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PURE AND DOPED MESOPOROUS TIO_2 FILMS MADE FROM REVERSE MICELLES AND THEIR USE FOR THE PHOTOCATALYTIC DEGRADATION OF ADSORBED BASIC BLUE DYE

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ABSTRACT. Films transparentes de TiO_2 ont été déposés sur des plâques de verre par une procedure sol-gel en présence de micelles inversées de Triton X-100 in cyclohexane. Solutions aqueuses de Basic Blue, (2- [[4- ethyl(2- hydroxyethyl)- amino)] phenyl]azo]- 5- metoxy-3-methyl (T-4)metoxysulfate), ont été absorbées sur ces films et leur photodégradation a été suivi par la spectrophotométry d'absoption. Pour obtenir le maximum du rendement de la photodégradation, la nanostructure du film a été optimisée en souivant le temps de géfication, la nature et la concentration du ion dopant et par l'irradiation du film avec des rayons UV. Les films qui ont incorporré, par micelles inversées, des ions d'argent et du chrôme sont plus efficaces que les films pures de TiO_2. Les films dopées avec Ag devient plus efficaces par irradiation UV. Les films dopées avec Au sont moins actifs, mais elles aussi devient plus éfficaces que les films pures de TiO_2 apres l'irradiation UV.

INTRODUCTION

Photodegradation catalyzed by TiO_2 particles provides a technological method for the treatment of air and water pollutant. This heterogeneous photocatalysis is an extensively studied process in the recent years[1-3]. In most of the applied technologies, TiO_2 aqueous suspensions have been employed[4,5]. Because the manipulation of TiO_2 powders and their removal is difficult, the most recent research is focused on the preparation of the immobilized catalysts, e.g. in the form of thin films on solid supports. These thin films are particularly interesting for applications to open-air purification panels[6,7]. The efficiency of thin films is lower than that of suspended powders[8]. For this reason, an intensive effort has been made to enrich titania with species that can enhance its photocatalytic capacity. Noble metals, in particular, silver have been used for this goal. Silver increases the photocatalytic capacity of titania by some different physical mechanisms that may act separately or simultaneously. Reduced silver particles of colloidal dimension (metallic silver) are considered to be electron scavengers. Thus, by trapping electrons produced in electron-hole pair after photons absorption, they prevent electron-hole recombination and liberate holes to participate in degradation reactions[9]. Plasmon resonance effects in metallic silver nanoparticles are also held responsible for local enhancement of the electric field, facilitating electron-hole pair production and separation[8,10,11]. Finally, silver is also reported to affect the structure of titania, leading to modification of its photocatalytic activity[12]. In the present work, we study the photocatalytic efficiency of transparent mesoporous titania thin films, made by a sol-gel method involving reverse micellar templates[13-15]. Films are structured in nanoparticles of controlled and uniform size, both in pure form or doped with silver, chromium, gold and potassium. The metal ion is introduced in the films by initial solubilization in the reverse micellar solution. It has found that the presence of the impurity results in increasing photodegradation rate and it thus search for ways to optimize it.

The samples were tasted by monitoring rates of photodegradation of a model dye, Basic Blue (BB) absorbed on pure or doped titania mesoporous films. This choice was dictated by the following reasons: dye photodegradation on a transparent film can be easily monitored by absorption spectrophotometry; a large amount of water-borne pollutants is synthetic textile dyes and industrial dyes stuffs[16]; dye photodegradation can be carried out by visible light through photosensitization, i.e. by light absorption from the dye and subsequent electron separation by transfer to the semiconductor[16-18]; finally, TiO_2 photodegradation reactions in thin film configuration is a process acquiring increasing industrial interest since applications can be envisaged by deposition on large surfaces for both indoors and outdoors air-purifications system[1-3, 19].

EXPERIMENTAL

Materials. Titanium (IV) isopropoxide, polyoxiethilene(10)isooctyl- phenyl ether (triton X-100), $Ag(NO_3)$ hydrated, KNO_3, $NaAuCl_4xH_2O$, $Cr(NO_3)_3x9H_2O$ and benzothiazolium, (2-[[4-ethyl(2-hydroxyethyl)-amino)] phenyl]azo]-5-metoxy-3-methyl(T-4)-metoxysulfate) (Basic Blue, BB, cf. chemical structure from fig.1) were purchased from Aldrich and used as received. The rest of the reagents were from Merck, while millipore water was used in all experiments.

