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Determination of catalytic properties of TiO_2 coatings using aqueous solution of coumarin: Standardization efforts

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ABSTRACT

Many types of supported photocatalytic TiO_2 continue to be the subject of extensive development worldwide. Besides industrial production and practical use of the new photocatalytic materials, there is an increasing need for a simple and reliable procedure for characterization of photocatalytic activities of newly developed materials. The aim of our work was to develop a method for the determination of quantum yields of supported photocatalysts by employing an aqueous solution of a model organic compound and different thin TiO_2 films. Additionally, also a newly defined parameter, the so-called mass efficiency, was introduced as an advantageous way of defining the photocatalytic activities. Coumarin (CM) was found to be an appropriate candidate for being a probe molecule when the photocatalytic degradation mainly occurs via the $HO^\bullet$ radical-mediated mechanism. An advantage of using CM is easy determination of highly fluorescent 7-hydroxycoumarin (7OHC). Different TiO_2 films were deposited via sol–gel methods on soda-lime glass slides that were precovered with a thin SiO_2 film, and via the sedimentation process from aqueous suspensions. Aqueous solutions of CM were irradiated using 365 nm radiation in the presence of titania films. Although Degussa P25 films showed approximately four times higher degradation rates compared to the sol–gel processed, its quantum yield was not more than 2.5 times higher. This could be explained by higher absorbance of Degussa P25 films per amount of the catalyst compared to sol–gel films. Since no information on the absorption characteristics of the material per unit of mass of the catalyst is included within the calculation of quantum yield, mass efficiency is suggested for the evaluation of photocatalytic properties of the coatings. It is evident from the present study that it is obligatory to evaluate the photocatalytic efficiencies of different area densities of the same photocatalyst in order to properly characterize the material's efficiency.

1. Introduction

The evaluations of photocatalytic efficiencies of different catalysts are usually presented as the percentage of degradation, degradation rate, or the half-life of a model compound. However, because of different experimental factors, it is difficult to use these data for comparison. Although there are numerous different ways of defining the efficiency of the photocatalyst to degrade an organic molecule, the only absolute parameter is the overall quantum yield ($\Phi_{overall}$) [1]. It is defined as the ratio between the number of molecules undergoing a physical or chemical event in a unit of time (r) and the number of photons absorbed by the reactant within the same unit of time (I_{abs}) (Eq. (1)). In case of photocatalysis, the number of photons absorbed by the reactant corresponds to the number of photons absorbed by the photocatalyst:

$$\Phi_{overall} = \frac{r(\text{mol s}^{-1})}{I_{abs}(\text{einstein s}^{-1})} \quad (1)$$

In case of titanium dioxide, the value of true absorption is difficult to evaluate due to the absorption, transmission and scattering of the semiconductor particles. Additionally, $\Phi_{overall}$ does not only depend on the physical and chemical characteristics of the material, but also on many other parameters, such as the intensity and the wavelength of the irradiation, the amount of the catalyst, the nature and concentration of the organic molecules, the concentration of dissolved molecular oxygen, etc. Concerning the evaluation of the quantum yield, the reported studies in the literature mostly deal

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Abbreviations: 7HOC, 7-hydroxycoumarin; CM, coumarin; Films C, sol–gel produced films with the addition of surfactant in the sol; Films D, sol–gel produced films without the addition of surfactant in the sol; Films P, Degussa P25 films; FLD, fluorescence detector; RSD, relative standard deviation.

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Nomenclature

A	absorption
E	irradiance (mW m^{-2})
E_p	photon irradiance (einstein min^{-1} cm^{-2})
I_{abs}	absorbed photon flow (einstein s^{-1})
r	rate of degradation (formation) (mol s^{-1})
R	reflectance
T	transmittance

Greek letters

ζ	photonic efficiency
ζ_m	mass efficiency (cm^2 g^{-1})
ζ_r	relative photonic efficiency
Φ_p	incident photon flow (einstein s^{-1})
Φ_{365}	quantum yield at 365 nm

with some mechanistic investigations and are not intended to serve as a method of evaluating photocatalytic activities of different TiO_2 materials [2–5]. Photonic efficiency (ζ) [1] is the parameter which could be more easily evaluated and consequently become useful in standardization procedures. It avoids the inherent difficulties encountered in the precise evaluation of the number of photons absorbed by the photocatalyst, the difficulties with utilization of different light sources, as well as different reactor geometries and other unspecified factors by referring all the results to an equivalent experiment carried out under identical conditions for a standard process. ζ describes the number of reactant molecules transformed or product molecules formed, divided by the number of incident photons, measured at a given wavelength, inside the front window of the photocatalytic cell. Next, relative photonic efficiency (ζ_r) as a standard measure for different TiO_2 materials and different organic substrates was established by Serpone [1] and this procedure was proposed also to the Commission on photochemistry under the IUPAC [6,7]. The ζ_r is defined as a rate of disappearance of the substrate divided by the rate of disappearance of a standard molecule and should be therefore related to an acceptable standard process, a standard photocatalyst material and a standard secondary actinometer in the photocatalyzed process [1]. Ultimately, these ζ_r values can be converted into photochemically defined quantum yields, once the standard quantum yield for a given photocatalyst and a given substrate (in their case phenol) has been determined.

Mills and Le Hunte [8] argued that there was no advantage of this methodology compared with the classical measurement of the quantum yields, since the standard quantum yield would vary enormously with different reaction conditions, and the value would have to be determined for each set of specific reaction conditions.

The evaluation of photocatalytic activities of TiO_2 slurries is a far more difficult task than the one concerning TiO_2 films [9]. Despite this and the fact that a large number of supported photocatalysts were prepared in the last years, not many attempts have been made to quantify the activity of immobilized materials in terms of the standardized parameters such as photonic efficiencies. Many different methods can be used to determine the activity of photocatalytic surfaces in aqueous solutions. The photocatalytic destruction of the thiazine dye – methylene blue – is probably the most extensively studied one [10]. It is commonly used as a standard molecule in the demonstration experiments of photocatalysis as it provides an excellent visual representation of the process. It should be pointed out that it is a tricky standard molecule, because it also undergoes simultaneous reduction to a colourless leuco dye, which is not a photocatalytically initiated process [11]. Additionally, the testing methods based on the decolourisation of different dyes are based on the relative comparison of the photoefficiency of the probe to the photoefficiency of the standard under constant conditions, which generates the problem of constant conditions that may differ among laboratories.

