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Photodegradation of dyes in aqueous solutions catalyzed by highly efficient nanocrystalline titania films

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Abstract

Thin nanocrystalline titanium dioxide films were deposited on glass rings by the sol-gel method in the presence of ethanol, acetic acid and the non-ionic surfactant Triton X-100. Nanocrystallites are formed due to surfactant self-organization that acts as a template. These films have high active surface area and are very efficient for the photodegradation of dyes in aqueous solutions. In addition, the catalyst can be easily recovered and can be repeatedly used without loss of efficiency. Three dyes were used: Basic Blue 41, Acid Orange 7, and Crystal Violet. Decoloration of solutions of Basic Blue is much faster than those of the other two dyes. A very low load of catalyst, i.e. 120 mg l^{-1}, is capable of bleaching dilute solutions in only a few hours by shining black light of 0.7 mW cm^{-2}. An inexpensive and simple reactor of cylindrical symmetry is described which employs a 4 W black-light tube as light source.

1. Introduction

TiO_2 is an efficient photocatalyst for organic compound photodegradation both on aerated surfaces and in aqueous suspensions. In the present work we have studied photodegradation of a few chosen dyes in aqueous solutions by using a titania catalyst that can be easily recovered; it is efficient, it can be reused without loss in efficiency and can be sensitized by employing inexpensive installations. Thus the catalyst was in the form of thin nanocrystalline titania films, deposited on glass rings by using a sol-gel method and appropriate surfactant templates. Titania immobilized on solid substrates so as to be easily recovered after photodegradation has been reported previously [1–6]. The originality of the present method lies with an optimal combination of reactor design, use of black light radiation and employment of highly efficient nanocrystalline titania films.

Synthesis of nanocrystalline titania can be routinely carried out by the sol-gel method and by employing appropriate templating techniques. Transparent nanocrystalline titania has been presently deposited as thin film on both inner and outer side of glass rings. Photodegradation of dyes in water was achieved by immersing rings in the dye solution and by shining black light on it (see reactor design below). Titania has been synthesized by solvolysis of $Ti(OiPr)_4$ in the presence of the non-ionic surfactant Triton X-100. Nanocrystallites were made in very small and uniform size by exploiting two main factors: slow water release and surfactant templating [7]. A typical and best known sol-gel process is based on hydrolysis of an alkoxide, according to the reaction

$$\mathrm{Ti{-}OR} + H_2O \rightarrow \mathrm{Ti{-}OH} + \mathrm{ROH} \qquad (1)$$

where R is a short aliphatic group (isopropyl, in our case). The highly reactive Ti–OH thus created can polymerize (Ti–O–Ti) and lead to gelation only if it is kept in suspension. However, hydrolysis is exothermic and violent, particularly, in the case of transition metal alkoxides and usually it leads to undesirable routes, that is, precipitation of particles of large size and uncontrollable shape and, generally, to poor quality gels. It is then necessary to seek for ways to make this process slow and controllable. There are several alternatives [7], however, in recent work titania is synthesized by slow water intake from the environment and from the water attached to the reagents in the precursor sol [7–10]. In this respect, the best way is to choose a controlled water release from the system itself within the precursor sol. One way that leads to controlled water release is to introduce alcohol (EtOH) and an organic acid (for example, acetic acid: AcOH) in the original sol. Ethanol and acetic acid interact according to the esterification reaction

$$\mathrm{EtOH + AcOH \rightarrow EtOAc + H_2O} \quad (2)$$

slowly producing water [11]. Slow water production leads to slow hydrolysis and to formation of hydroxide species, which can polymerize to yield a Ti–O–Ti network. However, nonhydrolytic routes for the production of Ti–O–Ti cannot be excluded. Thus the following possible reactions can also lead to a Ti–O–Ti network [7]:

$$\mathrm{Ti{-}OR + AcOH \rightarrow Ti{-}OAc + ROH} \quad (3)$$

$$\mathrm{ROH + AcOH \rightarrow ROAc + H_2O} \quad (4)$$

$$\mathrm{Ti{-}OAc + ROH \rightarrow ROAc + Ti{-}OH} \quad (5)$$

$$\mathrm{Ti{-}OR + Ti{-}OAc \rightarrow ROAc + Ti{-}O{-}Ti} \quad (6)$$

(In reactions 1 and 3–6, only one of four reacting alkoxy groups is taken into account, for reasons of simplicity). Reactions 1–6 show that the end product of the sol-gel process in the presence of organic acids can be obtained by a variety of chemical routes. Reaction 3, followed by 6 can lead to Ti–O–Ti, while water released through esterification reaction 4 can yield oxide by the hydrolysis route. Furthermore, intermediate Ti–OAc ester or Ti–O–Ti oligomers may create entities which offer polymorphism to the sol-gel evolution. Thus the presence of a non-ionic surfactant, Triton X-100 in our case, which bears a chain of approximately 10 ether groups, plays a crucial role in organizing the structure of the material and in creating well defined and reproducible nanophases. As has been previously shown [9], this group of surfactants participates in the formation and organization of clusters in solution, subsequently, organizing the structure of the ensuing gel.

2. Experimental

All reagents used were purchased from Aldrich. The following protocol was observed to deposit films on glass rings. 20.75 ml EtOH, 3.82 g of the non-ionic surfactant Triton X-100 [polyoxyethylene-(10) isooctylphenyl ether], 3.71 ml AcOH and 1.96 ml $\mathrm{Ti(OiPr)_4}$ were mixed in this order under vigorous stirring and under ambient conditions. After 30 min stirring, a Pyrex glass ring (external diameter 36 mm, height 15 mm, thickness 1.5 mm), previously cleaned in sulfochromic solution, sonicated in ethanol and dried in a stream of N_2, was dipped in the sol and drawn out by hand. After drying in an air stream for a few minutes, the ring with nanocomposite organic-inorganic film was introduced to the oven and calcined at 550 °C for 10 min. Dipping and calcination procedure was repeated one more time. The second time, the ring was left in the oven for 20 min to ensure that all organic residues were completely calcined. The final quantity of titania deposited on inner and outer side of the ring was 3.0 mg per ring. Six such rings were used in the reactor making a glass tube of 9 cm high and a total titania load of 18 mg that makes approximately 0.09 mg $\mathrm{cm^{-2}}$. The volume of the solution in the reactor was 150 ml, giving 120 mg of catalyst per liter of solution. This catalyst load is much lower than used in other work [1–4] and it is a first indication of the efficiency of the employed titania films. In some cases the quantity of the catalyst was increased or decreased by a factor of 2 to study the effect of catalyst content on photodegradation efficiency.

UV–vis absorption measurements were made with a Cary 1E spectrophotometer. To monitor the photodegradation process, sampling of the decoloring solution was made at different time intervals according to the decoloration rate. The reactor design is shown in Figure 1. The whole system was built of Pyrex glass. The lamp was a 4 W commercial black-light tube [12]. The intensity of radiation at the position of the catalyst was around 0.7 mW $\mathrm{cm^{-2}}$ as measured by an Oriel Radiant Power Meter. An air flow produced by a small pump ensured agitation and oxygenation of the solution.

3. Results and discussion

Nanocrystalline titania films can be deposited on solid substrates through sol-gel procedures and by employing templating techniques. A large variety of preparation protocols can be proposed. The resulting nanocrystalline films can extensively vary in structure, depending on the type of the organic substance used for the template

