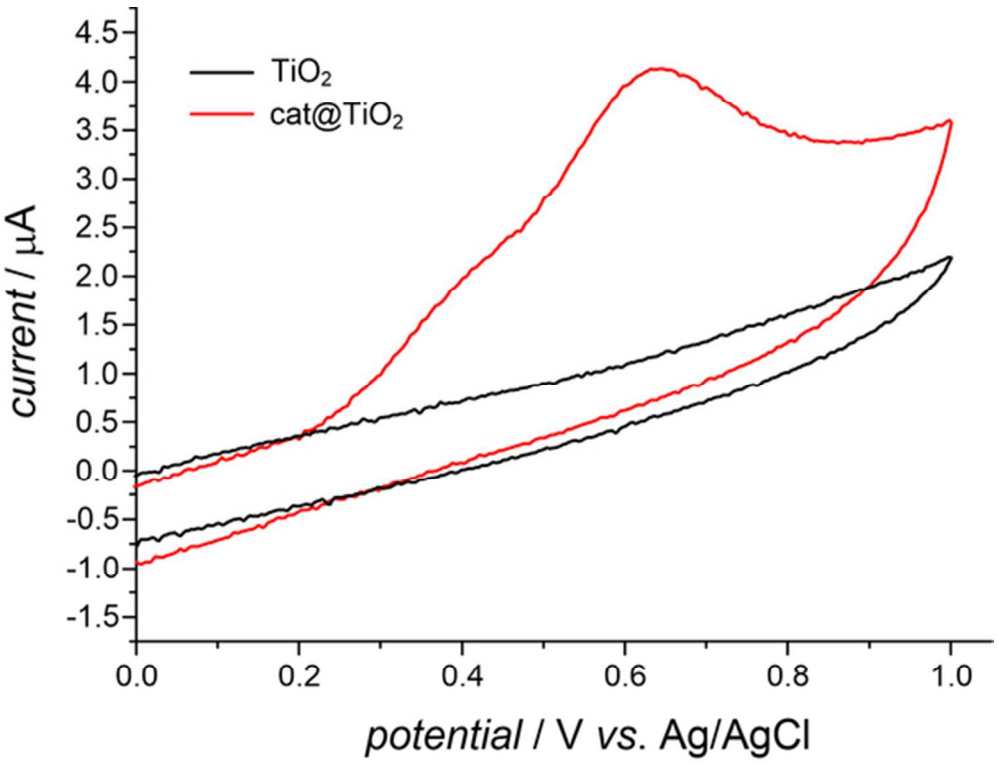


Figure 4
51x39mm (300 x 300 DPI)

