

# Enhanced activity of silver modified thin-film TiO<sub>2</sub> photocatalysts

P. Falaras,<sup>1,†</sup> I. M. Arabatzis,<sup>1</sup> T. Stergiopoulos,<sup>1</sup> and M. C. Bernard<sup>2</sup>

<sup>1</sup> Institute of Physical Chemistry, NCSR "Demokritos", 153 10 Aghia Paraskevi Attikis, Greece

<sup>2</sup> UPR 15 du CNRS "Physique de Liquides et Électrochimie", Université Pierre et Marie Curie, 75252 Paris, Cedex 05, France

**ABSTRACT.** Novel, composite silver/titania immobilized on glass substrates were prepared, characterized and their photocatalytic activity was evaluated. The undoped original material consists of rough, high surface area nanocrystalline titanium dioxide (TiO<sub>2</sub>) thin films. To increase their efficiency, the TiO<sub>2</sub> films were modified by silver cations deposition and subsequent UV-C irradiation. SEM pictures confirmed the existence of an open porous network of interconnected titania particles on the semiconductor surface. AFM analysis proved the presence of spherical silver particles on the catalyst surface and provided quantitative surface parameters as fractal dimension, surface roughness and mean particle diameter. Spectroreflectometry showed the presence of an increase in optical absorbance attributed to plasmon resonance absorption of the silver clusters. The photocatalytic properties of the surface modified materials were investigated through photodegradation of Methyl Orange. The silver deposition conditions were optimized for maximum photocatalytic efficiency and crucial parameters such as dipping period, UV irradiation time, and concentration of the dipping solution were determined. The optimum silver nitrate concentration of the dipping solution was found to be 10<sup>-3</sup> M. This silver doped photocatalyst decomposes the azo-dye pollutant 3-times faster than the un-doped Degussa P25 TiO<sub>2</sub> film. A concentration increase results in a decrease of the films photocatalytic performance. Strength and reproducibility tests proved that the photocatalytic activity of the silver doped titania was perfectly reproducible.

## 1. INTRODUCTION

Heterogeneous photocatalysis involving titanium dioxide, a well-established advanced oxidation process (AOP), is used for environmental cleaning, especially for water pollutant photodecomposition [1, 2]. Although other AOPs are currently similar or more widely used (e.g. hydrogen peroxide/UV, ozone, ozone/UV, and ozone/hydrogen peroxide) [3], titania photocatalysis technology is currently at the stage of commercialisation [4] and the size of the newly created market in Japan is estimated that may grow to \$5 billion [5]. Recently, the main interest is focused on the development of photocatalytic surfaces by immobilizing the catalyst in the form of a thin film [6, 7]. The immobilization technique enables industrial application benefits eliminating the majority of the problems encountered with slurries such as the need for separation or filtration steps, the problematic use in continuous flow systems and the particle aggregation, especially at high concentrations. However, the efficiency of the immobilized systems is significantly lower than that of the corresponding slurries. To enhance the photocatalytic reaction rate, the addition of noble metals (Au, Pt, Ag, Pd, Ru, Rh) has been performed on TiO<sub>2</sub> surfaces [8-12], thus hindering the photogenerated electron/hole pair recombination and accelerating the photoexcitation and formation of oxidizing species.

In this work we present new immobilized photocatalysts of increased efficiency. They consist of rough high surface area nanocrystalline TiO<sub>2</sub> thin films modified by silver particles deposited via dipping in AgNO<sub>3</sub> and subsequent UV irradiation. Dipping time and irradiation time of the catalyst as well as dipping solution concentration are of vital importance for the performance of the photocatalyst; therefore we focused on the preparation method to optimize the deposition process. The photocatalytic activity of the composite catalyst is investigated through the photodegradation of Methyl Orange, a well-known azo-dye pollutant in the textile industry.

## 2. MATERIALS AND METHODOLOGY

Rough, high surface area titanium dioxide thin films (about 3.5 μm in thickness) were deposited on optically transparent microscopy glass substrates by using the doctor-blade technique [7]. The precursor was a viscous paste consisting of 0.5 g TiO<sub>2</sub> powder (Degussa P25), ground with 1 ml of water containing 0.1 ml acetylacetone. This paste was further diluted by very slow addition of 1.7 ml of water. Finally, 1 drop of Triton X-100 was added and the paste was smeared on a glass substrate immobilized by an adhesive tape strip. After drying at 120 °C for about 10 min, the film was annealed in an oven at 450 °C for 30 min. To elucidate the dopant structure and morphology via AFM analysis

<sup>†</sup>E-mail: papi@chem.demokritos.gr

(visualize the deposited silver particles onto the titanium dioxide surface), very thin (about 300 nm in thickness) and smooth (Surface Roughness Rms = 0.35 nm) titania films were also prepared following a sol-gel procedure. The sol precursor was prepared following controlled hydrolysis and condensation of titanium butoxide in n-butanol [13]. To form the film, a sol drop on the substrate was spin-coated using a Model KW-4A (from PI-KEM, England) spin coating apparatus. After spin coating, the films were transformed to TiO<sub>2</sub> through heating at 100 °C for 15 min and subsequent annealing at 450 °C for 30 min [7].