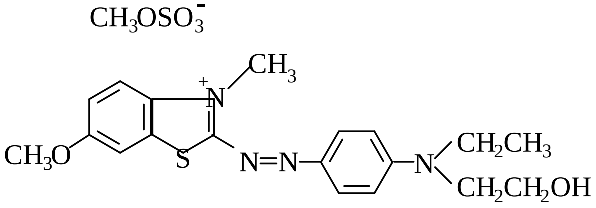

Fig.1. The chemical structure of Basic Blue.

Preparation of TiO_2 mesoporous films deposited on glass slides

Reverse micellar solutions of 0.2M Triton X-100 were prepared in cyclohexane. To each of these solutions it was added 0.2M titanium isopropoxide under vigorous stirring and at ambient conditions[13-15]. Hydrolysis and condensation of titanium isopropoxide begins as soon as it is introduced in the reverse micellar solution, but it may take more than one hour before the solution becomes a visible gel. This prepared composite material was deposited as thin film on a glass slide by dip-coating. The slide was previously sonicated for 20 min. in ethanol and was finally copiously washed with millipore water and dried in a stream of N_2. The thus prepared slide was dipped into the gelling solution and was fast withdrawn at a speed of 2cm/s. The composite of organic-inorganic film was left to dry in air and then it was slowly heated in air, up to 450℃ at a rate of 3.5℃/min. The film was finally sintered at 450℃ f or about 15 more minutes. The procedure was repeated two additional times. Thicker films could be made by further successive coatings. However thickness grows at the expense of transparency. AFM and SEM images of the films prepared by the above method and published in previous publicati- ons[13-15] reveal a mesoporous structure that consists of TiO_2 nanoparticles of practi- cally monodisperse size with exceptional reproducibility. It was observed that choosing the water/surfactant ratio in the original solution easily controls the size of the nanoparticles[7]. Larger nanoparticles are made when more water exists in the solution. The advantage of the reverse micellar route in making TiO_2 particles, as compared with other methods, exactly lies on this capacity to control the mesoporous structure of the obtained films. The diameter of the nanoparticles employed in the present work, as estimated by using AFM images, was around 30 nm in the case of samples made with a water/surfactant ratio equal to two (0.2 M Triton X-100, 0.4M water). The TiO_2 films are too thin to give a detectable X-ray diffraction spectrum. The powder of TiO_2 obtained by the freeze drying procedure (in the same conditions) was study by X-ray diffraction. It gave a diffusion pattern, which corresponds to anatase nanocrystallites.

Incorporation of metal ions

Silver, chromium, gold and potassium ions were been directly incorporated in titania film by solubilization in the original reverse micellar solution, i.e. instead of pure water, it was used aqueous salt solution so that the final metal ion concentration is well defined. The rest of the procedure remained the same as above. The ions concentration was 0.005-0.05M, i.e. at 2.5-25% doping level with respect to titanium.

Adsorption of the dye on the films

Both pure titania and doped films adsorb a substantial amount of Basic Blue, when they are dipped in an aqueous solution of the dye. Adsorption is instantaneous and the films are immediately deeply colored (cf. figures 2 and 3). In typical preparations, dye concentration in solution was 10^{-2}M.

Methods

Absorption measurements were made with a Cary 1E spectrophotometer. UV-treatment of the films has been obtained by illumination with a mercury-containing 400W UV lamp. Illumination of the samples for dye photodegradation was achieved with a commercial 250W tungsten-halogen spotlight satisfactorily simulating solar radiation. The light intensity at the surface of the sample was 600 mW/cm^2. Measuring the absorbance of the dye at its maximum monitored photodegradation.