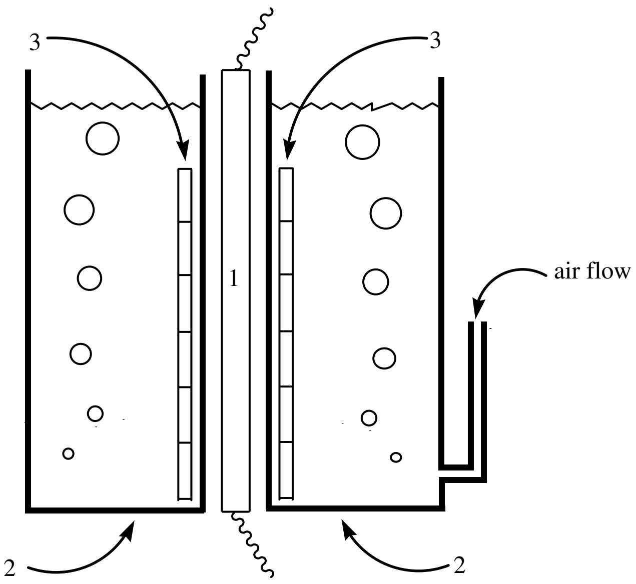


Fig. 1. Cross-sectional view of the reactor: (1) Black-light lamp; (2) Reactor walls; (3) Stack of rings supporting titania.

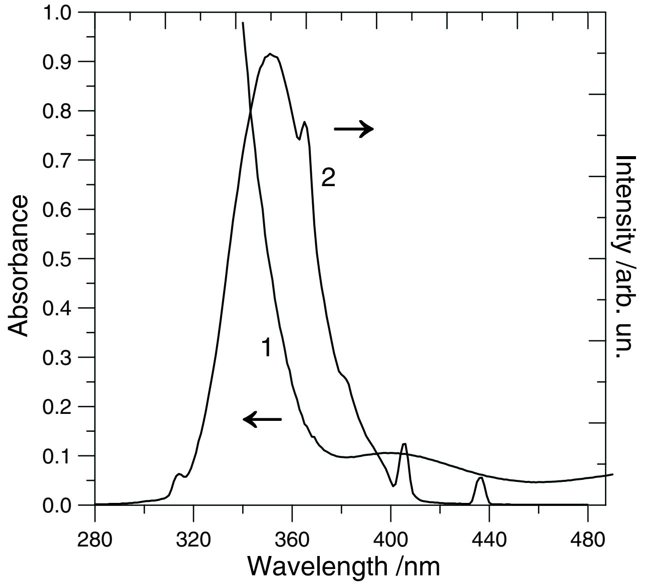


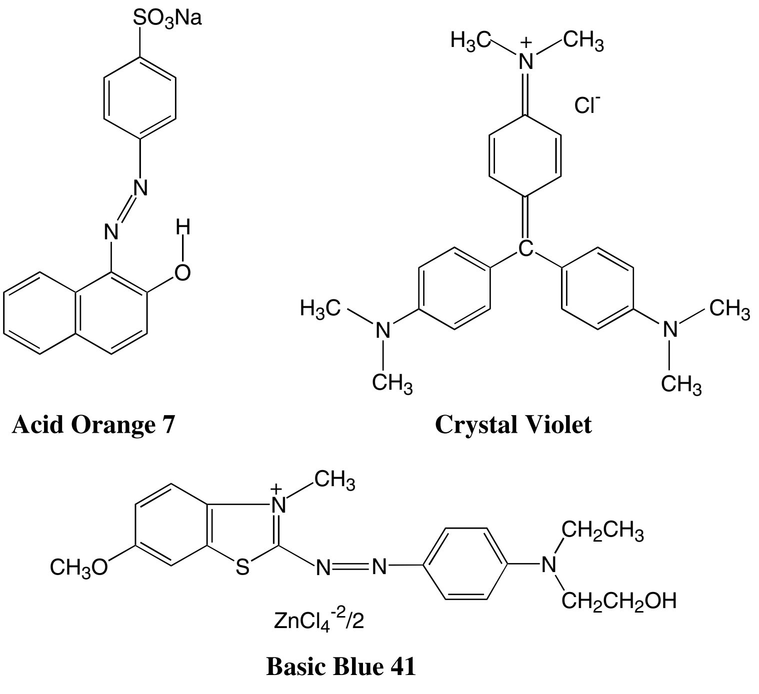
Fig. 2. (1) Absorption spectrum of a titania film; (2) Emission profile of the employed black-light lamp.