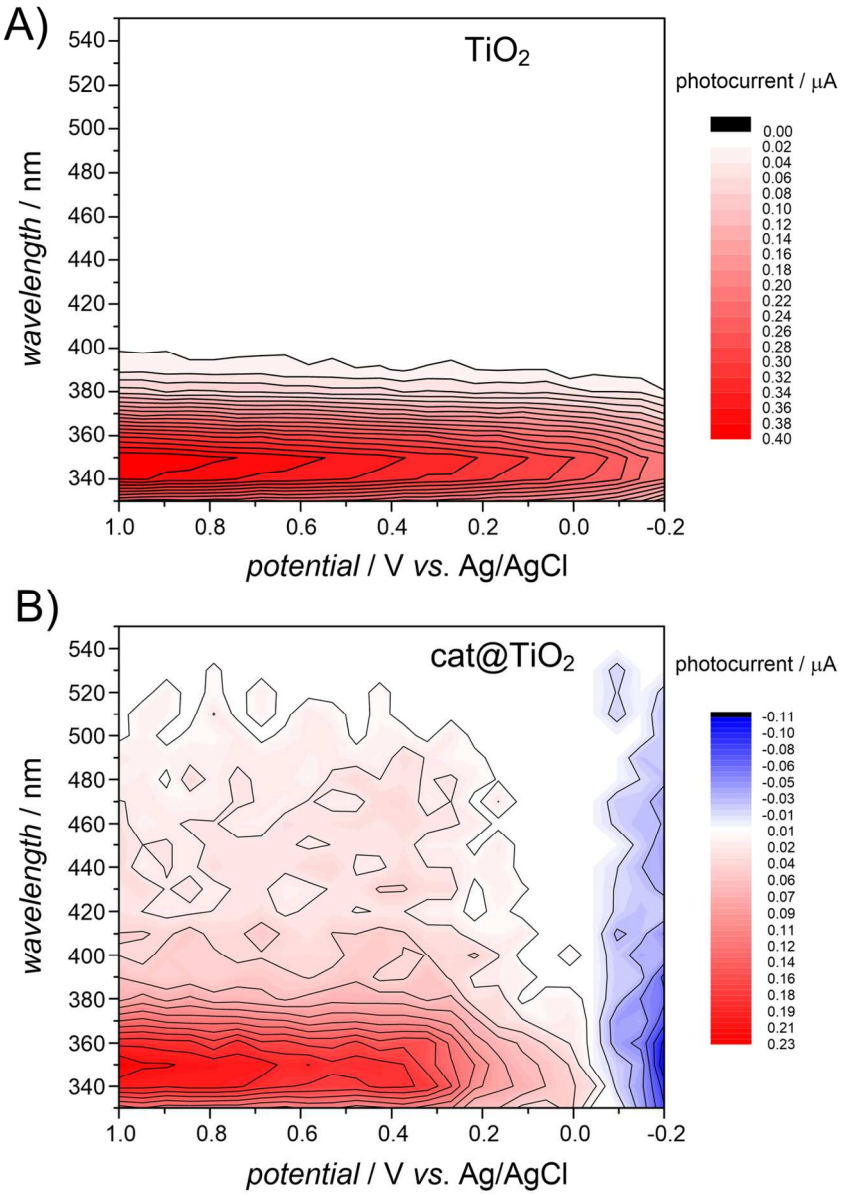


Figure 5
113x162mm (300 x 300 DPI)

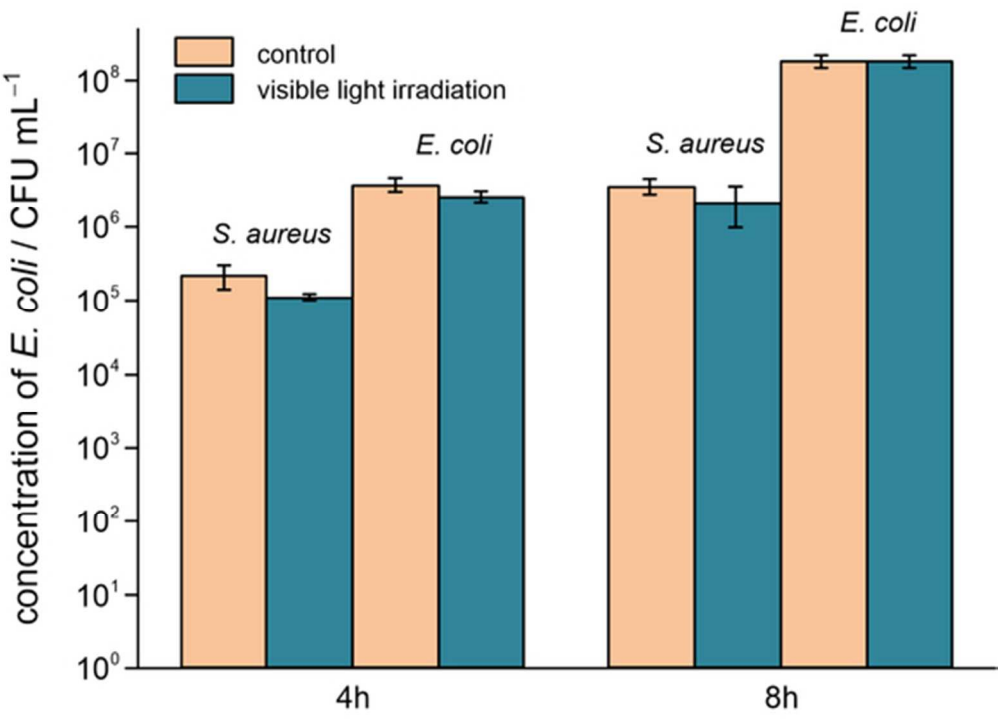


Figure 6
48x34mm (300 x 300 DPI)