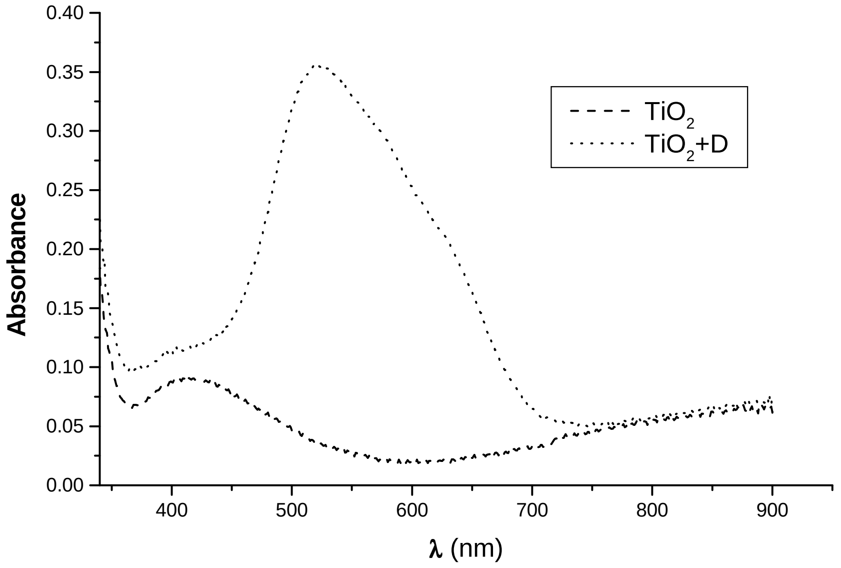

Fig.2. Absorbtion spectrum of pure titania film without and with adsorbed BB.

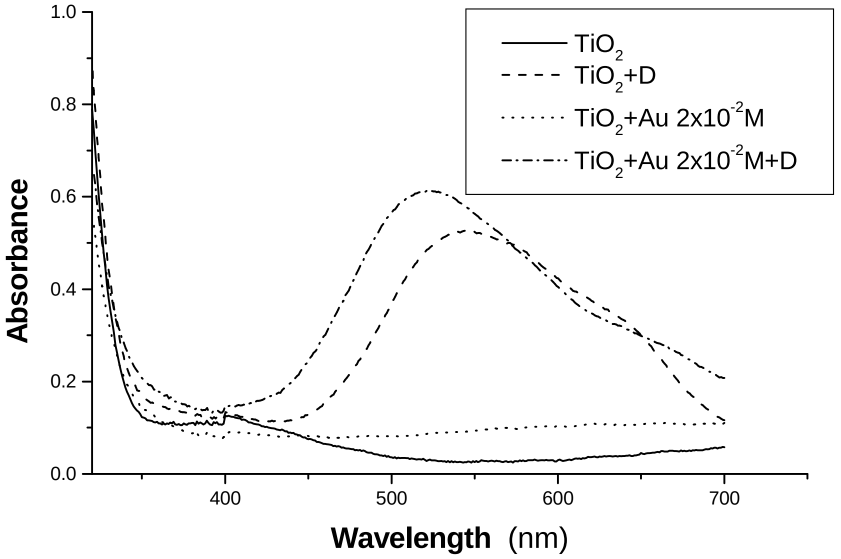

Fig.3. Absorption spectrum of a typical pure titania film (with and without adsorbed BB) and Au-doped titania film (with and without adsorbed BB).

RESULTS AND DISCUSSION

Figure 4 shows the variation of absorbance of pure titania films with adsorbed BB as a function of illumination time with visible light. The two curves correspond to two films made with the same reverse micellar solution but a different time of gelation. The chemical structure of BB is also presented in figures 1.

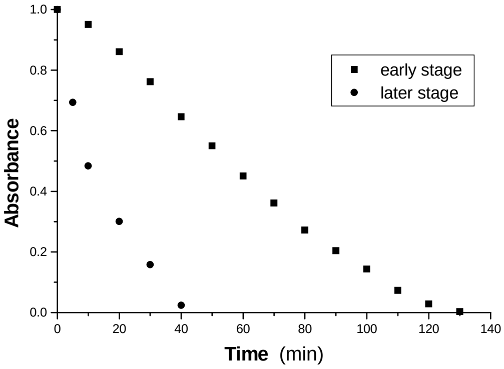

Fig.4. Variation of absorbance of pure titania films with adsorbed BB as a function of illumination time with visible light. The two curves correspond to two films made with the same reverse micellar solution but a different stage of gelation.

Fig. 5 shows the absorption spectrum of a representative titania film alone.