Other techniques to determine the activities of photocatalytic surfaces are based on the photo-oxidation of organic films (such as stearic acid deposited on the surfaces) [12] and contact angle changes [13]. The photocatalytic destruction of such solid compounds is of practical interest since it represents a reasonable model system for the type of solid organic films which are often deposited on exterior glass surfaces. Therefore, such treatment is proposed as a standard method for determination of activities of self-cleaning surfaces. Recently, an alternative test based upon the colour change of a dye in water has been presented by Evans et al. [14]. The formulation comprises the redox dye resazurin (a sacrificial electron donor), glycerol and a polymer (hydroxyethyl cellulose), all dissolved in water. Whether wet or dry, upon irradiation of the ink on the photocatalytic surface, the photogenerated holes oxidize the glycerol and the electrons reduce the blue resazurin to the pink resorufin. The test is quick and the comparison of photoactivity using the dye and stearic acid tests indicates a strong correlation. But still, the drawback of the all three methods described is their relativity. They are not absolute methods and a standard photocatalytic surface (i.e. Degussa P25 for slurries) must be evaluated first. Mills et al. proposed as such standard photocatalytic surface [15] commercially available Pilkington Activ^{TM} self-cleaning glass. Although not as active as a P25 TiO_2 film, the vastly superior mechanical stability of Activ^{TM}, along with its highly reproducible activity and widespread commercial availability make it a suitable and necessary substitute for P25 TiO_2. The problem of Activ ^{TM} is its low photocatalytic efficiency in applications such as removing the organic pollutants from the polluted drinking waters, therefore it can be used as a standard material only in self-cleaning applications.

In case of determination of photocatalytic activities of photocatalytic surfaces in aqueous solutions a different method should be proposed. Another, more quantitative and absolute, approach for evaluating the photocatalytic surfaces is based on the measurement of the rate of the hydroxyl radical generation by the oxidation of methanol, 2-propanol etc. Measurements lead to useful results for the comparison of the photoactivity of different materials, independently on the specific degradation mechanism of the selected pollutants. Marugan et al. [16] evaluated the photonic efficiency for the hydroxyl radical generation on several silica-supported TiO_2 photocatalysts. The study has been carried out using methanol as the hydroxyl radical scavenger. Methanol was chosen because previous studies have demonstrated the possibility of using high concentrations of methanol to quantify the complete hydroxyl radical production from the photogenerated holes at the semiconductor surface [17].

The generation of $HO^\bullet$ radicals is quantitatively detected also by using specific fluorescent probes. These are molecules which upon reaction with the substrate generate highly fluorescent products which can be easily detected by the very sensitive fluorescent techniques when compared to absorption measurements. There are a few known fluorescence probes for detection of $HO^\bullet$ radicals, i.e. sodium terephtalate, 1,3-cyclohexanedione, fluorescein, 4-(9-anthroyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl, etc. [18]. Coumarin (CM) is a poorly fluorescent molecule that has been known to form many different products when reacting with hydroxyl radical, among them, the very fluorescent 7-hydroxycoumarin (7OHC) [19]. The reaction of the hydroxylation of CM and the consequent formation of 7OHC is shown in Fig. 1. An advantage of using CM as the probe is that 7OHC fluoresces in the visible spectral range. Newton and Milligan [20] showed in

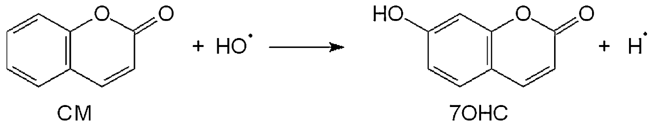

Fig. 1. Chemical structures of CM and 7OHC and reaction representing hydroxylation of CM forming fluorescent 7OHC.

their radiolysis experiments that the yield of generation of 7OHC is around 4.7% per generated HO•. CM has already been used as a probe molecule for the detection of active oxidative species in TiO_2 photocatalysis [21], but the quantitative evaluation of hydroxyl radical production has not been yet performed.

According to the lack of reliable evaluation methodology of the catalyst in the liquid phase, we decided, in the present work, to develop a method for the evaluation of quantum yields and mass efficiencies for photocatalytic surfaces, which is based on the formation rates of 7OHC (HO• radicals) by the fluorescence detection in a liquid–solid system. The sol–gel derived TiO_2 films prepared and characterized elsewhere [22] were compared with standard Degussa P25 films.

2. Experimental

2.1. Chemicals, preparation of sols and deposition of photocatalytic films

The chemicals in this study were used as purchased: methanol (HPLC grade), tetraethoxysilane, concentrated sulphuric(VI) acid, 65% nitric(V) acid and acetic acid from J. T. Baker, titanium(IV) isopropoxide ($Ti(OiPr)_4$), CM and 2-methoxyethanol from Fluka, Pluronic F-127 from Sigma, 7OHC and 1,10-phenanthroline from Aldrich, 96% ethanol, ferrous sulphate(VI), sodium acetate and ethyl acetoacetate (EAA) from Riedel-de Haen. All aqueous solutions of the organic pollutants were prepared by using highly pure water ($18\,M\Omega\,cm^{-1}$) from the NANOpure system (Barnstead).

