

Metal-Modified Nanostructured Titania Films as the Materials for Planar Photocatalysts, Photocontrollable Coatings and Photocatalytic Lithography

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Novel photocatalytic systems based on nano- and mesostructured titania modified with photodeposited metal nanoparticles and bimetallic nanoparticles grown by combination of photochemical and electroless deposition have 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 photomicrobiocidal activity.

The investigation of the photodegradation of model organic compounds with different polarity at the surface of thin films of TiO₂ and TiO₂-based nanocomposites (TiO₂:SiO₂, TiO₂:In₂O₃ derived from the mixed sols of individual oxides 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 [1]. 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, this effect manifesting itself only in a rather narrow range of metal loadings (1-2 monolayers according to the Rutherford backscattering measurements). The photocatalytic, photoelectrochemical, chemiluminescent and contact angle investigations have evidenced that the observed enhancement of photoactivity can be attributed to the decreased level of recombination, high yield of photoproduced superoxide (which is involved into the photodegradation together with photoholes and photogenerated hydroxyl radicals) and increased hydrophilicity of the photocatalyst surface. By contrast, deposition of base metals (Cu, Ni) results in the passivation of the TiO₂ photocatalyst due to drastic increase of the recombination losses. However, the bimetallic Ag/Ni particles obtained by growing small nickel caps over the initial silver particles via the electroless plating technique ensure further increase of the photocatalytic activity due to the enhancement of superoxide yield while the recombination level remains untaken.

The effect of deposition of metallic (Ag) and bimetallic (Ag/Ni) nanoparticles on the photoinduced pathophysiological activity of nanostructured TiO₂ films have been also investigated with the use of the representative strains of Gram (+) and Gram (-) bacteria: *P. fluorescens* • -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 TiO₂/Ag films which demonstrate the enhanced efficiency of cell adsorption as compared to the naked TiO₂ (the adsorption increases 6-fold) and a high yield of both photogenerated hydroxyl radicals (the major lethal factor) and superoxide (which is predominantly involved in the inactivation of microorganisms initially damaged by hydroxyl radicals). The photocatalytically-active TiO₂/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. By contrast, the differences in the breathing mechanism have appeared to be the minor factor which only slightly affects the efficiency of cell deactivation at the photocatalyst surface.

(ii) **photocontrollable coatings** consisting of metallized titania-based nanocontainers incorporated in the hybrid SiO_x:ZrO_x film which demonstrate an ability of efficient light-driven release of the loaded materials from the embedded nanocontainers.

The incorporation of nano- and microdispersed titania particles into the hybrid SiO_x:ZrO_x-based films permits immobilization of different catalysts (including commercial ones specially designed for

photocatalytic purification purposes) and obtaining photocatalytically-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 $\text{SiO}_x:\text{ZrO}_x$ -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 $\text{SiO}_x:\text{ZrO}_x$ 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.

(iii) **photosensitive layers** made of Pd^{2+} -doped amorphous TiO_2 which enables generation of metal patterns (grids, circuits, catalytic pads for growing of carbon nanotubes, etc.) on conducting and nonconducting substrates with the resolution down to $3 \cdot \mu\text{m}$ employing the UV light exposure and below 100 nm in the case of exposure with the e-beam.

The photopatterning with $\text{TiO}_2:\text{Pd}^{2+}$ films involves their photoactivation towards electroless deposition of nickel or copper [2]. Under UV irradiation, photoreduction of Pd^{2+} residing in the photolayer occurs predominantly as a one-electron reaction yielding Pd(I) compound stabilized in the titania matrix, while the hydroxyl groups of TiO_2 and hole scavenger contained in the $\text{TiO}_2:\text{Pd}^{2+}$ film are oxidized by photoholes. Actinic illumination also results in photopolymerization of hydrated titania, leading to profound losses in solubility of the photolayer at exposed areas. Washing results in the removal of the photolayer from the unexposed areas and facilitates the formation of a Pd nanophase at exposed areas via a disproportionation mechanism, the structure and dispersity of the resultant Pd particles being dependent on the intensity of UV irradiation. Pd particles of crystalline structure and a size of ca. 4 nm produced upon low intensity UV irradiation can catalyze the subsequent Ni electroless deposition, providing formation of negative metal pattern. On the other hand, amorphous Pd particles of smaller size produced upon high intensity illumination do not possess catalytic activity and electroless nickel plating results in the generation of metal pattern of positive type. This opens the possibility of straightforward switching of the photopatterning process by changing the illumination intensity.

References

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