The silver was photodeposited on both the doctor-blade and sol-gel films using a two-step method. The TiO<sub>2</sub> films were dipped in an aqueous solution of AgNO<sub>3</sub> (from BDH Laboratory supplies-England). After dipping, the films were thoroughly washed with ultra pure water and dried under N<sub>2</sub> stream. Finally, they were irradiated under UV radiation (254 nm).

To evaluate the photocatalytic activity of the silver modified TiO<sub>2</sub> thin film catalysts, the photodegradation of Methyl Orange (4-[[[4-Dimethylamino) phenyl]azo] benzene sulfonic acid sodium salt of analytical grade from Fluka-Switzerland) was investigated. Photocatalysis experiments were carried out in round-bottomed Pyrex glass cells (cutoff wavelength: 320 nm). A laboratory constructed "solarbox" equipped with four F15W/T8 blacklight tubes (Sylvania GTE) provided the UV-A irradiation source. This UV-A source has a maximum emission at 350 nm, Figure 1, and emits 71.7 μW·cm<sup>-2</sup> at a distance of 25 cm (the irradiance of the radiation source (W/cm<sup>2</sup>) was measured using an 28-0925 Ealing Research Radiometer-Photometer operating in conjunction with a 28-0982 silicon detector and a 28-0727 flat response filter). 5 ml of aqueous solution of Methyl Orange (initial concentration 1.9 × 10<sup>-5</sup> M) in the presence of doped TiO<sub>2</sub> thin films (adjusted in surface area at 1 cm<sup>2</sup>) were photolyzed under magnetic

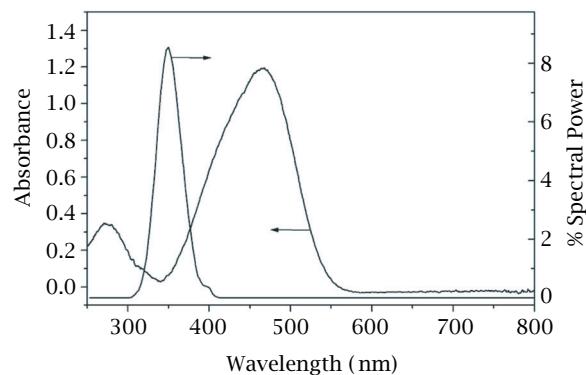


Figure 1. Aqueous Methyl Orange absorbance spectrum. Molar absorbance coefficient  $\epsilon = 25100 \text{ M}^{-1} \text{ cm}^{-1}$  at 466.5 nm. The spectral power distribution of the UV-A irradiation lamps is also given.

stirring. The immobilized films were positioned at the center of the round-bottomed cell.

The characterization of the films optical properties was performed using a Hitachi U-4001 UV-VIS spectrophotometer equipped with an integrating sphere. Surface morphology, roughness and fractality of the silver/titania films were examined with a Digital Instruments Nanoscope III atomic force microscope (AFM), operating in the tapping mode (TM). For the fractal analysis the V423r3 algorithm was used. Detailed surface images were also obtained by means of a scanning electron microscope (SEM) with numerical image acquisition (LEICA S440).

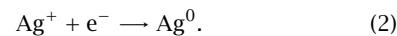
### 3. RESULTS AND DISCUSSION

During the catalyst preparation procedure, titania films are immersed in silver nitrate solution. The pH of the solution drops during immersion as TiO<sub>2</sub> surface protons are replaced by silver cations [14]. Consequently an overall reaction can be written:



The modified films are thoroughly washed after immersion and the nitrate anions are removed from the surface.

The UV-C irradiation process (254 nm) is a very important step as it assures the stabilization of the composite catalyst via photoreduction of Ag(I) to Ag(0) [15]. In fact titania absorbs UV radiation and produces electron-hole pairs at the semiconductor surface. The photoinduced conduction band electrons are responsible for reducing silver cations to metallic silver [16, 17].



The texture and morphology of the silver layer deposited on the titania surface are very important parameters and might influence the photocatalytic activity. In fact, Herrmann *et al.* [18] principally attributed the apparent increase in photocatalytic efficiency to the increase in the exposed surface due to textural characteristics of the Ag/TiO<sub>2</sub> layer. To better understand the differences between the Ag/TiO<sub>2</sub> films and express this in terms of surface parameters, we have undertaken their characterization by both scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM image (Figure 2) confirms that the TiO<sub>2</sub> film presents a porous, sponge like network of high roughness and complexity. This results in a high surface area titania substrate which has been proved to be extremely efficient for the photodegradation of 3,5-dichlorophenol and related compounds [6]. In agreement with the literature data [18], silver deposition affects the surface characteristics of the resulting Ag/TiO<sub>2</sub> films. Despite the importance of the surface