Transparent TiO_2-anatase films deposited on both sides of SiO_2-precoated soda-lime glass slides (25 mm × 70 mm) were produced by sol–gel processing route, already described in detail in our previous publications [22,23]. $Ti(OiPr)_4$ was added to EAA ($n(EAA)/n(Ti(OiPr)_4) = 1$) during constant stirring. The prepared solution was dissolved in 2-methoxyethanol ($n(MeOCH_2CH_2OH)/n(Ti) = 13.6$) after 5 min. The resultant alkoxide solution (sol D) was stirred at room temperature for solvolysis and condensation reactions at least for 3 h. After using, the sol was kept in the refrigerator. It was conditioned at room temperature for at least 1 h before the next use. The procedure for the preparation of the sols with added Pluronic F-127 was basically the same as described above. The only difference was that the triblock copolymer Pluronic F-127 (4.7 g) was dissolved in the sol (35.0 g) after the addition of 2-methoxyethanol (sol C). SiO_2-precovered soda-lime glass slides were used as substrates for the deposition of titania films. They were deposited with a pulling speed of up to $10\,cm\,min^{-1}$ from a TiO_2 sol and similarly heat-treated at 500 °C for 30 min. The thicknesses of the TiO_2 films were increased by repeating the dipping and heat-treatment cycles. The amount of the catalyst on a glass slide was determined by weighing. The names of the TiO_2 samples are composed of two characters: (1) D or C = the symbol of titania sol; (2) 1–9 = number of dipping–heating cycles.

Beside sol–gel derived films, non-transparent Degussa P25 films were also deposited on soda-lime glass slides (dimensions of 25 mm × 70 mm) as it is described in detail in our previous publication [24]. A series of different types of immobilized TiO_2 layers were prepared on SiO_2-precovered soda-lime glass slides by sedimentation from aqueous suspension of TiO_2 P25 ($10\,g\,L^{-1}$) for different times, with additional drying and annealing at 500 °C for 15 min. The amount of the catalyst on the glass slide was determined by weighing. The names of the samples are composed of two characters: (1) P denotes Degussa P25; (2) numbers from 1 to 7 denote progressive amounts of TiO_2.

TiO_2 was physically removed from one side of the substrate by applying zinc powder and conc. hydrochloric acid. The substrate was then cut to the appropriate dimensions (9.5 mm × 40 mm) to fit into the fluorescence cell. The area densities of all deposited TiO_2 are collected in Table 1. The area densities were calculated as a ratio between the amount of the deposited TiO_2 and the covered area of the substrate.

Nitrogen sorption measurements were performed on a Micromeritics accelerated surface and porosity analyzer (ASAP 2020). The "film powder" samples were used for this purpose instead of immobilized films, because we were not able to characterize the surface area of TiO_2 on immobilized samples. To prepare "film powders" the TiO_2 was deposited onto a glass substrate as a thin layer. After 30 min of drying under atmospheric conditions the film was mechanically scratched from the substrate. Many glass plates were covered by the film, in order to get sufficient amount of the powder sample (>100 mg) which was then calcined for 1 h at 500 °C.

2.2. Photocatalytic degradation of CM

TiO_2 film, deposited on SiO_2-precoated soda-lime glass (40 mm × 9.5 mm) was at first activated by 1 h irradiation in water with the help of black tubes (polychromatic radiation with the maximum at 365 nm). After pretreatment, the TiO_2 film was positioned on the back wall of 4 mL standard fluorescence quartz cell (10 mm × 10 mm) containing 3.6 mL of aqueous solution of CM (5.0×10^{-4} M). The solution was then irradiated by a steady-state 365 nm monochromatic radiation, obtained from a 1600 W Xe lamp in conjunction with a high-intensity monochromator (Schoeffel). The half-width was about 10 nm. The solution was also continuously stirred and purged with O_2 during irradiation. The photon flow (Φ_p) in the cell was evaluated by potassium ferrioxalate actinometry [25], and determined to be 1.1×10^{-8} einstein s^{-1}. This value gives the irradiance (E) of the photocatalyst, which is $1.0\,mW\,cm^{-2}$ if the energy of the photons with the wavelengths of 365 nm are used in calculations. The temperature was kept constant at 20 °C during the experiment. The samples (0.4 mL) were taken from the cell at different times during the irradiation for analysis with HPLC. The samples were analyzed without additional filtration, extraction or centrifugation. The photodegradation experiments lasted between 30 and 150 min. At least two runs with each film were performed to evaluate the reproducibility of the measurements. The cell and the film were washed with deionised water before starting a new experiment.

2.3. Analytical procedures

The HPLC analyses of CM and 7OHC were made on a Spectra-Physics chromatograph, coupled with a UV (Spectra-Physics SP8450) and fluorescence detector (Shimadzu RF-530). The chromatographic separations were run on the Eclipse XDB-C8 column (Zorbax, 150 mm × 4.6 mm, 3.5 μm) using a 68:32 isocratic mixture of aqueous acetic acid (1%) and methanol as the mobile phase. The flow rate was $1.0\,mL\,min^{-1}$. The injection volume was 50 μL. The elution of CM was monitored by a UV detector at 275 nm, while 7OHC was monitored by a fluorescence detector (FLD) with the excitation wavelength at 332 nm and emission wavelength positioned at 456 nm. The calibration curves were performed for the aqueous solutions of CM and 7OHC.

Table 1

Different parameters of TiO_2 films, used in the calculations of quantum yields and mass efficiencies of the catalysts.