The oscillating part in the spectrum of titania is due to interference fringes. The photodegradation is realized by the photosensitizing procedure[16-18], i.e. light is almost exclusively absorbed by the dye. Then the excited electron is transferred into the conduction band of the semiconductor leaving behind a hole localized on the dye. The thus separated electron is scavenged by atmospheric molecular oxygen so that e^--h^+ recombination is prevented and the dye is destroyed by the remaining hole. Photodegradation by direct excitation of titania is not excluded but it is very limited. Indeed use of filters cutting off the Near UV radiation of the lamp (400nm cutoff filter) only slightly diminishes photodegradation rates. Hydrolysis of titanium isopropoxide and subsequent gelation by inorganic (i.e., -Ti-O-Ti-) polymerization, according to the sol-gel procedure, is very rapid for $w/s \geq 3$. Fast gelation leads to very rough, light-scattering films that are not appropriate for the present studies. Thus the highest exploitable ratio was w/s = 2.5(0.2M Triton X-100 + 0.5M water). SEM, TEM and AFM9-11 have previously characterized titania films made by using different w/s ratios. As a general rule, later stage of gelation leads to mesoporous titania films composed of larger nanoparticles. The total active surface of the mesoporous structure is larger in smaller particles, i.e. in the case of early stage of gelation. Increase of time of gelation, i.e. increase of the nanoparticle size, makes rougher films with smaller active surface expansion. For this reason, it has found that films made after 1 h of gelation have smaller capacity of BB absorption. It seems reasonable that no more than one BB molecule can be absorbed on a single titania nanoparticle. For this reason, smaller but more numerous nanoparticles can adsorb more dye than larger but less numerous nanoparticles. However, bigger particles are more effective in photodegradating BB than smaller particles, as can be seen in figure 4. It is obvious that photodegradation rates are much faster for later stage than for early stage of gelation. Even though more extensive studies are needed to explain this phenomenon, there may be plausible explanations. It is known, that according to Brus effective mass model for nanosize semiconductors[20], absorption occurs at longer wavelength for bigger particles due to the size effects on the electronic properties of the semiconductor. Indeed, as seen in fig. 5 showing absorption spectra of films made with different growth times, larger particles (longer growth) absorb light at longer wavelength than smaller particles (short times). One then possible reason for higher rates with later stage of gelation is the larger percentage of direct Near UV absorption of photons by the larger particles. However, this seems to us a rather weak argument since the direct participation of titania in photon absorption is, as already said, very limited. Meanwhile, smaller particles have a higher energy band-gap. It is then possible that the electron transfer from the dye to the higher - laying Conduction Band of the smaller-size semiconductor particles during photosensitization, is more difficult than in larger particles, which have a smaller band-gap. This can partly explain the smaller efficiency of smaller particles[21]. A second explanation is that in smaller particles it

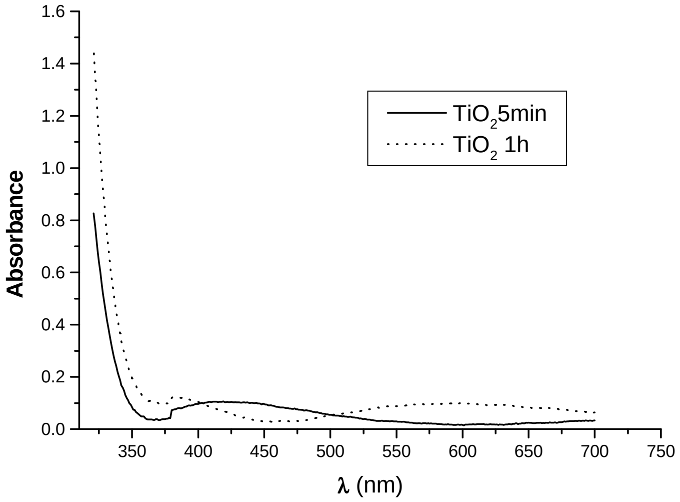

Fig.5. Absorption spectrum of a typical titania film made with the same reverse micellar solution but a different stage of gelation.

is more probable to have extended surface defects that will quench the excited species by providing electron - hole recombination sites and thus give lower photodegradation rates. As a conclusion the above information indicated that more material is adsorbed on a film that has a finer mesoporous structure but it offers lower photodegradation rates. For this reason and in order to compensate the two opposing effects it has opted for 1h of gelation (0.2M Triton X-100 and 0.4 M water) as the best combination for both satisfactory adsorption capacity and photodegradation efficiency.

Photocatalytic degradation of BB has also been studied with doped TiO_2 films made by the above procedure, using a standard water/surfactant ratio w/s = 2. Four dopants were tried, Ag^+, Cr^{+3}, Au^{+3}, and K^+. Salts of these metals have been introduced at concentration 0.005 - 0.05M, i.e. at 2.5 - 25% doping level with respect to titanium, by solubilizing them in the water used to make Triton X-100 reverse micelles. Formation of films by dipping and subsequent heating up to 450℃ as well as BB adsorption for photodegradation experiments followed the same procedure as for pure titania films. The incorporation of dopants by the reverse micellar route introduces metal ions in titanium substitution sites in the nanocrystallite lattice. The present study is focused on the question of the photodegradation efficiency itself.

