# Photocatalytic activity of TiO$_2$:In$_2$O$_3$ nanocomposite films towards the degradation of arylmethane and azo dyes

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## Abstract

The photocatalytic activity of TiO$_2$:In$_2$O$_3$ nanocomposite films derived from the mixed sols of individual oxides was investigated using a photodegradation of adsorbed arylmethane and azo dyes under UV illumination in contact with air. It has been shown that the photoactivity of TiO$_2$:In$_2$O$_3$ films towards the destruction of polar dyes exhibits non-additive variations with Ti/In ratio and correlates well with the intrinsic hydrophilicity of nanocomposite films, whereas the photodegradation of non-polar dyes occurs most rapidly at pure titania. The observed effects are discussed in terms of different mechanisms of the photodegradation of probing dyes and inhomogeneity of photocatalyst surface.
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## 1. Introduction

In recent years, the investigations on titania photocatalysis, traditionally directed towards the photodecomposition of chemical and bacterial pollutants in aqueous phase [1–3], were also focused on the photocatalytically-active coatings (so-called self-cleaning materials) capable of removing adsorbed organic contaminants under solar or artificial illumination [1,3–7]. The self-cleaning characteristics of TiO$_2$ result not only from its strong oxidation power under UV irradiation but also from the recently discovered phenomenon of the photoinduced superhydrophylicity inherent in titania surface [1,7,8]. The contributions of these factors in the self-cleaning function of the titania coating are essentially dependent on its structure, acidity, concentration of defects and doping density which are very sensitive to the photocatalyst preparation route. Composite films, permitting to combine titanium dioxide with photoactive [9–15] and non-photoactive [6,16,17] compounds, open fresh opportunities for controlling the specific adsorption properties, the surface morphology and the photoreactivity of the photocatalytically-active coatings, thus imparting them additional functionalities.

In the present work we have studied the photocatalytic activity of TiO$_2$:In$_2$O$_3$ composite in the contact with air using, as the probing photocatalytic reaction, the light-induced degradation of adsorbed dyes. It has been demonstrated previously that TiO$_2$:In$_2$O$_3$ composite in a form of mesoporous spheres [18] and nanocrystalline powders [19] possesses a surprisingly high activity towards the photodegradation of organics in aqueous medium; of principle meaning is also the fact that structural, optical and conducting properties of TiO$_2$:In$_2$O$_3$ composite (*i.e.*, the factors governing its photocatalytic activity) can be effectively controlled by changing the Ti/In ratio [20,21].

## 2. Experimental

The titanium dioxide and indium hydroxide sols used for the preparation of the photocatalytic coatings were obtained by controlled hydrolysis followed by ultrasonic dispergation. To prepare titania sol, 2.5 M TiCl$_4$ + 0.65 M HCl aqueous solution cooled to 0 °C was slowly titrated with 12.5% NH$_4$OH under continuous mechanical stirring up to a final pH of *ca.* 5. The precipitate was then centrifuged, washed out with distilled water, and, after adding HNO$_3$ as a stabilizer (the TiO$_2$:HNO$_3$ mole ratio was 5:1), exposed to ultrasound (22 kHz). The aqueous sol of indium hydroxide was prepared in the similar manner by adding 12.5% NH$_4$OH dropwise to 0.25 M In(NO$_3$)$_3$ at room

temperature until pH $\sim 4$ was reached. Before the sonication of the resultant precipitate, $HNO_3$ was added as the stabilizer in an amount corresponding to the $In(OH)_3$: $HNO_3$ mole ratio of 20:1. Thus obtained transparent sols (64 g/l in the case of titanium dioxide and 46 g/l in the case of indium hydroxide) were stable at room temperature at least for several months. For further details concerning preparation of sols see Refs. [20,21].

Thin-film photocatalysts were prepared by spraying aqueous sols of titanium dioxide and indium hydroxide as well as their mixtures onto the glazed ceramic tiles heated to 200 °C. The resultant $TiO_2$, $In_2O_3$ and $TiO_2:In_2O_3$ coatings were then annealed at 450 °C for 1.5 h in air. No signs of the chemical interaction between titanium and indium oxides as the result of heat treatment of composite film was observed in the XRD patterns. Before the photocatalyst deposition, the surface of the substrate was coated with a silicon dioxide intermediate layer by spraying the $SiO_2$ sol to prevent migration of sodium ions from a glaze during annealing (the latter factor could adversary affect the photoactivity of titania [22]). Thus obtained photocatalytic coatings were robust and highly adhesive; according to the Rutherford backscattering spectra their thickness was of *ca.* 0.2 μm. After preparation, the samples were left for 2 weeks in the dark to ensure complete conversion of non-equilibrium OH groups at the photocatalyst surface into oxygen bridging ones [23].