[7, 10], the type of its self-organization, the relative ratios of the constituents, the presence of acid catalysts, etc. We have tested samples made in the presence of ethanol and acetic acid in several cases, some of them reported in previous publications, and we have found optimal results by using the synthesis protocol described in the experimental section. Films deposited by this procedure consist of nanoparticles of about 11–15 nm size and 65% anatase –35% rutile crystalline mixture [7]. The film active area was about 110 m^2 g^{-1}, as measured by BET [7]. Nanoparticle size distribution was narrow and film roughness was relatively low. The absorption spectrum of such a titania film, recorded by depositing film on a flat glass slide, is shown in Figure 2. On the same figure, the emission profile of the employed black-light lamp is also presented, revealing a significant overlap between the two spectra. Obviously, direct excitation of titania is obtained by this type of lamp.

Two azo-dye and one triarylmethane dye solution were subjected to photodegradation by using the installation of Figure 1: Basic Blue 41 (BB), Acid Orange 7 (AO7) and Crystal Violet (CV). Their chemical structures are shown in Figure 3. Aqueous solutions of the above dyes were bleached at satisfactory rates by using the reactor of Figure 1. Figure 4 shows the variation of the concentration of the non-degraded dye vs. irradiation time, as monitored by absorption spectrophotometry of the solution. AO7 and CV solutions gave similar decoloration rates while BB solution was decolored much faster. The curves of Figure 4 fit Langmuir–Hinshelwood kinetics [13] very well

$$\ln(C_0/C) = k_{\mathrm{app}}t \tag{7}$$

and gives the apparent first-order reaction rate k_{app}. The corresponding calculated values were 1.9×10^{-2} min^{-1} (BB), 0.59×10^{-2} min^{-1} (AO7) and 0.53×10^{-2} min^{-1} (CV). The bleaching efficiency of BB was almost four times higher than that of AO7 and CV. By looking at the chemical structure of the dyes, the faster decoloration of BB could be expected, since it contains the heteroaromatic ring which is more vulnerable to splitting. For the same catalyst quantity, bleaching was slower when the dye concentration in solution was higher. This is demonstrated by the data of Figure 5. The corresponding k_{app} values were 1.9×10^{-2} min^{-1} in



Acid Orange 7

Crystal Violet

Basic Blue 41

Fig. 3. Chemical structure of the dyes used.

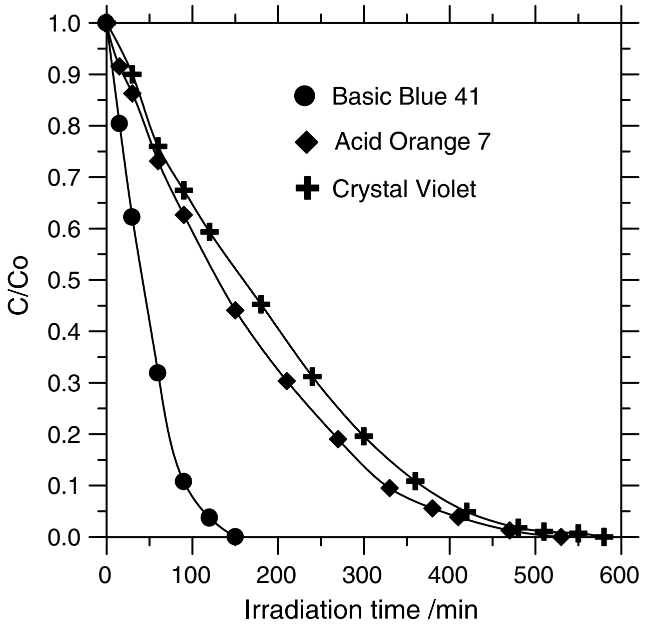


Fig. 4. Variation of the relative concentration of the non-degraded dye vs. irradiation time. Dye concentration 10^{-5} M.

