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NOVEL PHOTOCATALYTIC SYSTEMS BASED ON NANO- AND MESOSTRUCTURED TITANIA

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Novel photocatalytic systems based on nano- and mesostructured titania modified with metallic nanoparticles has been proposed and investigated:

(I) thin-film photocatalysts operating in air conditions, which exhibit extra high activity towards photooxidation of the adsorbed organics and demonstrate enhanced photomicrobiocidic activity.

The investigation of the photodegradation of model organic compounds with different polarity at the surface of thin films of TiO_2 and TiO_2-based has evidenced that the catalytic photolysis of polar organics involves the attack by hydroxyl radicals, whereas the photodestruction of non-polar organic compounds occurs via direct photohole trapping. Deposition of nanoparticles of noble metals (Ag, Pd, Pt) results in drastic (4-fold) increase in the efficiency of the photodestruction of both polar and non-polar probing organic compounds. By contrast, deposition of base metals (Cu, Ni) results in the passivation of the TiO_2 photocatalyst due to drastic increase of the recombination losses. The photoinduced pathophysiological activity of nanostructured TiO_2 films have been also investigated with the use of the representative strains of Gram (+) and Gram (-) bacteria: *P. fluorescens* B-22, *Lactococcus lactis* ssp. lactis 411, *Lactococcus lactis* ssp. *cremoris* 502, *Escherichia coli* K-12 HfrH, and *Bacillus subtilis*. It has been shown that the highest photobiocide activity is inherent in TiO_2/Ag films which demonstrate the enhanced efficiency of cell adsorption as compared to the naked TiO_2 (the adsorption increases 6-fold) and a high yield of both photogenerated hydroxyl radicals and superoxide. TiO_2/Ag coatings demonstrate higher biocide activity towards the G(-) bacteria than towards G(+) ones that can be explained by different morphology of the cell walls resulted in different resistance against the attack of active oxygen species.

(II) photocontrollable coatings consisting of titania-based nanocontainers incorporated in the hybrid SiO_x:ZrO_x film; the embedded nanocontainers demonstrate an ability of efficient light-driven release of the loaded materials,

The incorporation of nano- and microdispersed titania particles into the hybrid SiO_x:ZrO_x-based films permits immobilization of different catalysts and obtaining photacatalytically-active coatings at low temperatures. The resultant thin-film photocatalysts reveal high activity towards photodestruction of organics both in aqueous solutions and in air conditions. The enhanced hydrophilicity inherent to the titania-loaded hybrid sol-gel films makes them a promising material for air purification and for self-cleaning coatings. These films also show high affinity to microorganisms and demonstrate enhanced photoinduced pathophysiological activity towards both gram-negative and gram-positive bacteria. Of principle meaning is also the fact that the hybrid SiO_x:ZrO_x-based films used as the photocatalyst carrier are highly adhesive and, being deposited onto the metal surface, behave as the anticorrosion coatings. The proposed approach permits one to change radically the whole scheme of assembling the photocatalytically-active coatings since the titania particles to be embedded into the hybrid sol-gel film can be synthesized, annealed and then modified (if needed) separately. Moreover, the dispersions of different photocatalysts can be embedded in the SiO_x:ZrO_x matrix yielding photocatalytically-active coatings with mosaic surface that opens strong possibilities of controlling the adsorption of chemical and bacterial contaminants.

By applying polyelectrolyte shell over the particles of mesoporous titania via layer-by-layer assembly of oppositely charged polyelectrolytes it is possible to fabricate micro- and nano-scaled reservoirs which being immobilized by hybrid sol-gel film demonstrate an ability of light-driven release of the loaded materials. On this basis novel photocontrollable coatings (e.g, with extra high pathophysiological activity if the embedded nanocontainers are loaded with the bactericidal material) can be developed. In a broad sense, the use of photocatalytic reactions to exert the remote control over the permeability of polyelectrolyte capsules (both in the immobilized state and in the solution) opens up fresh opportunities for delivery and controllable release of chemical compounds, in particularly, for analytical and biomedical applications.