The photocatalytic activity of the samples was evaluated by the photodegradation of Rhodamine 6G (*o*-[6-(ethylamino)-3-(ethylimino)-2,7-dimethyl-3*H*-xanthen-9-yl]benzoic acid ethyl ester monohydrochloride) as a model polar dye and Sudan I (1-(phenylazo)-2-naphthol) as a dye of low polarity; for comparison, a set of arylmethane dyes: Bromothymol Blue (3′,3″-dibromothymolsulphophtalein), Rhodamine B ([9-(*o*-carboxyphenyl)-6-(diethylamino)-3*H*-xanthen-3-ylidene]diethyl-ammonium chloride), Eosin (9-(*o*-carboxyphenyl)-6-hydroxy-3*H*-xanten-3-one, potassium salt) and azo dyes: Methyl Orange (4′-dimethylaminoazobenzene-4-sulphonic acid, sodium salt), Sudan IV (1-[[2-methyl-4-[(2-methylphenyl)azo]phenyl]azo]-2-naphthalenol), PAN (1-(2-piridylazo)-2-naphthol) was used to probe the photoactivity of composite films. Dye solutions (in water for polar dyes and in acetone for non-polar dyes) were applied onto the photocatalyst surface in an amount corresponding to the surface concentration of *ca.* $2 \times 10^{-8}$ mol/cm$^2$ and samples were left for drying. The dye photodegradation was followed by measuring a diffuse reflectance, $R$; to obtain on this basis the value proportional to the surface dye concentration, $\Gamma$, the Kubelka–Munk function [24] was used:

$$\Gamma \sim \frac{(1-R)^2}{2R}$$

The measurements of $R$ were carried out at 530 nm; this value corresponds well to the absorption of the probing dyes in the adsorbed state. As the measure of the photoactivity, $Y_{ph}$, we have used the relative drop of a dye concentration after 5 min-illumination:

$$Y_{ph} = \frac{1 - \Gamma_5}{\Gamma_0}$$

where $\Gamma_0$ and $\Gamma_5$ are the concentrations of a probing dye before and after the illumination, respectively.

The photocatalytic tests were performed in 1-liter cylindrical reactor with quartz window in which the desired humidity was maintained using the fired silica gel or saturated aqueous solutions of LiCl, KBr, and $Na_2HPO_4$ (ensuring the humidity of 2–3%, 15–16%, 70–72% and 86–94%, respectively). The humidity in the interior of the photocatalytic reactor was measured using the humidity meter Testo 625 (Hotek Technologies). To equilibrate the system, the samples were left in the reactor for 1 h before photocatalytic experiments. Ultraviolet illumination was carried out using high-pressure mercury lamp (120 W) equipped with 310–400 nm bandwidth filter.

The superoxide production at the air-photocatalyst interface due to the trapping of photoelectrons with molecular oxygen was studied by measuring chemiluminescence according to the procedure similar to that employed by Ishibashi et al. to identify the long-lived active oxygen species formed on the $TiO_2$ surface under the UV illumination [25]. The glass plates coated with $TiO_2$, $In_2O_3$, and $TiO_2:In_2O_3$ films were illuminated in an empty quartz cell with UV light during 10 min. Immediately after the illumination, the cell was placed in the homemade set-up permitting the measurement of the chemiluminescence as a function of time. During the course of the chemiluminescence measurement, the cell was filled with luminol solution (to prepare this solution, 20 mg of luminol was dissolved in 0.5 ml of dimethyl sulfoxide an then diluted 1:10 with 0.1 M KOH). The integrated intensity of chemiluminescence emitted by luminol was used to compare the amount of the active oxygen species photoproduced at the surface of different pohotocatalysts. The addition of mannitol (a selective scavenger of hydroxyl radicals) into the luminol solution did not result in the decrease of the chemiluminescence intensity evidencing that only superoxide species accumulated at the photoadsorption sites at the photocatalyst surface contribute to the detected chemiluminescent signal [25].