the case of $C_0 = 10^{-5}$ M and 0.42×10^{-2} min^{-1} in the case $C_0 = 5 \times 10^{-5}$ M. If we define a second-order rate constant k, so that $k_{app} = kC_0$, then k is approximately the same in the two cases. This result may be due to two possible and equally important reasons [13]: (1) the quantity of the catalyst is small so the (photo) generated $OH^{\bullet}$ radicals do not suffice to degrade higher quantities of the dye; and (2) the increase in dye concentration causes a screening effect against the exciting radiation, resulting in slowing down degradation rates [13]. Concerning the quantity of catalyst in contact with solution, Figure 6 gives an interesting result. No substantial variation of photodegradation efficiency was observed by changing the quantity of catalyst from 120 to 240 mg l^{-1}, but a significant decrease in photodegradation rate was observed by decreasing the quantity of catalyst by a factor of 2. Thus the proposed quantity, i.e. 120 mg l^{-1}, is optimal under the above conditions, keeping in mind the fact that the present films are transparent and all catalyst is exposed to exciting radiation.

The decoloration of the solutions does not mean that all organic content has been mineralized. Several uncolored intermediates may persist which would necessitate a longer irradiation period to ensure degradation to a satisfactory degree. The absorption spectra of AO7 and CV suffered a continuous decrease in height without variation in spectral structure with irradiation time, as seen in Figure 7. However, in the case of BB changes were observed in the UV part of the spectrum. The same changes were also observed with this dye in acidic pH. The pH of pure aqueous solutions of BB varies between 7.0 and 8.0, depending on dye concentration. If a few drops of HCl are added to the solution, the structure of the absorption spectrum between 190 and 240 nm changes substantially. We may then indirectly conclude that acids may be formed during BB photodegradation. Such a conclusion is in accordance with what is so far known, particularly for AO7, the most studied azo-dye [13–15], where a long series of intermediates is created during photodegradation finally leading to aliphatic acids. Of course, the value of the pH of the above solutions could be monitored during photodegradation and is indeed found to continuously drift to lower values. This is, however, also observed in standing aerated solutions due to carbon dioxide solubilization from the

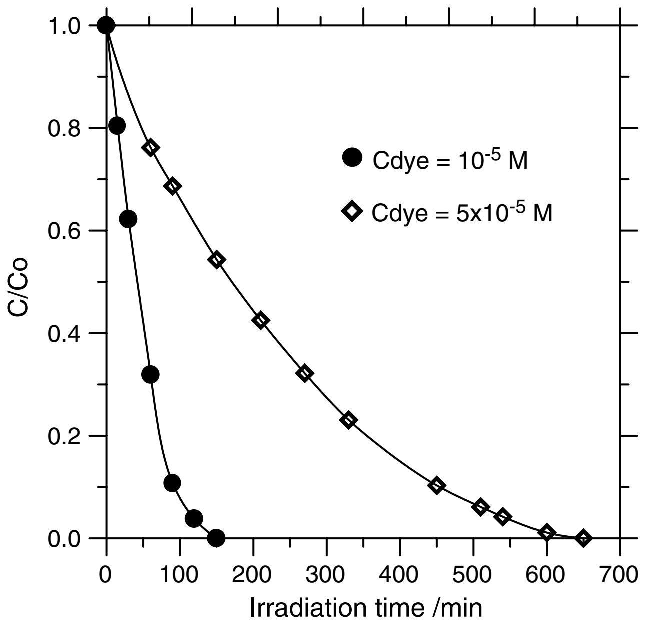


Fig. 5. Variation of the relative concentration of the non-degraded BB vs. irradiation time at two different original dye concentrations.