Film	Area density ($\mu g\ cm^{-2}$)	A at 365 nm (%)	CM degradation: $r = -dn/dt$ ($\times 10^{-9}$ mol min^{-1})	RSD (%)	Φ_{365} (CM degradation) (%)	7OHC formation: $r = dn/dt$ ($\times 10^{-11}$ mol min^{-1})	RSD (%)	Φ_{365} (7OHC formation) (%)	Mass efficiency ($cm^2\ g^{-1}$)
P1	60	19	3.3	6.5	2.7	10.3	0.4	0.08	2.7
P2	210	44	5.6	0.7	2.0	21.7	1.2	0.08	1.6
P3	250	46	5.8	4.0	1.9	21.8	2.4	0.07	1.4
P4	471	56	7.4	3.6	2.0	27.7	0.7	0.08	0.92
P5	690	67	9.0	4.1	2.1	35.5	2.2	0.08	0.80
P6	915	72	8.5	3.2	1.8	38.9	3.5	0.08	0.66
P7	1910	68	8.0	1.0	1.8	32.8	0.5	0.07	0.27
D1	29	2.9	0.50	2.8	2.7	1.8	3.1	0.09	0.95
D2	62	7.9	0.72	8.8	1.4	2.4	2.0	0.05	0.61
D3	93	9	0.83	2.5	1.4	2.7	4.9	0.05	0.45
D4	123	11	1.1	5.4	1.5	3.3	4.0	0.05	0.42
D9a[a]	281	22	1.6	8.9	1.1	5.3	6.4	0.04	0.29
D9b[a]	281	22	1.4	4.0	1.0	3.9	7.2	0.03	0.21
C1	62	5.6	0.65	0.6	1.8	2.2	0.3	0.06	0.56
C2	112	12	1.3	10.7	1.6	3.8	3.2	0.05	0.53
C3	191	15	1.8	2.7	1.9	5.1	3.4	0.05	0.42
C4	244	22	2.0	2.1	1.4	6.0	2.9	0.04	0.38
C7a[a]	430	39	2.4	7.7	1.0	7.7	9.3	0.03	0.27
C7b[a]	430	39	1.8	8.0	0.7	5.6	4.0	0.02	0.20

[a] a and b denote two films, prepared under exactly the same experimental conditions from the same sol.

The in situ fluorescence of the irradiated aqueous solution of CM was determined for each irradiated sample using a PerkinElmer MPF-3L instrument with excitation and emission bandwidths both at 4 nm. The excitation wavelength was at 332 nm, the maximum of the emission wavelength was at 456 nm.

2.4. Evaluation of quantum yield of different TiO_2 films

The transmittance (T) and reflectance (R) spectra (300–700 nm spectral range) of clean and calcined TiO_2 films deposited on SiO_2-precoated sodium glass were recorded on UV–vis–NIR spectrophotometer Lambda 950 (PerkinElmer) employing an integration sphere with inner diameter of 150 mm (PELA 1000, PerkinElmer). When measuring T spectra, the sample was inclined 11° from the normal direction of an incoming radiation beam of the spectrometer with the intention to get the optical interference maxima and minima at exactly the same wavelength values as in reflectance spectra. According to Eq. (2), the sum of T and R spectra was subtracted from 1 in order to obtain the real absorption (A) of the investigated TiO_2 film:

$$T + R + A = 1 \tag{2}$$

The rate of absorbed photons by TiO_2 sample was obtained by multiplying the photon flow in the photocatalytic cell with the A at 365 nm. The rate of the degradation of CM (or the rate of formation of 7OHC) was calculated from the HPLC analysis for each separate TiO_2 sample. In some cases, the formation rates of 7OHC were obtained also from the measurements of fluorescence of the irradiated solution. Finally, the quantum yield of each film for the degradation of CM (or formation of 7OHC) at 365 nm was calculated.

3. Results and discussions

Photocatalytic activities of C and D films made via sol–gel route have been recently evaluated by measuring of in situ decolourisation of aqueous solutions of Plasmocorinth B [22]. The photocatalytic activities of better performing films C were compared with standard Degussa P25 films in another study, where degradation of 4-chlorophenol was monitored [24]. Although a lot of information on studied material was obtained with such studies, these measurements were not standardized and therefore they cannot be easily repeated by laboratories worldwide. Therefore, our goal was to find out a simple way, how to evaluate the quantum yield for different (transparent, non-transparent) types of deposited films. For the determination of quantum yields, standard and reproducible conditions are of high importance. Temperature was kept constant at 20 °C and the solution was saturated with O_2 during the irradiation. To avoid problems with mass transfer to the surface of titania, constant stirring was applied to the system. Additionally, the concentration of CM was relatively high (5×10^{-4} M) with the intention to monitor only the degradation of 10% conversion (or even less). These conditions permit to assure that the majority of the formed hydroxyl radicals reacted with the parent molecule and not with the generated products. The irradiation wavelength was set at 365 nm because it is within the UVA region, which is also within the solar spectrum and TiO_2 is selectively excited.

The intrinsic absorption (A) of the TiO_2 films cannot be evaluated directly from the transmittance (T) spectra. In any case (sol–gel prepared films or Degussa films), the reflection on the prepared films must be evaluated and the sum of T and reflectance (R) spectra enables the calculation of the true A of TiO_2 at a given wavelength. Fig. 2A and B presents the measured T and R spectra and the sum of both spectra for P1 film and for C7S film, respectively. The same measurements were also performed for other films and the intrinsic percentages of absorbed radiation at 365 nm for all the studied films are gathered in Table 1. The absorption of the radiation on C and D films linearly increased with the number of layers (and consequently with the amount of the deposited catalyst). The trend was not the same on films P, where the A increased and leveled off. The reason is in the non-transparency of the material, so higher thickness of titania leads to the absorption of the photons only by the upper layers, whereas the reflectance was the same or it was even higher on less transparent films. This was not observed in case of transparent TiO_2 films.

Before the experiments, the films were firstly immersed in water and preactivated by UVA illumination for about 60 min. Within these conditions, such films showed stable and reproducible photocatalytic activities during the next few hours. We did not explore the activation phenomena in detail, but two possible reasons could be outlined. The first is the adsorption of organic and/or inorganic impurities from the atmosphere on the TiO_2 surface, thus decreasing its photocatalytic efficiency by blocking the active sites. The