The water contact angle measurements were performed at room temperature, with an experimental angle error of ±1°. The morphology of thin-film photocatalysts was investigated with atomic force microscope NanoScope 3a (Digital Instruments). Photoelectrochemical measurements were performed under potentiostatic conditions with the use of electrodes fabricated by deposition of $TiO_2$, $In_2O_3$ and $TiO_2:In_2O_3$ films onto the ITO glass plates.

## 3. Results and discussion

The photodegradation curves for Rhodamine 6G and Sudan I deposited onto the surface of $TiO_2$, $In_2O_3$ and $TiO_2:In_2O_3$ films shown in Fig. 1 evidence that for both probing dyes the photocatalytic degradation occurs much more efficiently as compared to the direct photolysis on the surface of a glazed tile free of the photocatalytic coating, with the rate of the dye photodegradation being strongly dependent on the photocatalyst composition. Fig. 2 discloses that the photocatalytic activity of $TiO_2:In_2O_3$
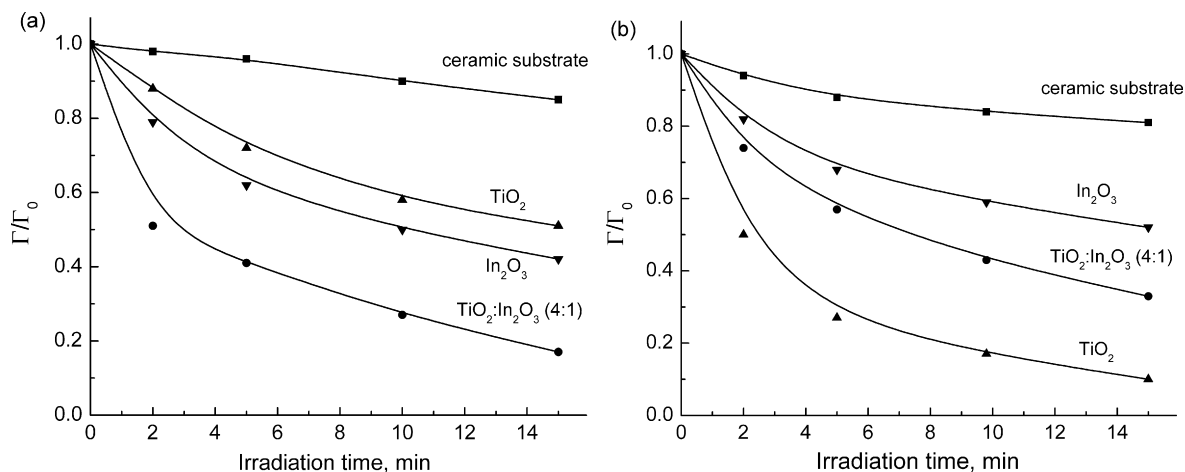
Fig. 1. Photodegradation kinetics of (a) Rhodamine 6G and (b) Sudan I on $TiO_2$, $In_2O_3$, $TiO_2$:$In_2O_3$ (4:1) thin-film photocatalysts and on the glazed tile used as the substrate. $\Gamma_0$, $\Gamma$ are the initial concentration of a probing dye and the concentration after illumination, respectively. Ambient humidity: 45%.

film towards the degradation of Rhodamine 6G and Sudan I varies with Ti/In ratio in a quite different manner: whereas in the case of Rhodamine 6G the photoactivity peaks for a composite containing 20 wt.% $In_2O_3$ (obtained by mixing $TiO_2$ and $In_2O_3$ colloids in a weight ratio of 4:1, further denoted as the $TiO_2$:$In_2O_3$ (4:1) composite), the photodegradation of Sudan I occurs most rapidly on the surface of $TiO_2$ film and slows down appreciably when going to the composite coatings.

The water contact angle measurements evidenced that the composite films exhibit higher hidrophylicity when compared to $TiO_2$ and $In_2O_3$. The hydrophilicity and the activity towards Rhodamine 6G photodegradation vary with $In_2O_3$ content in a

similar way (cf. Figs. 2a and 3), the photoactivity of the composite demonstrating more abrupt increase with the humidity of ambient air than in the case of individual oxides (Fig. 4). By contrast, no correlation between the hydrophilic properties of the composite films and their photocatalytic activity towards the photodestruction of Sudan I is observed (cf. Figs. 2b and 3); furthermore, in the case of catalytic photolysis of Sudan I the activities of $TiO_2$ and $TiO_2$:$In_2O_3$ exhibit only a slight dependence on the air humidity (Fig. 4).