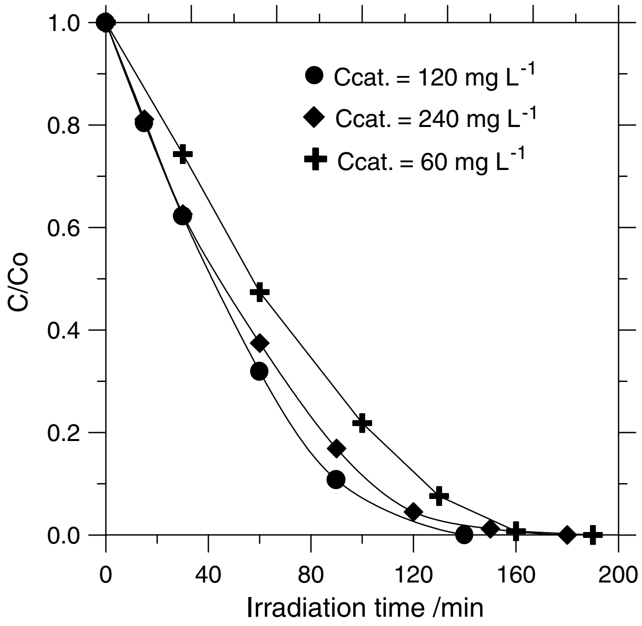


Fig. 6. Variation of the relative concentration of the non-degraded BB vs. irradiation time at three different catalyst loads.

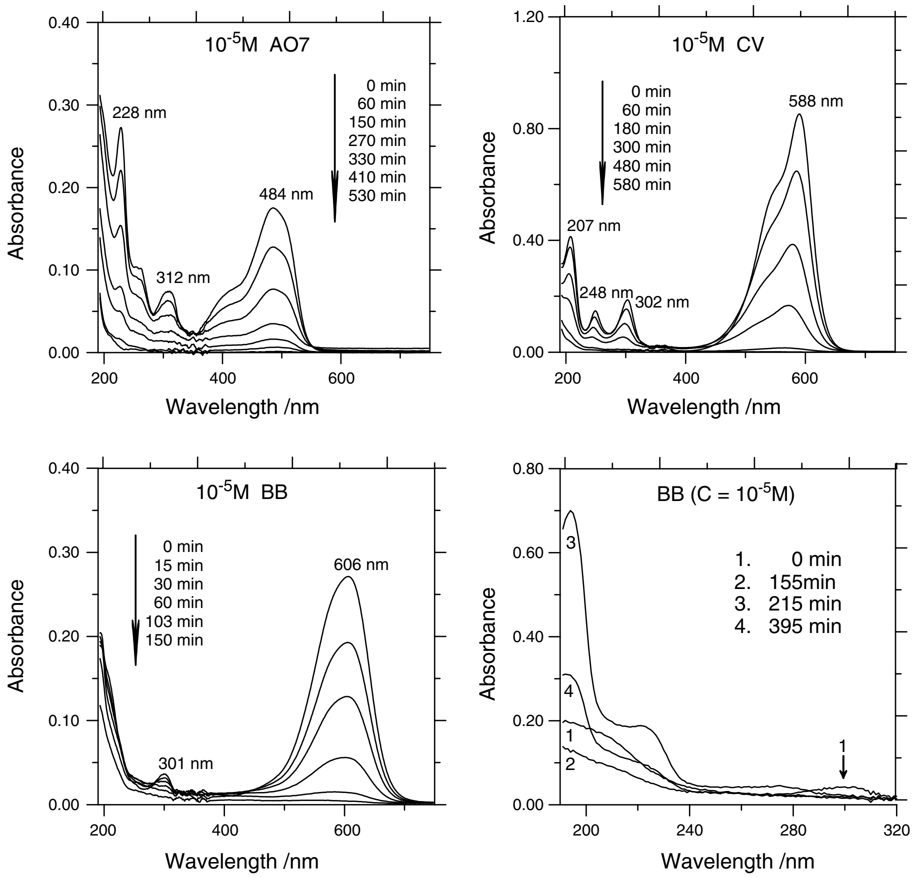


Fig. 7. Variation of the absorbance of 10^{-5} M aqueous solutions of the three dyes vs. irradiation time. The last figure expands the UV absorption spectrum of BB.

ambient, therefore, pH value is not a safe monitor of the photodegradation procedure. pH drift of standing non-illuminated aerated solutions did not affect the absorption spectrum of BB at any wavelength. Apparently, the system is complicated and further studies are needed. In any case, it is safe to the extend illumination period of the samples well beyond decoloration.