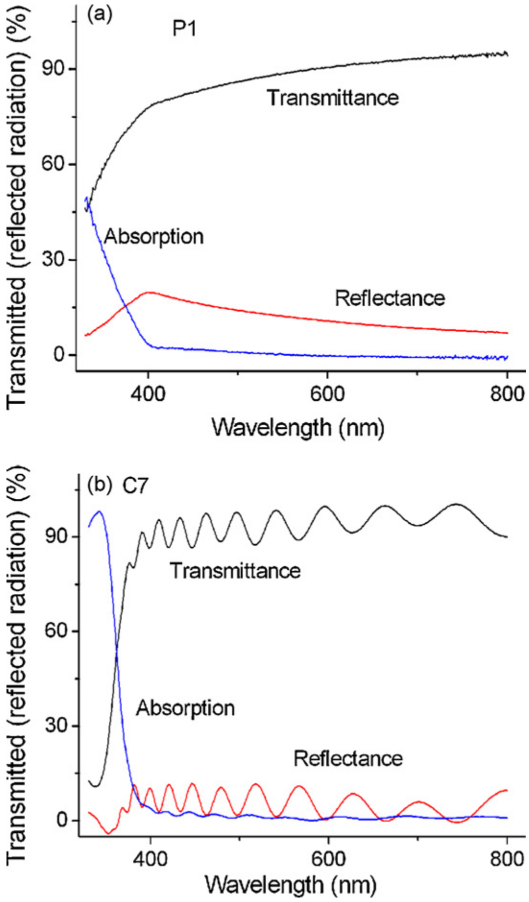

Fig. 2. Optical properties and evaluation of the intrinsic absorption of TiO_2 films: (A) non-transparent P1 film (area density 60 μg cm^{-2}); (B) sol–gel produced C7 film (area density 430 μg cm^{-2}).

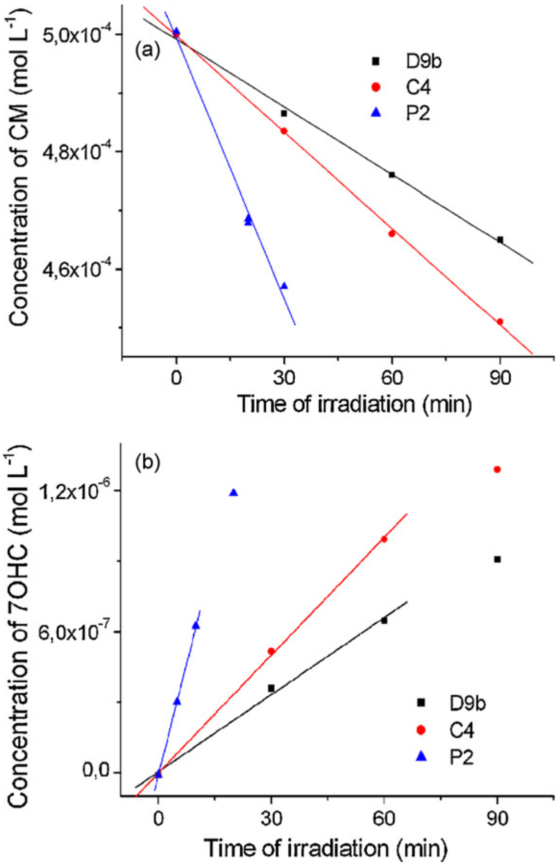

Fig. 3. Photocatalytic experiments with CM (3.6 mL, 5×10^{-4} M), constant stirring and purging with O_2, monochromatic irradiation at 365 nm: (A) degradation of CM, monitored by the HPLC–UV detector at 275 nm; (B) formation of 7OHC, monitored by HPLC-FLD at 456 nm.

second is photo-induced superhydrophilicity. It is a process where surface trapped holes weaken the bond between O and Ti and as a result, at such a weakened site, O_2 is released creating an oxygen vacancy, followed by the dissociative adsorption of water at the site to render it more hydroxylated [26]. Such surface becomes superhydrophilic. The photo-induced superhydrophilicity surface is converted to its original form when stored for long periods in the dark, which explains why the photocatalytic activity of the already used film decreased after a couple of days in darkness.

As it was mentioned before, both the degradation of the parent CM and the formation of 7OHC were monitored with HPLC analysis. Some representative experiments with different types of films are presented in Fig. 3A (degradation) and 3B (formation). The amount of 7OHC increases linearly only until its concentration reaches 10^{-6} M, afterwards the rate of its formation starts to decrease. Therefore, the degradation and formation rates were calculated only from the starting linear region. All the results together with the relative standard deviations (RSD) of degradation and formation rates are summarized in Table 1. According to the literature, many other hydroxycoumarins and also some other primary degradation products are formed in primary reactions of CM with hydroxyl radicals in radiolytic experiments and just a small amount of it is transformed to 7OHC (4.7% in the study conducted by Louit et al. [19]). Different degradation products were also detected in our HPLC–UV analysis and it was supposed that many of these molecules belonged to the group of hydroxycoumarins (Fig. 4A). But using HPLC-FLD it was proven that the only fluorescent species are CM and 7OHC, therefore a detailed analysis and characterization of other degradation products was not performed (Fig. 4A). However, by using a UV detector, the comparison of different photocatalytic materials based on transformation of a molecule, shows that (1) the ratio between degraded CM and formed 7OHC is constant for different materials and also that (2) the ratio between 7OHC and all other degradation products is constant for different types of TiO_2. The first condition is achieved for all studied samples, what is evident from Fig. 4B, where a good correlation between the amount of the degraded CM and the amount of formed 7OHC is presented.

The second condition, i.e. the ratio between the quantity of formed 7OHC and the quantity of other degradation products was also checked for different TiO_2 samples. The peak heights of three not characterized but detected products (peaks A, B and C from HPLC–UV chromatogram on Fig. 4A) were compared with the peak heights of 7OHC from the same chromatograms. The peak area ratios for the initial steps of CM degradation (wavelength of detection was 275 nm) were constant for all used samples and the obtained values are: 7OHC/A = 1.3 (±0.1); 7OHC/B = 1.4 (±0.1); 7OHC/C = 1.5 (±0.1). Using different HPLC conditions and different methods of detection also other degradation products could be clearly detected and the ratios between their formation and the formation of 7OHC could be obtained. This and the validity of obtained ratios also for other types of TiO_2 samples is a goal of our future work.