For a binary heterogeneous surface the contact-angle changes are generally satisfactorily described by Cassie equation [26]:

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 \qquad (1)$$

where $f_1$ is the fractional area of the surface with a contact angle of $\theta_1$ and $f_2$ is the fractional area of the surface with a contact angle of $\theta_2$. It is seen from Fig. 3 that water contact angles measured for $TiO_2$:$In_2O_3$ composite are much lower than those calculated from Eq. (1). It should be, however, noted that
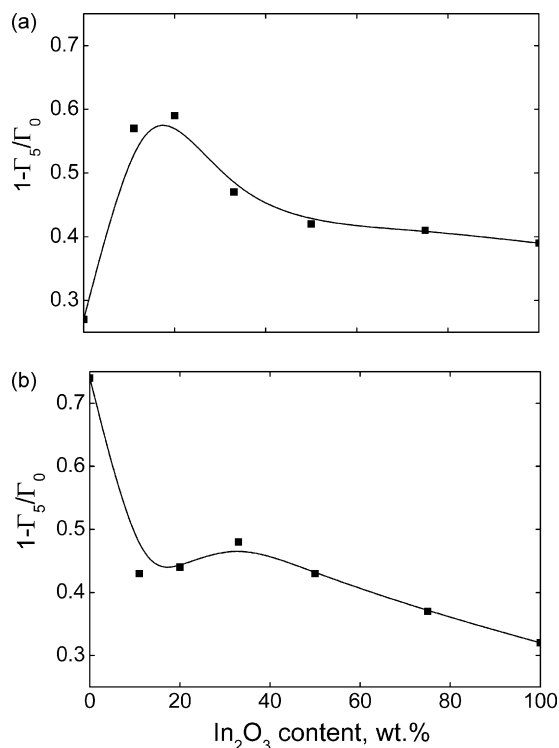


Fig. 2. Photocatalytic activity of $TiO_2$:$In_2O_3$ coating towards the photodegradation of (a) Rhodamine 6G and (b) Sudan I as a function of the $In_2O_3$ content.
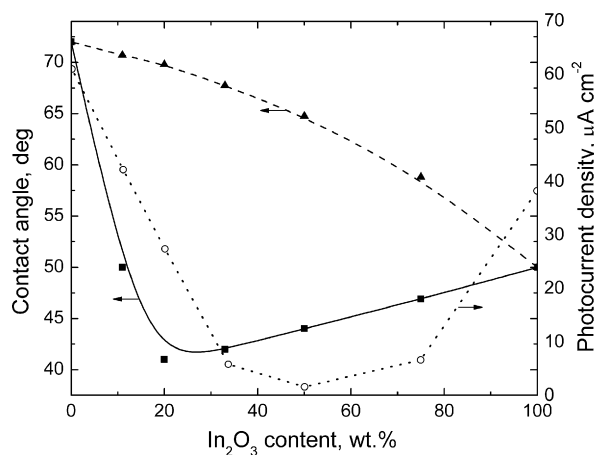


Fig. 3. Water contact angle and photocurrent response of $TiO_2$:$In_2O_3$ photocatalyst as a function of the $In_2O_3$ content. Squares show experimental contact angle values, triangles correspond to contact angle values calculated from Cassie equation. Photocurrents were measured in 0.1 M NaOH + 0.1 M $CH_3COONa$ at 0.5 V vs. Ag/AgCl (at this potential the photocurrent vs. potential dependencies exhibit complete saturation).
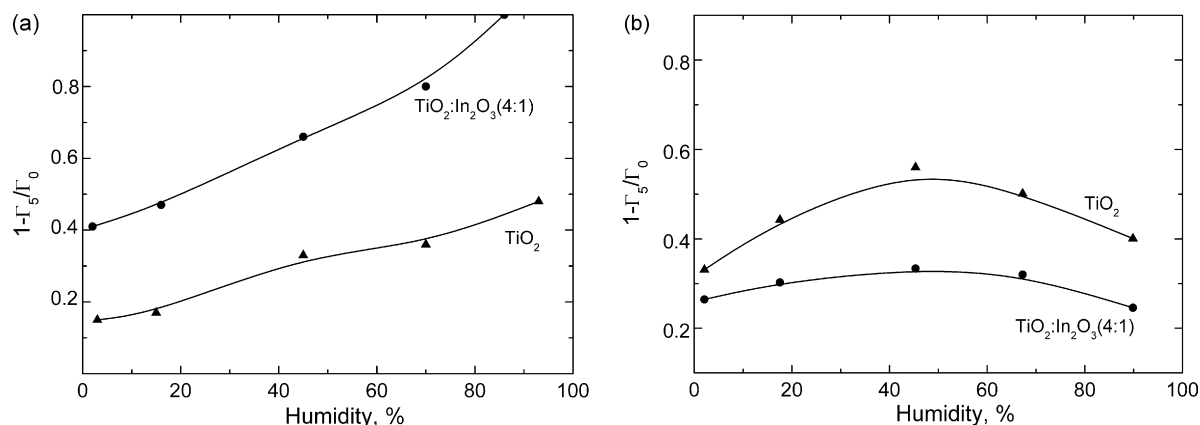
Fig. 4. Photocatalytic activity of $TiO_2$ and $TiO_2$:$In_2O_3$ (4:1) films towards the degradation of (a) Rhodamine 6G and (b) Sudan I as a function of the ambient humidity.