As a verification of the fact that smaller particles give lower photodegradation rates but higher dye adsorption capacity, it has produced films made with w/s = 2 and doped with Ag $2x10^{-2}$ F at two different stages of gelation, i.e. dipping in the solution was done 5 min and 15 min after component mixture. A longer waiting time means more extensive particle growth. In fact, approximately, the same effect is produced by using w/s = 2 and different concentrations of dopant ions and dipping a few minutes after preparation. Comparison of photodegradation rates between a film made at an early stage with a film made at a late stage of gelation is shown in fig. 6. Indeed the latter film adsorbs less dye but degrades it faster. The quantity of the adsorbed dye is not shown in fig. 6. Maximum absorbencies are normalized for the sake of comparison.

Two types of samples were examined. In the first type, immediately after the doped film was taken out of the furnace the absorption spectrum of the film was registered and then BB was adsorbed on the film by dipping. Finally, the film with adsorbed dye was illuminated with visible light and the photocatalytic degradation of the dye was monitored by absorption spectrophotometry. In the second type, after the films were taken out of the furnace, they were first subjected to UV treatment for about 15 min, and then the dye was adsorbed and finally was photodegradated by visible light illumination. UV treated doped films are much more efficient for dye photodegradation than untreated films. This can be seen in figures 7 and 8, where Ag-doped and Au-doped TiO_2 photocatalytic rates are, respectively, presented.

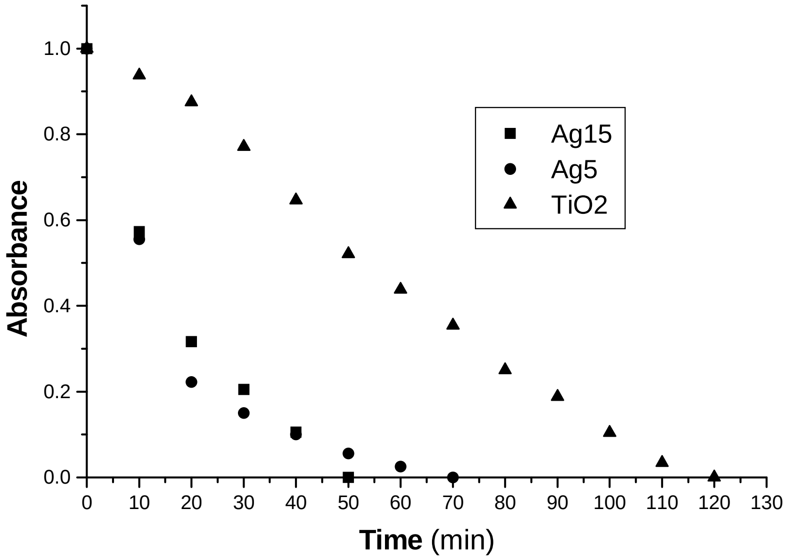

Fig.6. Variation of absorbance of pure titania film and Ag-doped titania films with adsorbed BB as a function of illumination time with visible light. The three curves correspond to three films: pure titania film, Ag-doped titania film after 5 min of gelation and Ag-doped titania film after 15 min of gelation

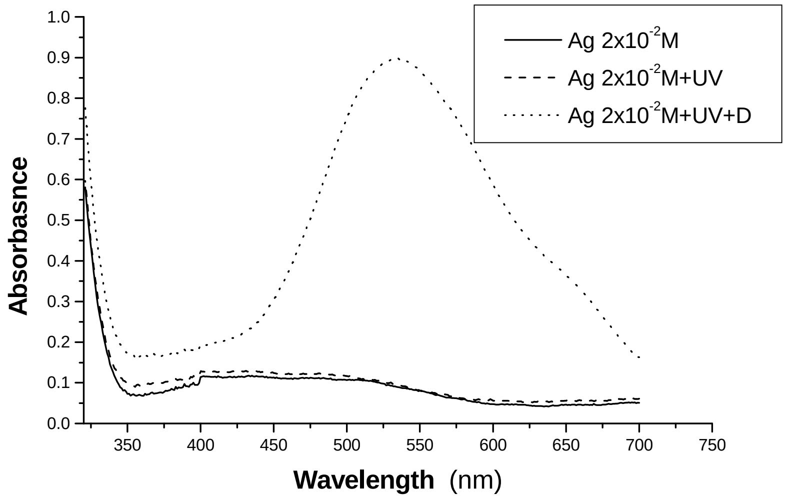

Fig.7a. Absorption spectrum of Ag-doped film. The three curves correspond to the same film before UV treatment, after UV treatment and after adsorption of BB