The error (RSD values) connected with measuring the fluorescence is smaller than in case of measuring the degradation of CM. An additional simplification of the method represents the use of the spectrofluorimeter instead HPLC-FLD system to evaluate

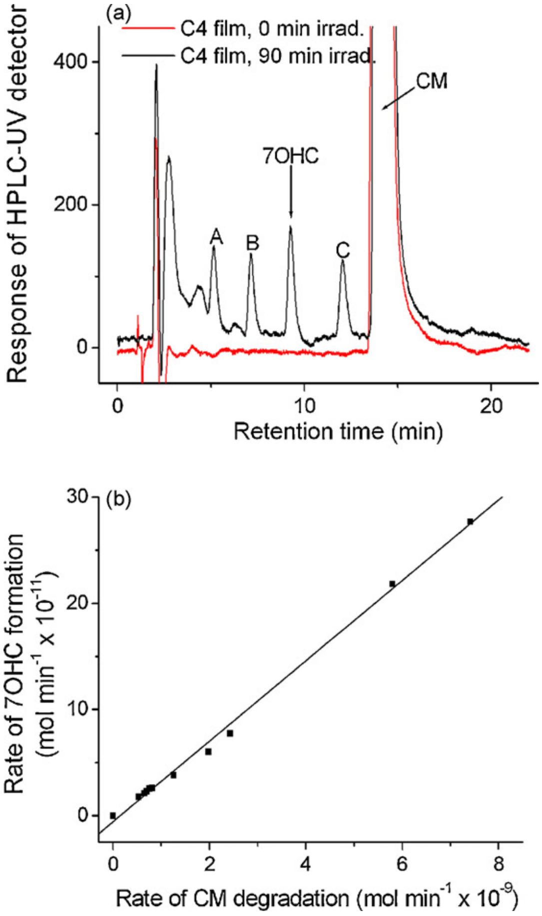

Fig. 4. (A) HPLC–UV chromatograms of CM solution before and after 90 min of irradiation; wavelength of detection 275 nm; (B) A correlation between the formation rates of 7OHC, obtained from HPLC-FLD, and degradation rates of CM, obtained from HPLC–UV analyses.

the formation rate of 7OHC. The results obtained with films P confirmed the advantage of such type of measurement (Fig. 5), because the values are readily obtained with the spectrofluorimeter and they completely correlate with the concentrations of 7OHC, obtained with HPLC-FLD. We believe that the in situ measuring of fluorescence could also enable fast determination and comparison of activities of suspended photocatalysts, because the fluorescence is theoretically not affected by suspended catalyst. The time-consuming separation of the powder is avoided in such case.

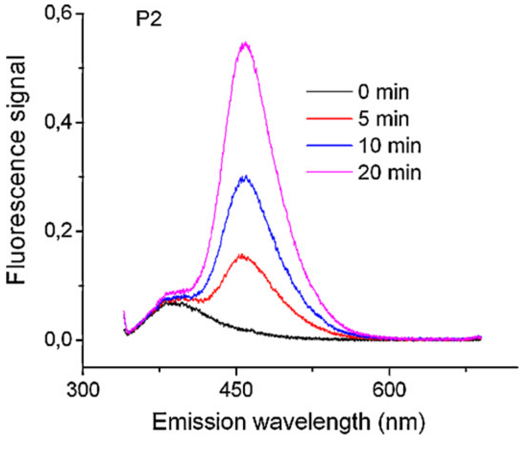

Fig. 5. Fluorescence measurements (spectrofluorimeter) of the irradiated solution of CM (3.6 mL, 5×10^{-4} M); P2 film (area density 210 μg cm^{-2}). Excitation wavelength was 332 nm.

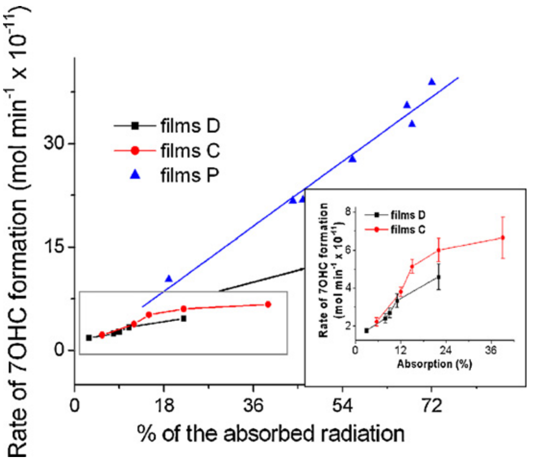

Fig. 6. Correlation between formation rates of 7OHC and the absorption of radiation (in %) at 365 nm by the TiO_2 films. Experimental conditions are identical to those in Fig. 3.

Films P are much more photocatalytically active compared to the sol–gel films with the same amount of titania. For example, comparing the rate of formation of 7OHC with two films with the same area density of titania, the rate of formation with P1 is 1.03×10^{-10} mol min^{-1}, on the other hand the rate of formation on D2 is 2.4×10^{-11} mol min^{-1}, which is approximately 4.2 times slower. Fig. 6 shows the correlation between the formation rates and the absorbed radiation by the titania films for non-transparent P and transparent C and D films. There is a linear dependence when studying this effect on non-transparent films indicating that percentage of recombined photogenerated electrons and holes is the same regardless the amount of the catalyst. The shadowed TiO_2 particles in the interior of the films do not absorb the radiation and cannot participate in the photocatalytic reactions.