Cassie equation was derived for composite smooth surfaces, whereas contact angle is very sensitive to the geometrical structure of a solid surface: an intrinsically hydrophobic surface becomes more hydrophobic as its roughness increases and, *vice versa*, the hydrophilicity shows an increase with a roughness for the intrinsically hydrophilic surfaces. Consideration of the effect of a roughness of composite films on their hydrophylicity led to a modification of classical Young's equation [27]:

$$\cos\theta_a = r\frac{\alpha_{13} - \alpha_{12}}{\alpha_{23}} = r\cos\theta$$

where $\alpha_{12}$, $\alpha_{13}$ and $\alpha_{23}$ denote the interfacial tensions of the solid–liquid, the solid–gas and the liquid-gas interfaces, $\theta_a$ is the apparent water contact angle which is reduced from the intrinsic contact angle, $\theta$, by the roughness, $r$, of the intrinsically hydrophilic surface. It is seen from AFM images in Fig. 5 that the size of building blocks forming the surface of the composite film is considerably larger as compared to $TiO_2$ film. As the result, the root mean square roughness evaluated from AFM 1.5 μm × 1.5 μm surface plots increases *ca.* fourfold (from 12.7 to 44.1 nm) as one goes from $TiO_2$ to $TiO_2$:$In_2O_3$. The increase in the roughness in the case of composite films can be attributed to the enlargement of gel particles due to an interaction of $TiO_2$

and $In(OH)_3$ sols during the formation of a nanocomposite and a mutual protective action of composite-forming components against crystallization that hampers rearrangements in the $TiO_2$:$In_2O_3$ film during an annealing [20]. For heterogeneities of small dimensions (several micrometers or less) an additional decrease of contact angle can also result from the line tension contribution [28]; however, taken into account that there exists a lower size limit of chemically distinct patches at the composite surface that affect the contact angle (somewhat lower than 0.1 μm [29]) and using the size of $TiO_2$ and $In_2O_3$ crystallites in the composite (amounting, according to XRD analysis, 5–7 and 10–12 nm, respectively) as the estimate of the size of heterogeneous regions at the surface of the sample one might expect that in our case the role of the above mentioned factor is relatively low.