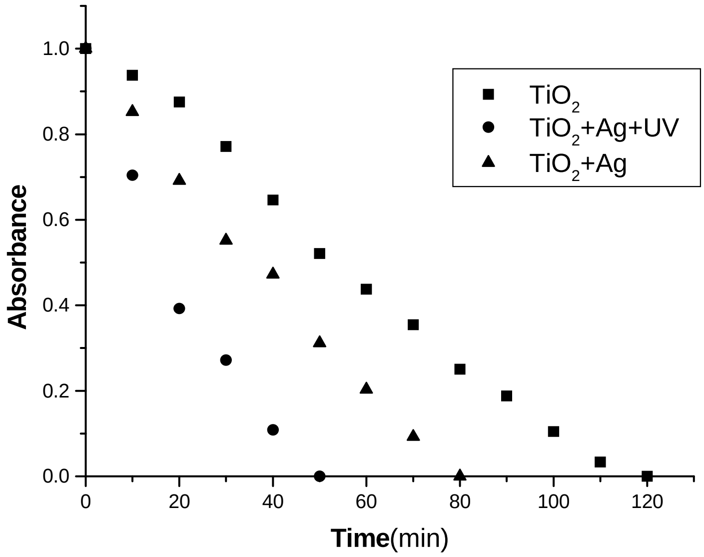

Fig.7b. Variation of absorbance of pure titania film, Ag-doped film with and without UV treatment.

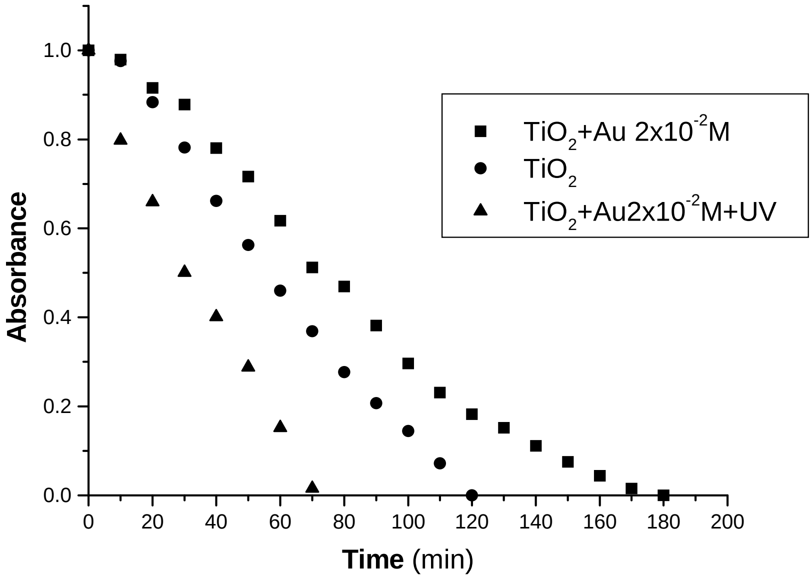

Fig.8. Variation of absorbance of pure titania film and Au-doped titania film with adsorbed BB as a function of illumination time with visible light. The three curves correspond

to three films: pure titania, Au-doped titania ($2x10^{-2}$M) with and without UV treatment.

Fig. 7 and 8 shows that it takes about two hours to photodegradate all adsorbed dye on pure TiO_2 films. Photodegradation diminishes with non-treated silver doped films and is limited to only 50 minutes when the films are previously treated with UV-radiation. The spectrum of this film can be seen in fig. 7a. In the case of Au, a markedly different behavior was observed. Non-treated Au-doped films decrease photodegradation efficiency, increasing photodegradation time from 2 hours, for pure TiO_2 films, to 3 hours, for untreated doped films. On the contrary, Au-doped films, previously treated with UV radiation decreased photodegradation time to 70 min. The Cr-doped films have a different comportment (cf. fig. 9). The spectrum of these films can be observed in fig.10.

Non treated Cr-doped films increase photodegradation efficiency, decreasing photodegradation time from 2 hours for pure titania films to 40 minutes for untreated doped films. On the contrary, Cr-doped films previously treated with UV radiation increase photodegradation time to 80 minutes.