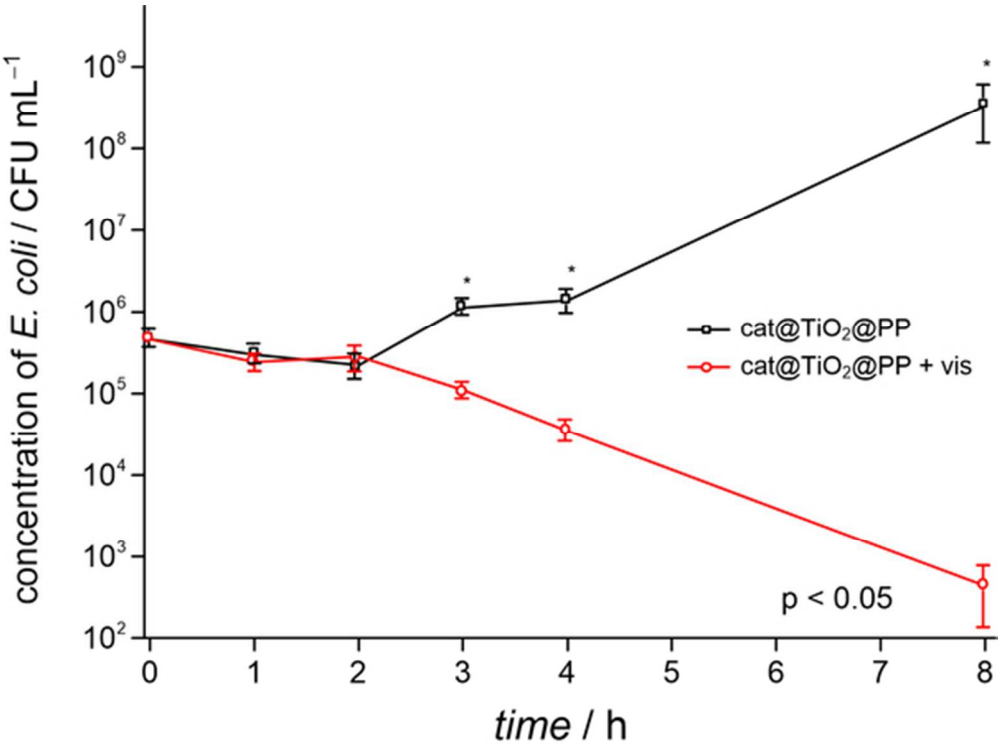


Figure 7
51x38mm (300 x 300 DPI)

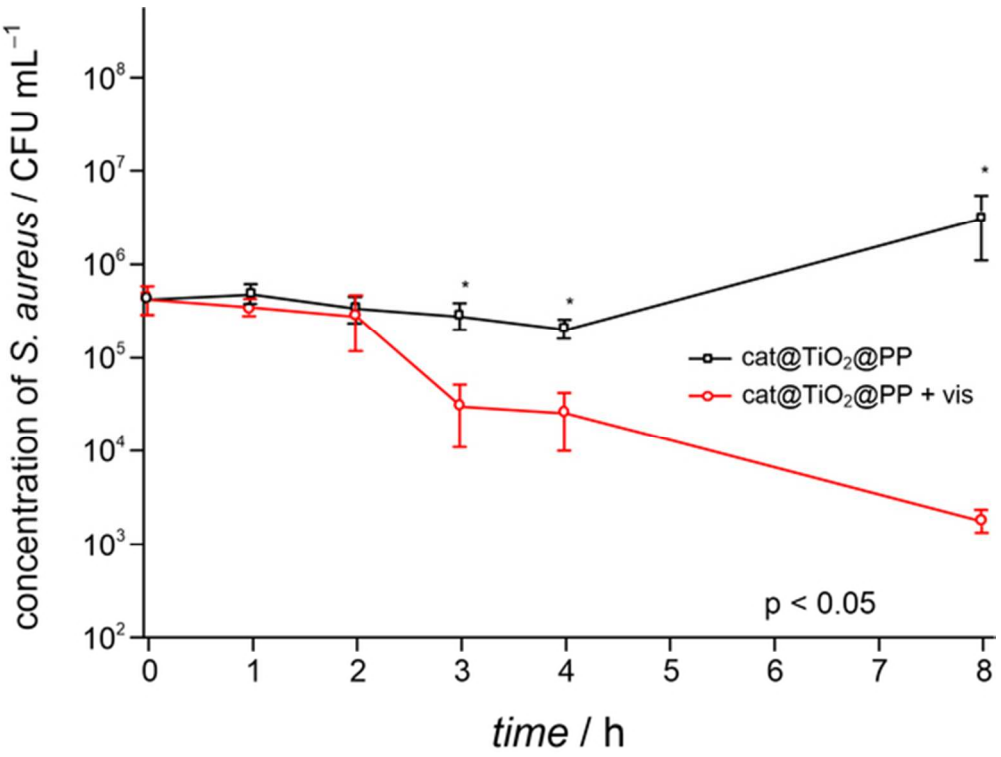


Figure 8
51x39mm (300 x 300 DPI)