***Materials Sciences and Applications*, 2011, 2, 564-571**
doi:10.4236/msa.2011.26075 Published Online June 2011 (http://www.SciRP.org/journal/msa)

TiO$_2$/CuO Films Obtained by Citrate Precursor Method for Photocatalytic Application

Leinig Perazolli[1*], Luciana Nuñez[1], Milady Renata Apolinário da Silva[2*], Guilherme Francisco Pegler[1], Ademir Geraldo Cavalarri Costalonga[1], Rossano Gimenes[2], Márcia Matiko Kondo[2], Maria Aparecida Zaghete Bertochi[1]

[1]Microwave Sintering and Photocatalysis Laboratory, Instituto de Química de Araraquara, Univ Estadual de São Paulo, Araraquara, Brazil; [2]UNIFEI-Federal University of Itajubá, Itajubá, Brazil.
Email: leinigp@iq.unesp.br, milady@unifei.edu.br

Received February 5th, 2011; revised March 20th, 2011; accepted April 12th, 2011.

ABSTRACT

In the present work, the hybrid catalyst films of TiO$_2$/CuO *containing up to* 10% *in mol of copper were deposited onto glass surface. Precursor solutions were obtained by citrate precursor method. Films were porous and the average particle size was* 20 nm *determined by FEG-SEM analysis. The photocatalytic activities of these films were studied using Rhodamine B as a target compound in a fixed bed reactor developed in our laboratory and UV lamp. It was observed that the addition of copper to* TiO$_2$ *increased significantly its photocatalytic activity during the oxidation of Rhodamine B. The degradation exceeded* 90% *within* 48 *hours of irradiation compared to* 38% *when pure* TiO$_2$ *was used. Moreover, there was a reduction in the particles band gap energy when compared to that of pure* TiO$_2$*. These results indicate that the* TiO$_2$/CuO *films are promising catalysts for the development of fixed bed reactors to be used to treat effluents containing azo dyes.*

Keywords: *TiO$_2$/CuO, Citrate Precursor Method, Thin Film, Rhodamine B, Photocatalytic Oxidation*

1. Introduction

The contamination of potable water supplies is one of the major problems that has drawn global attention. As a consequence of the growing global industrialization the water quality of rivers and reservoirs is compromised, mainly as a result of the complex nature of the industrial pollutants that are being released to the environment, in addition to the deficiency of domestic sewage treatment [1].

Because of the great amount of organic contaminated effluent generated and disposed without treatment, the textile industry can have a negative impact to the environment [2]. The problem continues even with the inappropriate disposal of dyes and pigments considered non toxic. These compounds when discharged in superficial water tend to inhibit the passage of solar light, leading to the reduction of the local biodiversity. Approximately 60% of the dyes used worldwide belong to the family of azo dyes (azo group, –N=N–), which in combination with other chromophoric groups promote their colors [3]. Nonetheless, the main problem is the presence of the groups of toxic chemical substances in the composition of these dyes, which are mostly carcinogenic and mutagenic [4,5]. The majority of azo dyes are toxic and non biodegradable, which inhibit or make it difficult to use biological treatment processes [6-8]. For this reason, there has been a constant search for more efficient, innovative, and less costly technologies for the treatment of industrial effluents.

Several researchers have investigated the mineralization of organics using Advanced Oxidative Processes (AOPs), in which the majority of these contaminants can be degraded into CO$_2$, H$_2$O and inorganic anions. These degradations are possible due to the reactions that include transitory oxidative species, mainly hydroxyl radicals [9]. These radicals present a oxidation potential of 2.8 V, that is only lower than that of fluorine which is 3.03 V [10].

Among AOPs, TiO$_2$ heterogenous photocatalysis has been successfully employed to destroy numerous classes of organic compounds [11], and also as a biocide agent [12-14]. This process was used initially by Pruden and Ollis [15,16] to degrade chloroform and trichloroethylene, which were totally mineralized by ultraviolet radiation in the presence of TiO_2.

The semiconductors, such as TiO_2, in their fundamental state do not present a continuous level of energy, and therefore they do not present electrical conductivity. However, when irradiated with photons with the same or higher energy of the band gap (3.2 eV), an electronic excitation occurs and the electron can be promoted from the valence band to the conduction band, thereby generating the electron/hole pair (e^-/h+) [17]. The photogenerated e^-/h+ pair can either recombine to release heat, or make their separate ways to the surface of TiO_2, where they can react with the adsorbed species on the catalyst, inducing the degradation of these substances.