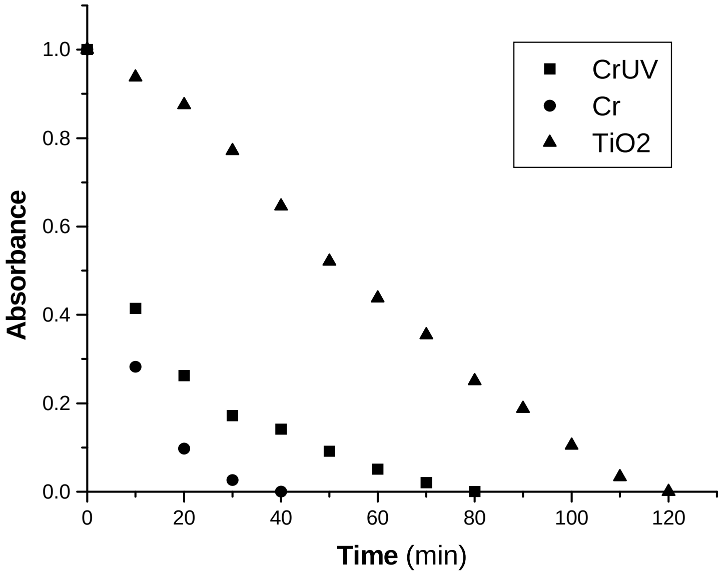

Fig.9. Variation of absorbance of pure titania film and Cr-doped titania films before and after UV treatment.

As already discussed in the introduction, silver doping of titania has beneficial effects on its photocatalytic activity owing to the existence of three mechanisms that may function separately or jointly. Metal particles created by silver ion reduction act as electron scavengers aiding electron-hole separation, dipole moment increase in the vicinity of metal particles also facilitates electron excitation and e^- - h^+ separation and silver dopants may structurally modify titania increasing its photocatalytic activity[8-10]. The enhancement of photocatalytic efficiency after UV irradiation is due to the creation of metal centers in the film, owing to reduction by electrons in the conduction band of the semiconductor. It was adopted the above model accepted for silver impurities. Titania absorbs UV-radiation, as can be seen fig. 5. Absorption of UV photons excites a large number of electrons, which can reduce Ag^+, Cr^{+3}, K^+ and Au^{+3}. Of course metal colloidal particle formation by reduction of the cationic species is easier in the case of the monovalent ions than in the case of the trivalent ions. For this reason only 15 minutes of UV-illumination are necessary to transform silver-doped films but it takes about 1 h in the case of trivalent ions-doped films. It is most probable that a large portion of silver ions are reduced during heating of the film, even before UV illumination, therefore the presence of silver always speeds up photodegradation. When silver or Au ions are incorporated into titania, they create traps, which aid electron-hole recombination and inhibit photodegradation[22]. This is obvious in the case of Au, the presence of which, before reduction by UV-treatment, largely decreases photodegradation rate (Fig. 8). This is not detected in Ag^+-doped films, since silver is easily reduced, so it acts to increase photodegradation rates even before UV-treatment (fig. 7). When the film was illuminated by UV-light, the electrons liberated by direct absorption of photons by titania eliminate these sites by reduction of silver ions. Whether silver metal particles are created is hard to say, since their density might be too small to be spectroscopically detected by plasmon resonance

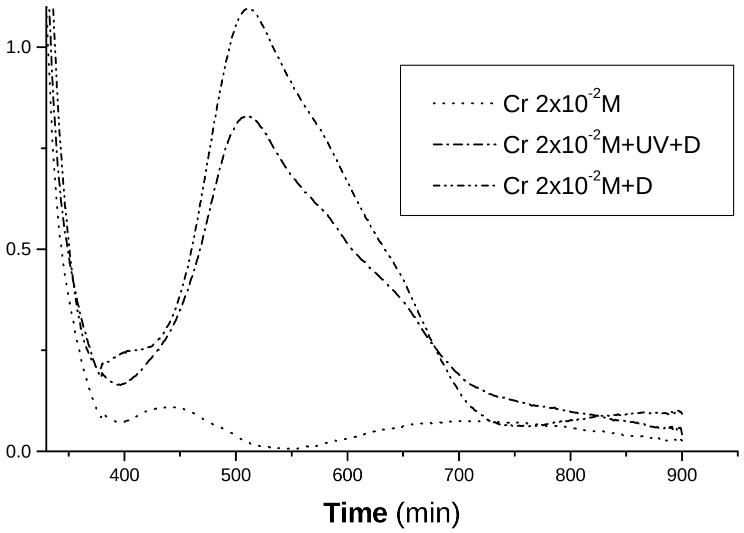

Fig.10. Absorbtion spectrum of Cr-doped titania film. The three curves correspond with the films made with the same reverse micellar solution doped with Cr^{+3} without the dye, with the dye and with UV treatment and after adsorbed the dye.

absorbtion[15]. UV treatment of the Au containing films gives dramatic effects on photocatalytic efficiency.

The influence of dopant ion concentration can be observed for some films. For Ag-doped titania films the photodegradation time decrease with the increase of dopant ion concentration for the same conditions of preparation. The absorbance spectrum can be observed in fig. 11.