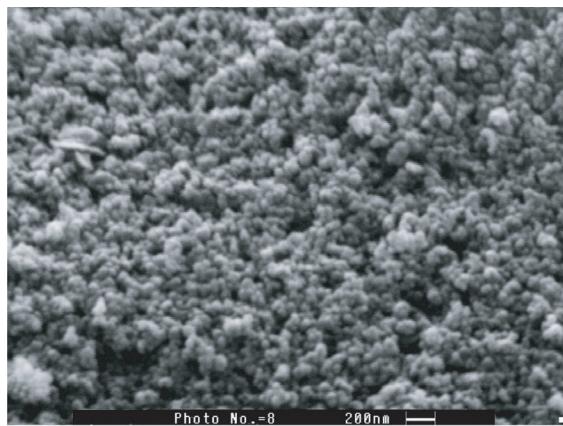


Figure 2. SEM image of doctor-blade titania film.

roughness for the efficiency of the photocatalytic process, the existence of an irregular and porous TiO<sub>2</sub> substrate with surface features of important height creates an insurmountable problem to the silver particles imaging. On such titanium dioxide morphology of high roughness, it is impossible to visualize the silver. In order to overcome the above problem, the silver deposition procedure was performed on very thin ( $\sim 300$  nm in thickness) and flat titanium dioxide films prepared via a sol-gel technique [7]. By using X-ray chemical analysis from a SEM microscope the Ag/Ti atomic concentration ratio on the surface of Ag/TiO<sub>2</sub> films was estimated. The analysis performed has shown similar results on both the doctor-blade and sol-gel films, thus confirming our hypothesis that the change of the titania substrate does not affect the silver deposition process. Thus, on relatively smooth modified surfaces, the use of AFM permitted to directly observe the silver particles ( $1 \times 1 \mu\text{m}^2$  top view images, Figures 3(a) and (b)). It is important to note that the silver particles are well distributed over the titania sol-gel films. Their surface density (number per surface unit) and average diameter depends on the AgNO<sub>3</sub> dipping solution. The higher the concentration of the dipping solution, the greater the particle number and diameter was observed.

As it can be seen on Figure 3, the silver is deposited in the form of well-defined and well-separated spherical nanoparticles. Their diameter has a Gaussian distribution with a maximum at 26 nm for dipping in a 10<sup>-3</sup> M Ag<sup>+</sup> solution. In the case of the sample dipped in 10<sup>-1</sup> M, the average grain diameter is about two times higher. Furthermore, grain size analysis proves that the height of the surface characteristics has a similar tendency. The height histogram presents a maximum at 4.7 nm against 11.9 nm respectively. These results are in excellent agreement with the roughness analysis performed on Figures 3(c) and (d). The Rms (Rms = the standard deviation of the Z values, Z being the total height range analysed) values show that

the TiO<sub>2</sub> films dipped in more dense solutions (10<sup>-1</sup> M AgNO<sub>3</sub>) present surface characteristics of higher roughness (10.4 nm) in comparison with those resulting from more dilute solutions (3.7 nm). In order to evaluate and compare the geometric complexity of the film surfaces, qualitative analysis including measurements of parameters such as feature frequency and fractal dimension (a parameter which reflects the scaling behaviour and is an intrinsic property of the material),  $D_f$  ( $3 \geq D_f \geq 2$ ) [19–23] was performed, Figures 3(e) and (f). The fractal analysis has shown that the silver doped films exhibit also self-affine scaling character over a significant range of length scales as a consequence of a “chaotic” dynamic deposition process, very sensitive to the initial conditions. It is worthwhile mentioning that the Ag(10<sup>-1</sup> M)/TiO<sub>2</sub> films have higher fractal dimension  $D_f$  than the Ag(10<sup>-3</sup> M)/TiO<sub>2</sub> films. The measured values were 2.41 ( $\pm 0.02$ ) and 2.36 ( $\pm 0.02$ ) respectively. This can be explained by taking into account the fact that the fractal dimension  $D_f$  characterizes mainly the complexity of the surface. The Ag(10<sup>-1</sup> M)/TiO<sub>2</sub> films present a more complex topography characterized by a greater number of surface features of higher height and frequency. The fractal property influences the effective surface extension ( $S = cL^{D_f}$ ) of the catalyst ( $c$  is a constant describing finite fluctuations around the 0-level and  $L$  the sample size within the fractal limits). As a result, the real surface area of such a fractal photocatalyst is several times higher than the corresponding flat, non-fractal material ( $S \sim L^2$ ) [7, 20].

Photocatalysis experiments were first performed by using visible light (L 15/12 Lumilux de luxe daylight lamp) but the photocatalytic efficiency was poor and the calculation of kinetic parameters led to very low values of rate constants. On the contrary, preliminary tests performed with aqueous solutions irradiated under UV-A (350 nm) have shown photodecomposition of methyl orange, in the presence of the photocatalyst. They also demonstrated that the photocatalytic performance of the composite materials strongly depends on the silver deposition conditions. The films activity was then evaluated in terms of the most crucial preparation parameters: dipping duration, UV irradiation time, and concentration of the AgNO<sub>3</sub> dipping solution. It must be pointed out that control experiments performed under the conditions of irradiation in the absence of the photocatalyst did not show any change of the azo-dye solution absorbance.