The anatase form of TiO_2 is widely used, mainly due to its properties that include higher photosensibility, non-toxic nature, band gap value considered ideal for use with ultraviolet radiation in the germicidal range of 254 nm to solar light, elevated chemical stability, relatively lower cost, and it can also be optimized using dopants [18,19]. The TiO_2 can be employed in suspension or with some kind of support, normally prepared by the sol-gel process [20,21]. However, the Pechini method [22] can also be used. This method uses polymeric precursors of citrate as well as ethylene glycol, which can facilitate the homogeneous distribution of cations in the crystalline structure and the acquisition of the thin films.

In despite of the wide use of TiO_2, several modifications have been proposed in the surface and/or structure trying to increase the photocatalytic efficiency of this semiconductor. Its combination with other semiconductors such as CdS, WO_3, SnO_2, including its doping with different metals have been largely studied [23-28]. Moreover, there have also been reports related to the combination of CuO with TiO_2 [29-31] and the main reason for such combination was the possibility to obtain a potential increase in the photocatalytic efficiency, especially when visible light is used [32-35].

In order to evaluate the photocatalytic activity of TiO_2/CuO binary system films, obtained by citrate precursor method, the present work studied the Rhodamine B degradation as the central parameter. Rhodamine B, which belongs to the dyes family known as fluorides, is an organic molecule considered to be very stable that does not suffer degradation with visible light, and therefore can be used in pulsed dye lasers.

2. Experimental

2.1. Chemicals

The reagents used in this study were 97% titanium isopropoxide; citric acid P.A., titanium citrate P.A. and copper nitrate P.A. purchased from Aldrich. Extran®, polyethylene glycol (PEG 20000) P.A. from Merck. Rhodamine B and ethylene glycol P.A. were purchase from Synth.

2.2. Catalyst and Film Preparation

Titanium isopropoxide, citric acid and ethylene glycol were used in the molar rations of 1:4:16. Ethylene glycol was heated to 60˚C under magnetic stirred and titanium isopropoxide was added the agitation until the solution become clear. Then, the citric acid was added and the temperature was raised to 90˚C under magnetic stirred for 120 minutes. Copper nitrate was dissolved in deionized water and added drop wise into the aqueous solution of titanium citrate. TiO_2/CuO catalyst with molar rations of 90/10 and 95/05 were obtained by the citrate precursor method. The precursor solution was magnetically stirred and heated at 110˚C. The pH was around 5 - 6 and in this pH the precipitation of titanium and copper salts was avoid. Ethylene glycol was added to start the polysterification reaction and the solution was stirred and heated for two hours. After cooling the solution 1 mL of Extran® and polyethylene glycol (PEG 20000) were added in a proportion of 80% w/w in relation to the expected mass of oxide. These solutions was deposited onto borosilicate glass surface using a spin coating technique (NS-400B-6NPP/LITE/10K model, Laurell Technologies) and it was thermally treated at 600˚C during 90 min, using a heating ration of 1˚C·min^{-1}. In order to compare the results and evaluated the influence of Cu, solutions of TiO_2 without Cu was prepared and deposited in the same way of TiO_2/CuO.

Crystalline phases of films were analyzed by X-Ray diffraction (Rigaku 2000 X-ray Diffractometer, $2\theta = 20$ to 80 degrees, step scan at 0.2 s^{-1}). Thickness and morphology of films were observed by scanning electron microscopy of field emission FEG-SEM (ZEISS™ FEG-UP Supra 35) and ultraviolet-visible region absorption on UV-vis spectrometer (Varian 5G).

2.3. Photocatalytic Reactor

The photocatalytic reactor was developed in our laboratory according to illustration of **Figure 1**. The system, *i.e.* beaker, catalyst supported film, silicone tubes, and pump were assembled into a closed box in order to avoid the entrance of external light during the degradation experiment. The beaker containing 50 mL solution of 0.01 mM Rhodamine B was placed inside the box. The solution was forced to flow from the top to the bottom of the oxide film by the pump and recycled at 20 mL·min^{-1} flow rate. The system was irradiated by germicidal ultraviolet light of 9 W, with maximum wavelength of 254 nm and a film exposition area of 12 cm^2. Samples of 2 mL solution were withdrawn taking into account the irradiation exposure time. The absorbance spectrum, in the range of