The enhanced hydrophilicity inherent in $TiO_2$:$In_2O_3$ films with highly developed surface facilitates water adsorption from humid air. This creates favorable conditions for photoproduction of hydroxyl radicals capable to induce oxidation reactions similar to those occurring in the aqueous suspensions of the photocatalyst during destruction of organics under actinic illumination [30,31]. Moreover, chemiluminescence measurements evidence that larger amount of superoxide is photoproduced
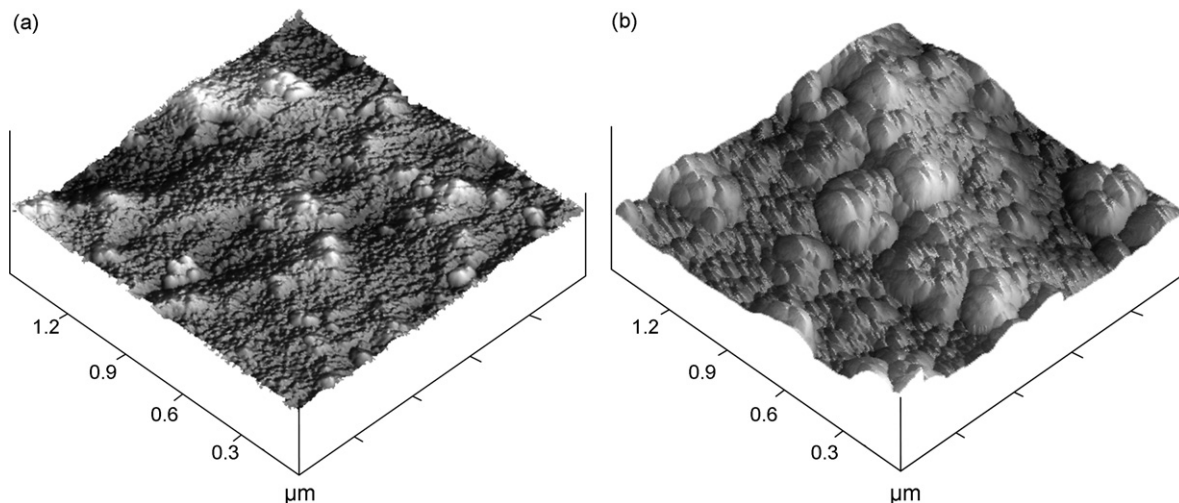


Fig. 5. AFM surface plots for (a) $TiO_2$ and (b) $TiO_2$:$In_2O_3$ (4:1) films.

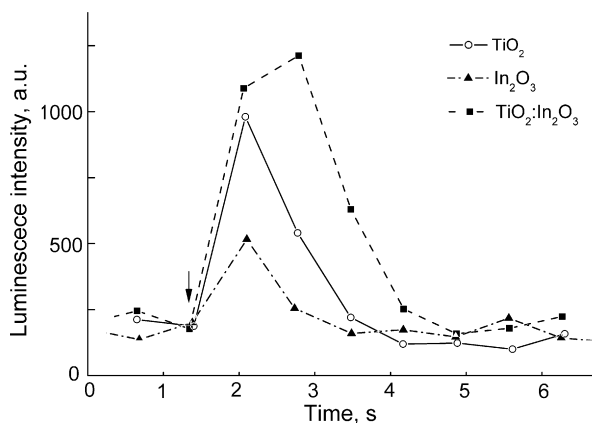Fig. 6. Time profiles of the chemiluminescence intensity for $TiO_2$, $In_2O_3$ and $TiO_2$:$In_2O_3$ (4:1) films. The arrow indicates the moment corresponding to the insertion of the luminol solution into the cell.
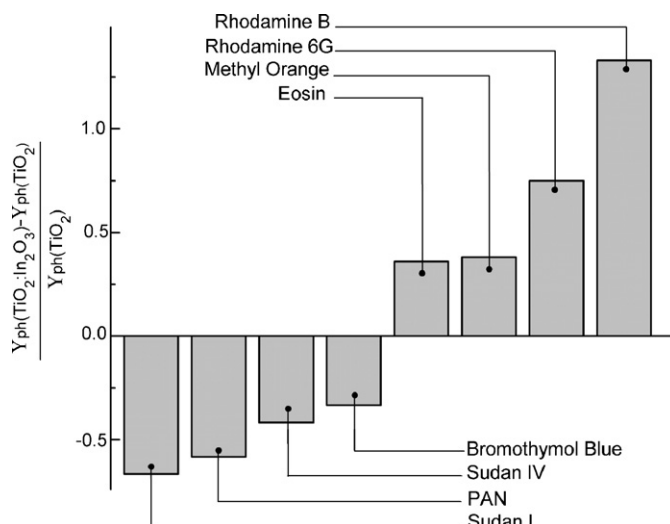


Fig. 7. Difference in the photocatalytic activity of $TiO_2$ and $TiO_2$:$In_2O_3$ (4:1) films towards the photodegradation of probing dyes of different polarity.

under UV illumination at the surface of $TiO_2$:$In_2O_3$ film than at the surface of $TiO_2$ and $In_2O_3$ films (Fig. 6). Together with hydroxyl radicals, superoxide can also be involved in the degradation of adsorbed probing dyes.