To define the optimum dipping duration, doctor-blade TiO<sub>2</sub> films were immersed in a 10<sup>-3</sup> M AgNO<sub>3</sub> solution for different time intervals (from 1 to 30 sec) and then they were UV irradiated for 2 h. The photocatalytic efficiency of these silver doped titania materials for the MO decomposition (% degradation percentage) is illustrated in Figure 4. The results show that the best efficiency corresponds to 3 s of dipping. Longer immersion in the silver nitrate solution results in an important

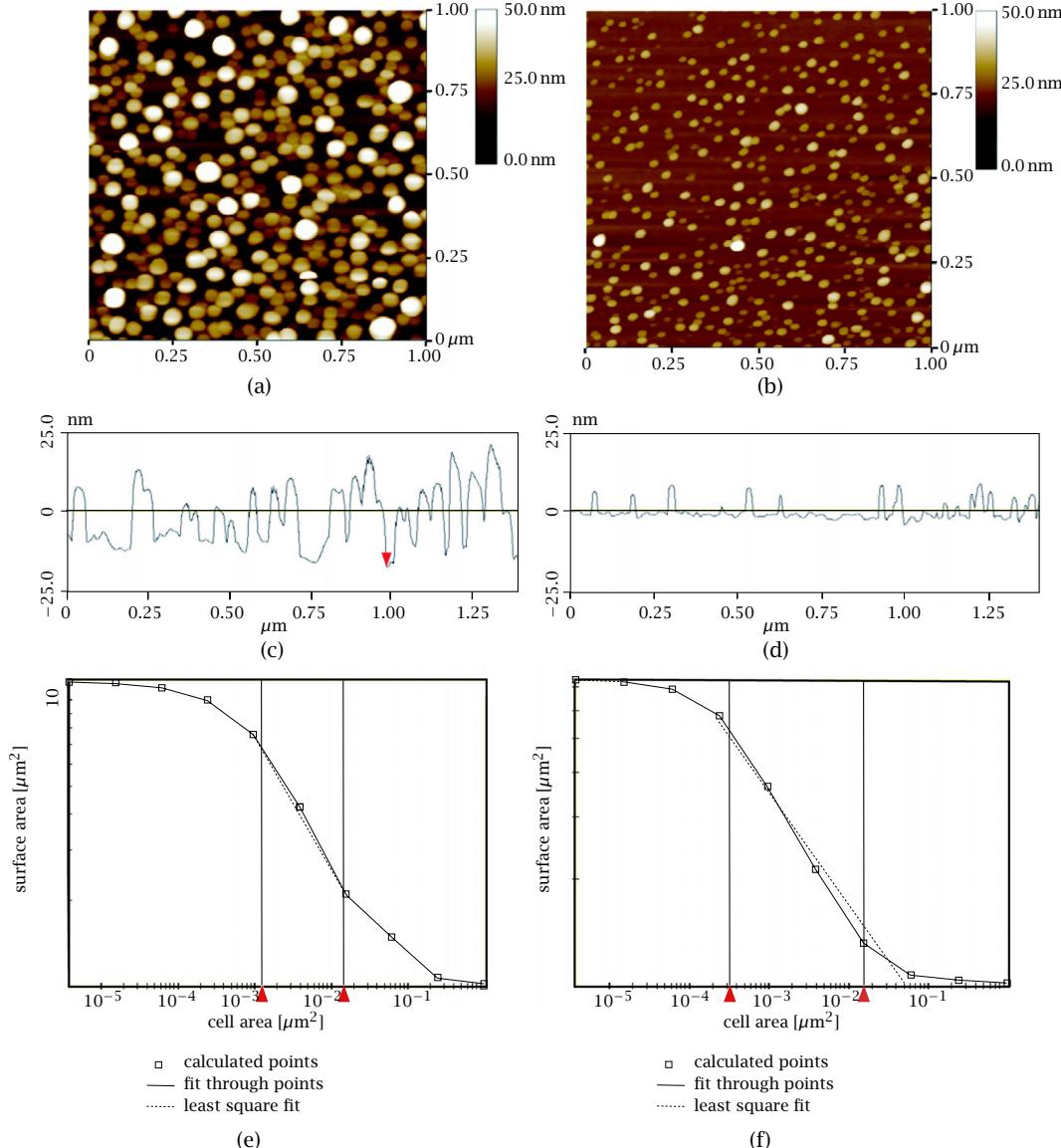


Figure 3. AFM analysis on silver particles deposited on titanium dioxide sol-gel thin films. Top-views of catalysts dipped in 10<sup>-1</sup> M (a) and 10<sup>-3</sup> M AgNO<sub>3</sub> solutions; Corresponding roughness graphs: (c) and (d); and fractal dimension calculation curves: (e) and (f).

decrease of the photocatalytic performance because of the existence of a large amount of silver on the semiconductor surface. The above behaviour does not depend on the concentration of the dipping solution. In fact, similar results were obtained with different AgNO<sub>3</sub> solutions whose concentration varied between 10<sup>-1</sup> and 10<sup>-3</sup> M.

Figure 5 shows that the photodegradation efficiency of methyl orange, using different silver modified TiO<sub>2</sub> films, increases, by increasing the irradiation time. It reaches a maximum at about 120 min and then remains practically stable. The existence of such a “plateau” can be attributed to a complete photoreduction of the silver cations.