It is very hard to make comparisons of the efficiency of the present system with others, since they come in a great variety with respect to the quantity of titania catalyst, the type of catalyst suspension, the quantity of pollutant in solution, the intensity and the wavelength of the employed light source, etc. However, the present system can give clear solutions by using a very small quantity of catalyst and very low illumination intensity in only a few hours while other systems necessitate many hours or several days [4, 14]. One of the important qualities of the present titania films is that they can be regenerated, simply by putting them in the oven at 550 °C for 10 min and can be reused without loss of efficiency. Indeed, the same films were tried for 10 subsequent photodegradation processes and gave exactly the same photodegradation rates as those represented by Figure 4. The proposed system is thus simple and inexpensive and valuable for many practical applications.

4. Conclusions

Thin titania nanocrystalline films deposited on glass supports by the sol-gel method in the presence of Triton X-100 are efficient for the photodegradation of aqueous solutions of BB, AO7, and CV. The reactor is simple and is made of inexpensive commercial materials. It employs a 4 W black-light tube as excitation source. The catalyst can be easily recovered and can be regenerated by simply heating it to get rid of any adsorbed organic residues. UV–Vis spectrophotometry of AO7 and CV fails to detect any intermediates but, in the case of BB, indications point toward acid formation in accordance with previous findings. The proposed reactor can be useful for practical applications where low pollutant load waters can be purified on line.

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References

1. M. Mehrvar, W.A. Anderson and M. Moo Young, *Adv. Env. Res.* **6** (2000) 411.
2. H.F. Lin and K.T. Valsaraj, *J. Hazard. Mat.* **B99** (2003) 203.
3. V. Subramanian, P.V. Kamat and E.E. Wolf, *Ind. Eng. Chem. Res.* **42** (2003) 2131.
4. G. Balasubramanian, D.D. Dionysiou, M.T. Suidan, I. Baudin and J.M. Laine, *Appl. Catal. B: Environ.* **47** (2004) 73.
5. J. Grzechulska and A. Waldemar Morawski, *Appl. Catal. B: Environ.* **46** (2003) 415.
6. M.R. Dhananjeyan, E. Mielczarski, K.R. Thampi, Ph. Buffat, M. Bensimon, A. Kulik, J. Mielczarski and J. Kiwi, *J. Phys. Chem. B* **105** (2001) 12046.
7. P. Bouras, E. Stathatos, P. Lianos and C. Tsakiroglou, *Appl. Catal. B: Environ.* **51** (2004) 275.
8. E. Stathatos, P. Lianos, F. Del Monte, D. Levy and D. Tsiourvas, *Langmuir* **13** (1997) 4295.
9. O. Dag, I. Soten, O. Celic, S. Polarz, N. Coombs and G.A. Ozin, *Adv. Funct. Mater.* **13** (2003) 30.
10. E. Stathatos, P. Lianos and P. Falaras, *Progr. Colloid Polym. Sci.* **118** (2001) 96.
11. M. Ivanda, S. Music, S. Popovic and M. Gotic, *J. Mol. Struct.* **480–481** (1999) 645.
12. T.N. Angelidis, M. Koutlemani and I. Poulios, *Appl. Catal. B: Environ.* **16** (1998) 347.
13. I.K. Konstantinou and T.A. Albanis, *Appl. Catal. B: Environ.* **49** (2004) 1.
14. M. Stylidi, D.I. Kontrides and X.E. Verykios, *Appl. Catal. B: Environ.* **40** (2003) 271.
15. C. Bauer, P. Jacques and A. Kalt, *J. Photochem. Photobiol. A Chem.* **140** (2001) 87.