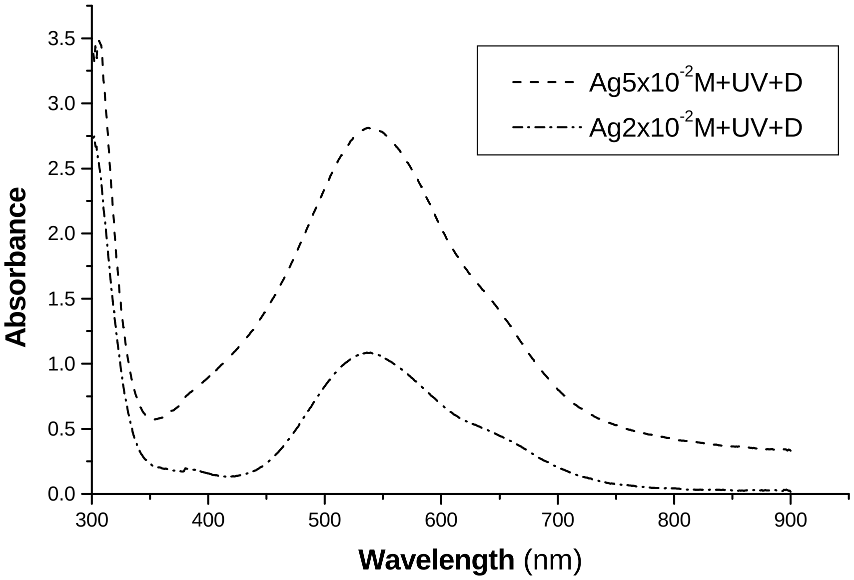

Fig.11. Absorption spectrum of Ag-doped films made at a different concentration of dopants on and after UV treatment.

The maximum of absorbance is three times greater for Ag $5x10^{-2}M$ than for Ag $2x10^{-2}M$. The quantity of BB adsorbed on doped film with Ag $5x10^{-2}$ is high, thus the film are much more efficient for the dye photodegradation.

K-doped titania films have a different comportment and the spectrum can be seen in fig. 12. All the films are made in the same conditions. The nanoparticles' size is bigger for low K^+ concentration.

Conclusion

The above mesoporous films are efficient photocatalysts for the degradation of adsorbed BB. More dye is adsorbed on films made with smaller titania nanoparticles but faster photodegradation rates are obtained with larger nanoparticles. More dye is also adsorbed on thicker films but thickness grows at the ex- pense of transparency. The reverse micellar route in combination with the sol-gel procedure can be successfully employed to optimize the efficiency of these films. Films doped with silver ions are very efficient photocatalysts when they are treated with UV radiation, i.e. when the ionic species are reduced. Films doped with silver and chromium ions, incorporated through the reverse micellar route, are more efficient photocatalysts than pure titania film. Films doped with gold ions are worse photocatalysts but when they are treated with UV-radiation, they also become more efficient photocatalysts than pure titania films.

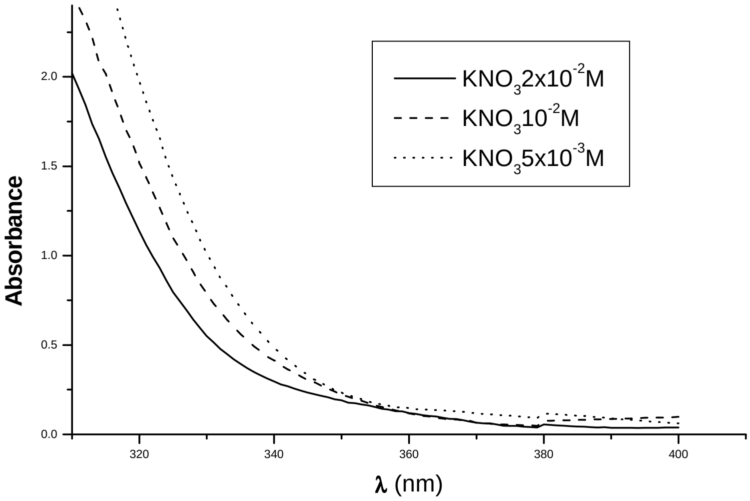

Fig.12. Absorption spectrum of three K-doped titania films made at different concentrations of dopant ion. The three curves correspond to three films prepared in the same conditions but at different concentrations of K-dopant: $5x10^{-3}$M, 10^{-2}M, and $2x10^{-2}$M.

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