However, the parameter that strongly influences the films photocatalytic activity is the concentration of the AgNO<sub>3</sub> dipping solution. Figure 6 illustrates the photocatalytic efficiency (degradation percentage after 1 hour irradiation) of the different silver doped titania materials for the MO decomposition and Table 1 regroups the obtained efficiencies. The results show that by increasing the concentration of the dipping solution, the photocatalytic efficiency increases. A maximum (90%) is observed for the titania films immersed in 10<sup>-3</sup> M AgNO<sub>3</sub> solution. Further increase of the Ag<sup>+</sup> concentration marks a considerable photocatalytic performance decrease. For instance, for films dipped in 10<sup>-2</sup> M AgNO<sub>3</sub> solution the MO decomposition

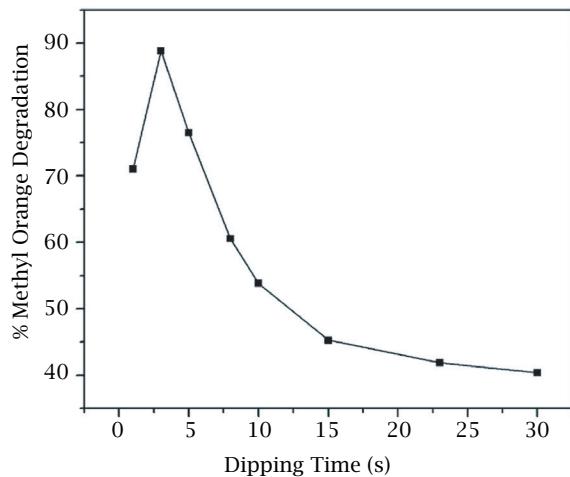


Figure 4. Photocatalytic activity of silver/titania composite films for methyl orange decomposition as a function of the dipping time (Initial MO concentration:  $1.9 \times 10^{-5}$  M; Concentration of  $\text{AgNO}_3$  solution:  $10^{-3}$  M; irradiation time: 3 h).

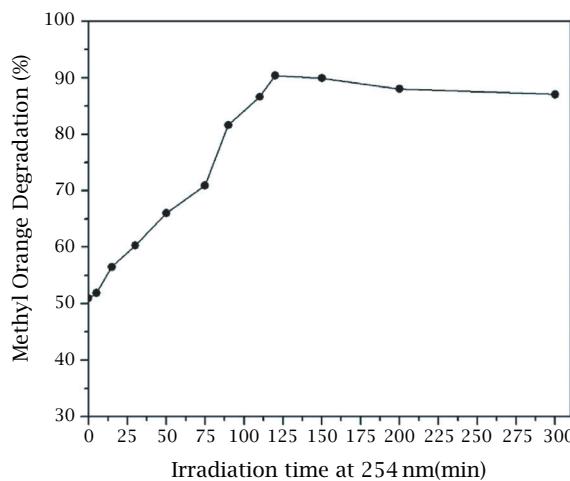


Figure 5. Photocatalytic activity of silver/titania composite films for methyl orange decomposition as a function of the irradiation time (Initial MO concentration:  $1.9 \times 10^{-5}$  M; Concentration of  $\text{AgNO}_3$  solution:  $10^{-3}$  M; dipping time: 3 s).

percentage goes to 70%. More spectacularly, the efficiency falls to 40% for  $10^{-1}$  M  $\text{AgNO}_3$ , a value lower than that obtained with the non-supported  $\text{TiO}_2$  films (50%). The corresponding time for complete pollutant degradation was found to be 110 min for the  $\text{Ag}(10^{-3}$  M)/ $\text{TiO}_2$  and about 5 h for the  $\text{TiO}_2$  films respectively. The above performance order can be roughly explained by the amount of absorbed photons. In fact, the addition of silver cations and subsequent UV irradiation causes significant changes to the absorption spectrum of  $\text{TiO}_2$  films. The reflectance spectra, presented on Figure 7, besides a shift of the absorption band edge, clearly show that the absorbance values of the  $\text{Ag}/\text{TiO}_2$  films around 350 nm (the region of the lamp emission

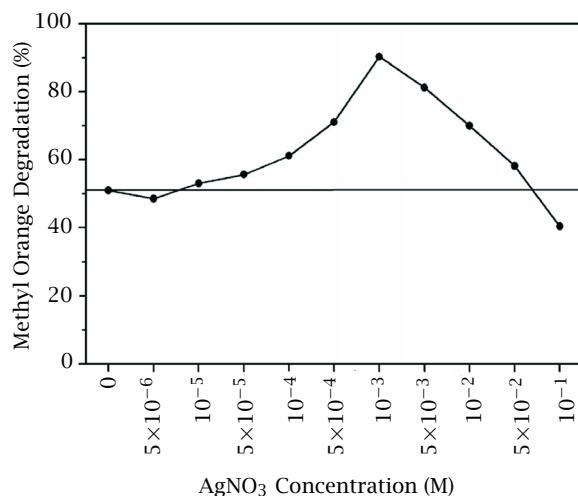


Figure 6. Photocatalytic activity of silver/titania composite films for methyl orange decomposition as a function of the concentration of the  $\text{AgNO}_3$  solution (Initial MO concentration:  $1.9 \times 10^{-5}$  M;  $10^{-3}$  M; dipping time: 3 s; irradiation time: 3 h).