In case of transparent films, the situation appears to be more complicated. As it was already explained, the absorption of radiation by transparent titania films increased linearly with the number of layers, e.g., with the amount of titania. Additionally, C and D films have almost the same *A* at 365 nm per amount of the catalyst independently of the number of layers (Table 1). It was supposed that the amount of crystalline anatase phase per amount of the catalyst was similar for both types of films. It seemed that the added surfactant in the preparation of films C did not significantly alter the crystallization of anatase phase. A more pronounced effect of the added surfactant was an increase of BET surface area of titania films. Films C have half lower macroscopic density [22] and “film powders” prepared from films C have a 14 times higher BET surface area compared to similarly prepared “film powders” from sol D (75 m^2 g^{-1} for films C and 5.5 m^2 g^{-1} for films D). According to the described features of prepared sol–gel films, the influence of the surfactant on the photocatalytic activity toward CM was evaluated. If the surface area had the influence on photocatalytic properties, the degradation rates of CM per unit of absorbed radiation at 365 nm would differ for C and D films. However, the degradation rates are comparable for the first four deposited layers (inset in Fig. 6). This is consistent with the fact that the surface area variations do not have an important impact on the photocatalytic activity of the material towards such kinds of molecules [27]. For other types of molecules, such as chloroacetic acids, the main photocatalytic mechanism is the one that requires direct contact between the pollutant and TiO_2, because TiO_2 holes are more efficient oxidants than

$HO^{\bullet}$ radicals. For such organic molecules, changing the surface area of the material has a large effect on degradation rates [27]. Due to different photocatalytic mechanisms towards the degradation of different organic molecules in water, a single compound could not be used as a standard probe for determination of photocatalytic activity of the studied material. According to the described results, CM is an acceptable candidate for being a probe molecule for the organic aqueous pollutants in case of which the photocatalytic degradation mainly occurs via a $HO^{\bullet}$ radical-mediated mechanism. This also makes the proposed method unsuitable for the determination of self-cleaning performances of the material, because in gas–solid photocatalytic systems the surface area has much higher influence than in liquid–solid systems.

With an increasing number of layers (C and D) from 4 to 9, the degradation rates no longer show linear dependence with the absorption properties. Despite the fact that at least the “film powder” sample from the sol C shows high porosity and that the macroscopic density of films C indirectly confirms the porosity of films themselves, the deposition of more than five layers increases the film’s thickness to such an extent (for example, five-layered film C is already approximately 1.4 μm thick [22]) that (1) the bottom TiO_2 layers are not in the contact with the CM solution; or (2) the diffusion of the CM solution into the interior of the film is too slow. The situation is even more distinctive in case of nonporous and denser films D. Because of the rapid recombination, the photogenerated holes and electrons from the bottom of the films could not reach the solid–liquid titania interface. Therefore, the photocatalytic activity cannot correlate indefinitely with the film thickness. Based on this, the thick C films (more than four layers) show higher rates compared to the thick D films (more than six layers) with the same amount of the catalyst, e.g., with the same absorption properties. Fig. 6 confirms the difference between both types of thick films, if the average rates are taken into account. Unfortunately, when depositing more than four layers, the reproducibility was lost. For instance, two D9 films (or C7) prepared under identical conditions, show formation rates which differ one from another for 15% in case of D9 (16% in case of C7).

The quantum yields for degradation of CM (and for formation of 7OHC) were calculated according to

$$\Phi_{365}(\mathrm{CM}) = \frac{-r_{\mathrm{CM}}}{I_{\mathrm{abs}}} = \frac{-r_{\mathrm{CM}}}{A\Phi_{\mathrm{p}}} \left(\Phi_{365}(7\mathrm{OHC}) = \frac{r_{7\mathrm{OHC}}}{I_{\mathrm{abs}}} = \frac{r_{7\mathrm{OHC}}}{A\Phi_{\mathrm{p}}}\right) \qquad (3)$$

where Φ_{365} is the quantum yield at 365 nm, $-r_{\mathrm{CM}}$ is number of degraded CM molecules per unit of time, $r_{7\mathrm{OHC}}$ is the number of formed 7OHC molecules per unit of time and I_{abs} is the absorbed photon flow at 365 nm. $\Phi_{\mathrm{p}}^{\mathrm{abs}}$ (mol s^{-1}) is calculated by multiplying the total photon flow (Φ_{p}) in the cuvette and the A of TiO_2 film. The results are presented in Table 1. The correlation between the quantum yields of different films and the amount of irradiated catalyst are shown in Fig. 7. Again, there is a very evident correlation between the Φ_{365}’s of CM degradation (Fig. 7A) and of 7OHC formation (Fig. 7B). During the first steps of CM degradation, approximately 3% of fluorescent 7OHC molecules were formed, what is in agreement with the literature data (4.7 molecules of formed 7OHC per 100 generated $HO^{\bullet}$ radicals [20]).

It should be pointed out that due to the reasons described above, the quantum yield values cannot be compared with the results obtained from the literature. According to the literature, it could be said that the values between 1% and 10% were expected [1], therefore the obtained values seem reasonable. Surprisingly, the differences in Φ_{365} between films P and films C and D are smaller than expected. According to the fact that films P showed approximately four times higher degradation rates when the same amount of titania is studied, also the four times higher Φ_{365} was expected. But Fig. 7 shows that the Degussa P25 has only twice higher Φ_{365} (in the range of the titania amount between 60 and 300 μg cm^{-2}) when the area density of TiO_2 between compared samples is similar. The phenomena could be explained by higher absorption characteristics of films P per amount of the catalyst, which could be the consequence of its more crystalline structure (a higher amount of anatase per amount of TiO_2) compared to the prepared sol–gel films. The second obvious observation is that in all three cases the decrease of quantum yield is noticed with the increase of the film thickness. This slope is much steeper in the case of films C and D than in case of films P. The higher the thickness, the more pronounced is the recombination of holes and electrons, before they could be trapped by the organic substrate. In case of films P, the decrease is not distinctive, because of their non-transparency. On the other hand, the decrease is steeper in the case of both denser, transparent films, which is also in accordance with the observations in Fig. 6.