Whereas a pronounced correlation exists between hydrophilic properties of $TiO_2$:$In_2O_3$ composite films and their activity towards photodegradation of adsorbed Rhodamine 6G, the rate of Sudan I photodegradation shows only a minor dependence on the hydrophilicity of the photocatalyst surface and the humidity of ambient air. This permits a suggestion that in the letter case the catalytic photolysis occurs predominantly *via* a direct attack of photoholes on dye molecules, followed by interaction of resultant dye cation radicals with molecular oxygen and/or $O_2^-$ to form peroxilated intermediates [32] capable of further rapid degradation in the direction of the mineralization. Taking into account that the surface of titania is composed of a nanoscale distribution of hydrophilic and oleophilic domains [7], it is likely that Rhodamine 6G and Sudan I appear to be adsorbed at different sites: polar Rhodamine 6G at the hydrophilic regions with high concentration of hydroxyl groups and adsorbed water, whereas Sudan I, exhibiting low polarity, concentrates at the oleophilic regions which are free from hydroxyl groups. By contrast, such amphiphilic properties are less pronounced for $In_2O_3$ exhibiting much higher hydrophilicity as compared to $TiO_2$ (the water contact angle is of 49° for $In_2O_3$ and 72° for $TiO_2$). For the direct hole-trapping mechanism, the photocatalytic activity is not dependent on the amount of the adsorbed water, being thus governed by the efficiency of the generation and the separation of electron–hole pairs. In favor of the hypothesis that adsorption of polar and non-polar organics is accompanied with segregation effects counts the fact that photodegradation of water-soluble polar arylmethane and azo dyes (Rhodamine 6G, Rhodamine B, Eosin, Methyl Orange) at the surface of $TiO_2$:$In_2O_3$ composite occurs much more efficient as compared to bare $TiO_2$ and, *vice versa*, water-insoluble dyes, both arylmethane and azo ones, exhibiting low polarity (Bromothymol Blue, Sudan I, Sudan IV, PAN) degrade more efficiently at the illuminated $TiO_2$ surface than at the surface of $TiO_2$:$In_2O_3$ film (Fig. 7).

The ability of $TiO_2$ to generate higher anodic photocurrent as compared to $In_2O_3$ (Fig. 3) points to higher photohole yield in the case of $TiO_2$ that agrees with the enhanced activity exhibited by $TiO_2$ films in the reaction of Sudan I photodegradation. On the other hand, it is seen from the photocurrent versus $In_2O_3$ content dependence (Fig. 3) that low photocurrent values are observed for nanocomposite films showing the high photoactivity towards Rhodamine 6G photodegradation. It should be, however, noted that due to the fact that the conduction band edge of $In_2O_3$ lies by 0.65 eV below the conduction band edge of $TiO_2$ [20], the favorable conditions are created in $TiO_2$:$In_2O_3$ film for separation of charge carriers at $TiO_2$/$In_2O_3$ junctions, with the photoelectrons generated in $TiO_2$ being collected in the $In_2O_3$ phase. This photoelectron trapping effect manifests itself also in a pronounced quenching of $TiO_2$ photoluminescence observed for $TiO_2$:$In_2O_3$ composite (spectra are not shown). When the $In_2O_3$ content is below 60 wt.% (the value corresponding to the formation of percolation cluster of interconnected conductive $In_2O_3$ nanoparticles [21]), the trapping of photoelectrons in $In_2O_3$ hampers the transport of major charge carriers in $TiO_2$:$In_2O_3$ film resulting in the photocurrent drop (Fig. 3). This trapping, however, does not affect adversary the photocatalytic processes responsible for the degradation of probing dye at the surface of composite film. The fact that the photodegradation of Sudan I appears to be much more efficient at titania films as compared to the composite ones suggests that the effects of the lateral separation of photogenerated charge carriers at the microheterojunctions at the surface of composite film are of minor importance as compared to the effects which are due to the adsorption of probing dyes at different sites at the photocatalyst surface.

The present study shows that the photocatalytic activity of $TiO_2$:$In_2O_3$ nanocomposite coatings towards photodestruction of adsorbed polar organics in contact with air is determined to large extent by the photocatalyst hydrophilicity which is dependent on the composition and morphology of the nanocomposite film. On the other hand, the photoactivity of these coatings towards degradation of non-polar organics exhibits a decrease

with the photocatalyst hydrophylicity, with the photodegradation occurring most rapidly at the surface of $TiO_2$ film.

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