Table 1. Photodegradation percentage of MO for different  $\text{Ag}/\text{TiO}_2$  photocatalysts.

$\text{AgNO}_3$ Solution Concentration (M)	M.O. Degradation Percentage (%)
0 ( $\text{TiO}_2$ only)	51
$5 \times 10^{-6}$	49
$10^{-5}$	53
$5 \times 10^{-5}$	56
$10^{-4}$	61
$5 \times 10^{-4}$	71
$10^{-3}$	90
$5 \times 10^{-3}$	81
$10^{-2}$	70
$5 \times 10^{-2}$	58
$10^{-1}$	40

spectrum) follow the same order. The slight increase of the absorbance between 350 and 450 nm indicates enhanced light capture, attributed to plasmon absorption of silver clusters [17]. Although a direct quantitative correlation between absorbance of the films and their photocatalytic efficiency is not possible, the existence of an optimum concentration for a silver nitrate solution can be understood. The presence of silver particles facilitates the charge separation. However, increased silver surface concentration leads to the shadowing of the semiconductor, thus reducing its photocatalytic activity.

To directly compare the performance of the silver modified photocatalyst to the non-supported material, methyl orange photodegradation kinetics are presented on Figure 8. The degradation of MO in the presence of

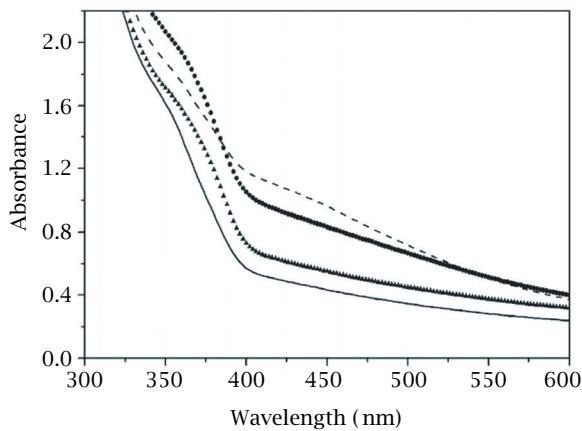


Figure 7. Absorption spectra of a Degussa P25 TiO<sub>2</sub> film (solid line) and of silver modified Degussa P25 TiO<sub>2</sub> films after dipping for 3 s in 10<sup>-1</sup> M (dashed line), 10<sup>-3</sup> M (circles) and 10<sup>-5</sup> M (triangles) AgNO<sub>3</sub> solutions respectively and subsequent UV (254 nm) irradiation.

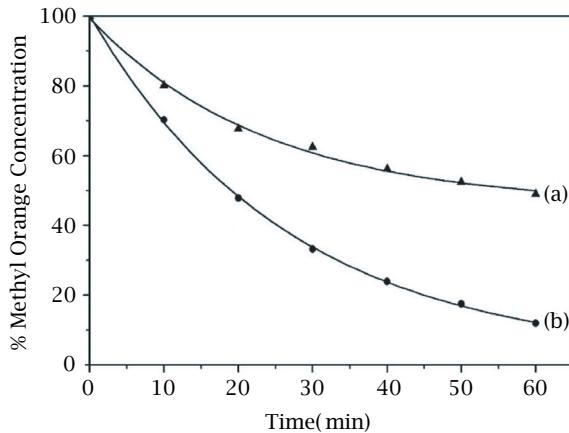


Figure 8. Decomposition kinetics of MO (10<sup>-3</sup> M) in the presence of a Degussa P25 TiO<sub>2</sub> film (a), a silver/titania film (b) (initial MO concentration: 1.9 × 10<sup>-5</sup> M; 10<sup>-3</sup> M; dipping time: 3 s; irradiation time: 3 h; concentration of AgNO<sub>3</sub> solution: 10<sup>-3</sup> M).

the silver modified TiO<sub>2</sub> photocatalysts follows apparent first order kinetics. Reaction rate constants (*k*) have been calculated from Figure 9, using the slope of the log plots:

$$\ln C = \ln C_o - kt, \quad (3)$$

(C<sub>*o*</sub> is the initial MO concentration and *C* the corresponding concentration at a given time, *t*). The correlation coefficients (*R*<sup>2</sup>) for the linear fitted log plots on Figure 9 concerning methyl orange photodegradation, were 0.998 for the silver modified and 0.996 for the original TiO<sub>2</sub> film. The corresponding rate constants were 0.03688 min<sup>-1</sup> (*t*<sub>1/2</sub> = 19.0 min) and 0.01158 min<sup>-1</sup> (*t*<sub>1/2</sub> = 59.5 min) respectively. It is worth mentioning that the photodegradation of methyl