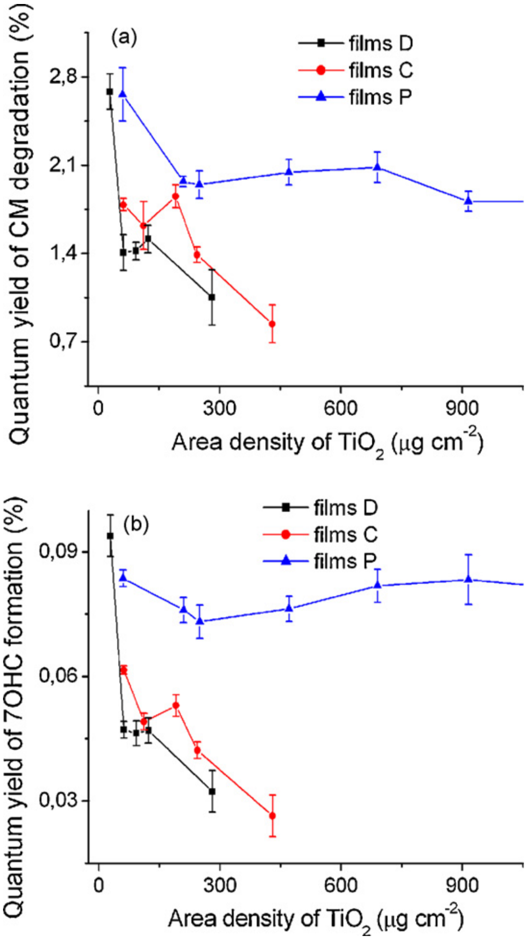

Fig. 7. Calculated Φ_{365} for (A) degradation of CM and (B) formation of 7OHC. Experimental conditions are identical to those in Fig. 3.

According to the presented results it could also be concluded that the evaluation of the quantum yield is not the only relevant quantity for standardization of photocatalytic activities of surfaces. The main problem is that no information on the absorption characteristics of the material per amount of the catalyst is included in the calculation. But the information which material is better per unit of mass is a prerequisite for industrial applications. Less material with the same efficiency leads to lower costs and therefore to a cheaper product. Since the determination of quantum yield does not give such information, we suggest a more appropriate parameter for the determination of photocatalytic properties of the photocatalytic

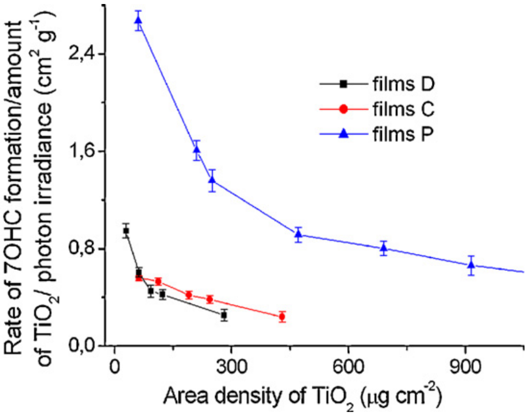

Fig. 8. Mass efficiency, i.e. the rate of formation of 7OHC per amount of catalyst per irradiance. Experimental conditions are identical to those in Fig. 3.

coatings–the rate of degradation (formation) of organic probe per amount of catalyst per photon irradiance:

$$\text{mass efficiency} = \xi_\text{m} = \frac{r/m(\text{TiO}_2)}{E_\text{p}} \quad (4)$$

where r represents the rate of degradation of organic probe or the rate of formation of some degradation product (mol min^{-1}), m represents the amount of irradiated catalyst (g) and E_p represents the photon irradiance, which is defined as the photon flow of monochromatic electromagnetic radiation per unit of irradiated area (einstein min^{-1} cm^{-2}). Because the new parameter is based on the photonic efficiency, it is named as mass efficiency (ζ_m) with the unit cm^2 g^{-1}.

One of the important advantages of determining ζ_m instead of quantum yield is to avoid the determination of absorption characteristics of the studied thin film. Only the number of photons which reach the thin film is needed and it can be obtained with chemical actinometry. To make the whole determination more comfortable, E should be in the range where r and E_p correlate linearly, as the ratio between r and E is then constant for the same photocatalyst. The E value of 25 mW cm^{-2} is the approximate limiting value and the reaction rate r is proportional to $E^{0.5}$ above it [28]. In our experiments, the E was constant and always 1.0 mW cm^{-2}, what is far below the limiting value. The advantage of a newly defined procedure is the use of a standard fluorescent cuvette with a volume 3.6 mL of CM. No complex reactors and complex geometry are necessary. The in situ determination of the fluorescent 7OHC simplifies the whole procedure of the evaluation of degradation rate of CM. The method could be used for transparent as well as for non-transparent samples.

Fig. 8 presents the correlation between the mass efficiency for the formation of 7OHC and the amount of the catalyst. Using a new parameter, the distinction in photocatalytic performance between Degussa P25 and sol–gel produced films is clearer. The increase of the amount of the catalyst leads to lower efficiency of the films. The obvious distinction between Figs. 7 and 8 is the behaviour of the slope of films P, where the high decrease of the efficiency with increasing amount of catalyst is noticed in Fig. 8 (but not in Fig. 7). This is an advantage of presenting a new parameter compared to presenting quantum yields, because the optimal amount of the deposited catalyst per unit of area could be more easily defined. One of the most important conclusions of the presented work is that when evaluating the photocatalytic property of a new material, it is of great interest to evaluate the photocatalytic efficiencies of different area densities of the same photocatalyst in order to obtain the whole picture of the process.

4. Conclusions

The proposed method for the evaluation of photocatalytic activity based on the measuring of the fluorescence of 7OHC seems to be simple and relevant. CM is an acceptable candidate for being a probe molecule for those organic aqueous pollutants, where the photocatalytic degradation occurs via HO$^\bullet$ radical-mediated mechanism. Although Degussa P25 films showed approximately four times higher degradation rates compared to sol–gel processed films with the same amount of the catalyst, the quantum yield of Degussa P25 was only two to three times higher. The phenomena could be explained by the higher absorbance of films P per amount of the catalyst, which could be the consequence of its more crystalline structure (higher amount of anatase per amount of TiO$_2$) compared to the prepared sol–gel films. Consequently, the disadvantage of calculating the quantum yield is that no information on the absorption characteristics of the material per unit of mass of the catalyst is included in the calculation. Therefore, a newly proposed parameter for evaluation of photocatalytic activities of the coatings (mass efficiency) is proposed, which is defined as the rate of degradation (formation) of organic probe per amount of catalyst per photon irradiance. Our future intentions are also to investigate the possibility of determining the photocatalytic activities of self-cleaning surfaces using the degradation of CM molecules deposited over TiO$_2$ surface as solid films.

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