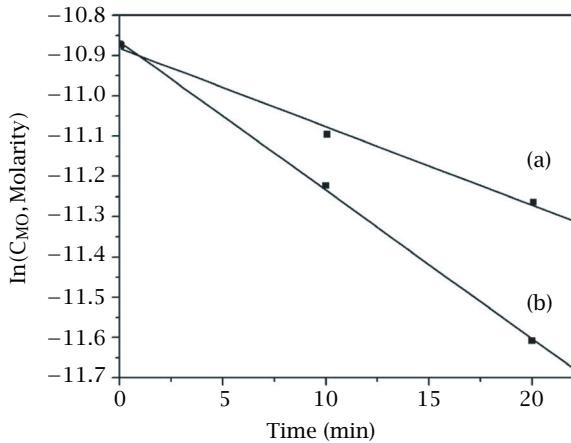


Figure 9. Log plots [ln *C* = ln *C*<sub>o</sub> - *kt*] for the calculation of the decomposition reaction rate constants (*k*) of methyl orange in the presence of a Degussa P25 TiO<sub>2</sub> film (a), a silver/titania film (b).

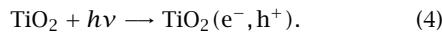
orange using the silver doped titania photocatalyst was perfectly reproducible. In fact, the same immobilized Ag/TiO<sub>2</sub> film surface was used in six consecutive irradiation experiments of new added pollutant quantities and each experiment reproduced the experimental points on Figure 8 within 2–4% error.

It must be pointed out that increased surface area is among the most important factors in the TiO<sub>2</sub> photocatalysis [24]. However, our results show that surface complexity is not the only parameter that determines the silver/titania composite films photocatalytic efficiency. Silver surface coverage and particle size distribution are also very important factors that might be taken into account. It is normal to assist at a competition between the silver synergistic action and a natural screening resulting from the presence of catalyst excess on the titania surface.

On the basis of the above remarks, the photocatalytic behavior of the silver modified titania samples can be explained. TiO<sub>2</sub> solar photocatalysis can operate under both visible and ultraviolet wavelengths involving two distinct mechanisms. Taking into account the fact that the MO optical spectrum is well centered in the visible (absorption maximum at 465 nm) and does not fit with the irradiation wavelengths (a narrow band around 350 nm), Figure 1, the sensitized photocatalysis route (involving first light absorption by the dye molecule and subsequent electron injection from the dye excited state to the semiconductor conduction band, followed by oxidation of the cation radical) must be excluded [25–27].

The mechanism for the heterogeneous photocatalysis on TiO<sub>2</sub> has been established on the basis of experimental measurements [1, 3, 27, 28]. Under irradiation of the TiO<sub>2</sub> semiconductor with photons of energy greater than the materials' gap (E<sub>g</sub> = 3.2 eV for pure

anatase), pairs of conduction band electrons ( $e^-$ ) and valence band holes ( $h^+$ ) are generated, following the reaction (4).



Then, the photogenerated holes migrate to the surface where they react with OH<sup>-</sup> or H<sub>2</sub>O to produce strongly oxidizing hydroxyl radicals ( $\bullet\text{OH}$ ) that can decompose the dye. Photogenerated electrons readily react with electron acceptors such as oxygen, to form superoxide anions (O<sub>2</sub> $\bullet^-$ ) [29, 30], which can then generate highly active  $\bullet\text{OOH}$  and  $\bullet\text{OH}$  radicals [31].

On the other hand it is important to notice that in the case of the Ag/TiO<sub>2</sub> catalysts, the photocatalysis mechanism must involve the participation of silver particles. Following Sclafani and co-workers [32], the effect of silver can be explained in terms of the separation of the photoinduced charges (e<sup>-</sup>, h<sup>+</sup>). Due to the difference in the work function of the two materials, a part of the photoproduced electrons are transferred to the silver cations, thus improving the charge carriers' separation. In addition, it must be pointed out that since silver possesses good catalytic properties for the reduction of oxygen, the formation of superoxide anions could occur on silver with lower overvoltage than on TiO<sub>2</sub>.

The proposed mechanism explains well the superiority of the silver modified films with respect to non-supported materials and it is compatible with the increase in the photocatalytic efficiency observed for catalysts with relatively low silver content (derived from 10<sup>-5</sup> to 10<sup>-3</sup> M AgNO<sub>3</sub> solutions). In fact, the unpaired holes would have a stronger oxidizing ability to the oxidation of methyl orange [33]. The model also justifies the significant activity decrease observed in the case of dipping in dense Ag<sup>+</sup> solutions, in excellent agreement with the surface characteristics of the catalysts. Lower photocatalytic efficiency means either higher recombination rate either (or/and) lower photon absorption ability. As the photocatalysis is a surface process and the silver supported catalysts have different surface characteristics, this results also in differences in the total surface area exposed to the radiation beam. In samples with high silver content not only the photochemically active TiO<sub>2</sub> surface is masked.

#### 4. CONCLUSIONS

A net improvement in the photocatalytic efficiency of titania films was obtained by silver photodeposition. This enhancement was attributed to the action of silver, which plays a key role by attracting conduction band photoelectrons and preventing electron-hole recombination. The obtained results make further work on the subject very encouraging. In fact, such a simple, two step deposition technique permits the silver incorporation onto the titania film and presents the advantage of

significant reduction in the composite catalyst preparation costs. In addition, this work opens the possibility to develop more efficient photocatalysts in the form of porous and high surface area inorganic oxide matrixes by depositing different other metal additives (i.e. gold, ruthenium).

#### ACKNOWLEDGEMENTS

Financial support from Greece-France bilateral cooperation (PLATON) and GSRT/Ministry of Development/Greece (Excellence in the Research Institutes-1422/B1/3.3.1/362/2002 project) as well as precious help and assistance from Fotini Papadimitriou and Georgios Katsaros are greatly acknowledged.

#### REFERENCES

- [1] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, Chem. Rev. **95** (1995), 69.
- [2] A. Fujishima, T. N. Rao, and D. A. Tryk, J. Photochem. Photobiol. C: Photochem. Rev. **1** (2000), 1.
- [3] O. Legrini, E. Oliveros, and A. M. Braun, Chem. Rev. **93** (1993), 671.
- [4] O. M. Alfano, D. Bahnemann, A. E. Cassano, R. Dillert, and R. Goslich, Catal. Today **58** (2000), 199.
- [5] A. Fujishima, K. Hashimoto, and T. Watanabe, TiO<sub>2</sub> Photocatalysis, Fundamentals and Applications Bkc, Inc, Tokyo, 1999.
- [6] I. Sopyan, M. Watanabe, S. Murasawa, K. Hashimoto, and A. Fujishima, J. Photochem. Photobiol. A: Chem. **98** (1996), 79.
- [7] I. M. Arabatzis, S. Antonaraki, T. Stergiopoulos, A. Hiskia, E. Papaconstantinou, and P. Falaras, J. Photochem. Photobiol. A: Chem. **149** (2002), 237.
- [8] M. Litter, Appl. Catal. B: Environ **23** (1999), 89.
- [9] W. Choi, A. Termin, and M. R. Hoffmann, J. Phys. Chem. **98** (1994), 13669.
- [10] M. A. Fox and M. T. Dulay, Chem. Rev. **93** (1993), 341.
- [11] M. Valden, X. Lai, and D. W. Goodman, Science **281** (1998), 1647.
- [12] X. Z. Li and F. B. Li, Environ. Sci. Technol. **35** (2001), 2381.
- [13] E. Scolan and C. Sanchez, Chem. Mater. **10**(10) (1998), 3217.
- [14] J.-M. Herrmann, J. Disdier, and P. Pichat, J. Catal. **113** (1988), 72.
- [15] P. A. Morris-Hotsenpiller, J. D. Bolt, W. E. Farneth, J. B. Lowekamp, and G. S. Rother, J. Phys. Chem. B. **102** (1998), 321.
- [16] M. R. V. Sahyum and N. Serpone, Langmuir **13** (1997), 5082.
- [17] E. Stathatos, T. Petrova, and P. Lianos, Langmuir **17** (2001), 5025.
- [18] J.-M. Herrmann, H. Tahiri, Y. Ait-Ichou, G. Lassaletta, A. R. González-Elipe, and A. Fernández, Appl. Catal. B: Environ. **13** (1997), 219.

- [19] A. P. Xagas, E. Androulaki, A. Hiskia, and P. Falaras, *Thin Solid Films* **357** (1999), 173.
- [20] A. Provata, P. Falaras, and A. Xagas, *Chem. Phys. Lett.* **297** (1998), 484.
- [21] P. Falaras, A. Hugot-Le Goff, M. C. Bernard, and A. Xagas, *Sol. Energy Mater. Sol. Cells* **64** (2000), 167.
- [22] B. Mandelbrot, *The Fractal Geometry of Nature*, W. H. Freeman and Co, New York, 1982.
- [23] P. Falaras, *Sol. Energy Mater. Sol. Cells* **53** (1998), 163.
- [24] W. Lee, H.-S. Shen, K. Dwight, and A. Wold, *J. Solid State Chem.* **106** (1993), 288.
- [25] F. Kiriakidou, D. I. Kondarides, and X. E. Verykios, *Catal. Today* **54** (1999), 119.
- [26] F. Zhang, J. Zhao, T. Shen, H. Hidaka, E. Pelizzetti, and N. Serpone, *Appl. Catal. B: Environ.* **15** (1998), 147.
- [27] F. Chen, Y. Xie, J. Zhao, and G. Lu, *Chemosphere* **44** (2001), 1159.
- [28] P. V. Kamat, S. Das, K. G. Thomas, and M. V. George, *Chem. Phys. Lett.* **178** (1991), 75.
- [29] C. Minero, E. Pelizzetti, P. Pichat, M. Sega, and M. Vincenti, *Environ. Sci. Technol.* **29**(9) (1995), 2226A.
- [30] N. Serpone, *J. Photochem. Photobiol. A: Chem.* **104** (1997), 1.
- [31] H. Gerisher and A. Heller, *J. Phys. Chem.* **95** (1991), 5261.
- [32] A. Sclafani, M.-N. Mozzanega, and P. Pichat, *J. Photochem. Photobiol. A: Chem.* **59** (1991), 181.
- [33] B. Ohtani, S. Zhang, J. Handa, H. Kajiwara, S. Nishimoto, and T. Kagiya, *J. Photochem. Photobiol. A: Chem.* **64** (1992), 223.