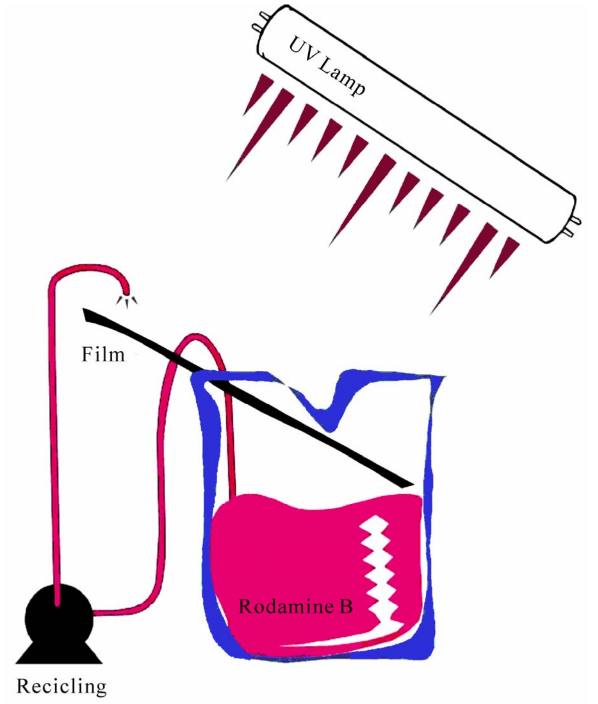


Figure 1. Reactor illustration for the study of Rhodamine B decomposition using TiO_2-CuO where a glass plate was used as a support. The recycle flow was 20 mL·min^{-1}.

300 to 700 nm, was obtained using a spectrophotometer UV-vis. Control experiments were also carried out irradiating the Rhodamine B solution using glass plate with films of pure TiO_2 as well as without the catalyst, placed under similar conditions to that of the TiO_2 film doped with Cu.

3. Results and Discussion

3.1. Films Characterization

3.1.1. X-Ray

The X-ray diffractograms of the pure TiO_2 and the films with 5 and 10 mol% of CuO are presented in **Figure 2**. The diffractograms allow only the identification of the anatase phase of TiO_2 by the presence of the peak (101) in $2\theta = 25.4^\circ$, which was observed for all the three compositions under study. The presence of CuO seems to favor the crystallization of anatase phase, since the FWHM of (101) peak narrows, as observed in **Figure 2**, for both TiO_2/CuO films.

3.1.2. Field Emission Scanning Electron Microscope (FEG-SEM)

Based on the analysis of the micrographic images of the pure TiO_2 and the films doped with 5% and 10% mol of CuO (**Figure 3**), it was possible to verify the morphology and its thickness, as well as the average size of their particles. The morphology of the films was homogeneous and appears almost spherical particles, with presence of porous forming a high porosity surface, which can enhance the catalytic activity of the films. Analyzing the results showed on the **Table 1** it is clear that the pure TiO_2 film is thicker than TiO_2/CuO films. This characteristic is due to the higher viscosity of precursor solution of the Ti than that of the Ti-CuO, since for the last ones, the solutions were diluted in order to guarantee the cooper ions stability.

Zhang [36] suggested that the optimum particle size is within the range of 11 - 21 nm to be a good photocatalyst. When the particle size is below the range of 5 - 10 nm, the surface recombination of electron-hole pairs was found to be significant, thus, leading to low photocatalytic efficiency. The present work showed particle size of 15 nm to the pure TiO_2 and 20 nm to the TiO_2/CuO. Those values are similar to the particle size of the P-25 Degussa, 20 nm, as calculated by Tseng [29]. These results suggest that it is possible to synthesize powders and films from the citrate precursor method, obtaining average sizes of ideal particles for the application in photocatalysis.

3.2. Rhodamine B Degradation

The UV-vis absorption spectra of the degradation of the Rhodamine B solutions using pure TiO_2 films are presented in **Figure 4**. It was observed that the Rhodamine B presented a maximum absorption peak within the region of 550 nm. This band was used as an indication of Rhodamine B degradation comparing the decrease of its absorption during irradiation with the initial absorption in each system. The reduction occurred due to the catalytic activity of the pure TiO_2 film.

Figure 5 illustrates the absorption decrease, at 550 nm of the Rhodamine B solutions, during exposition time

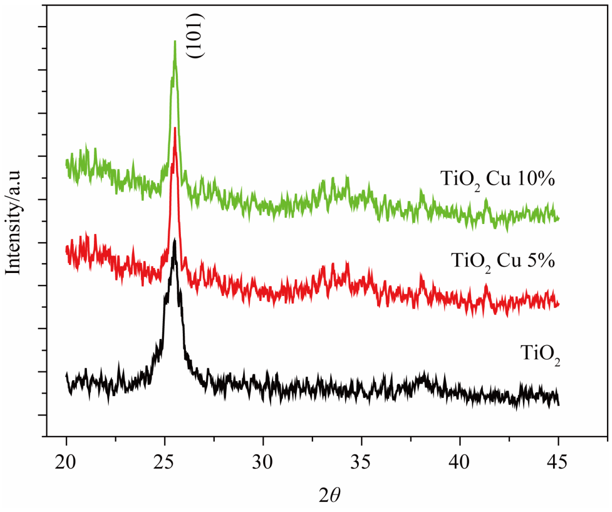
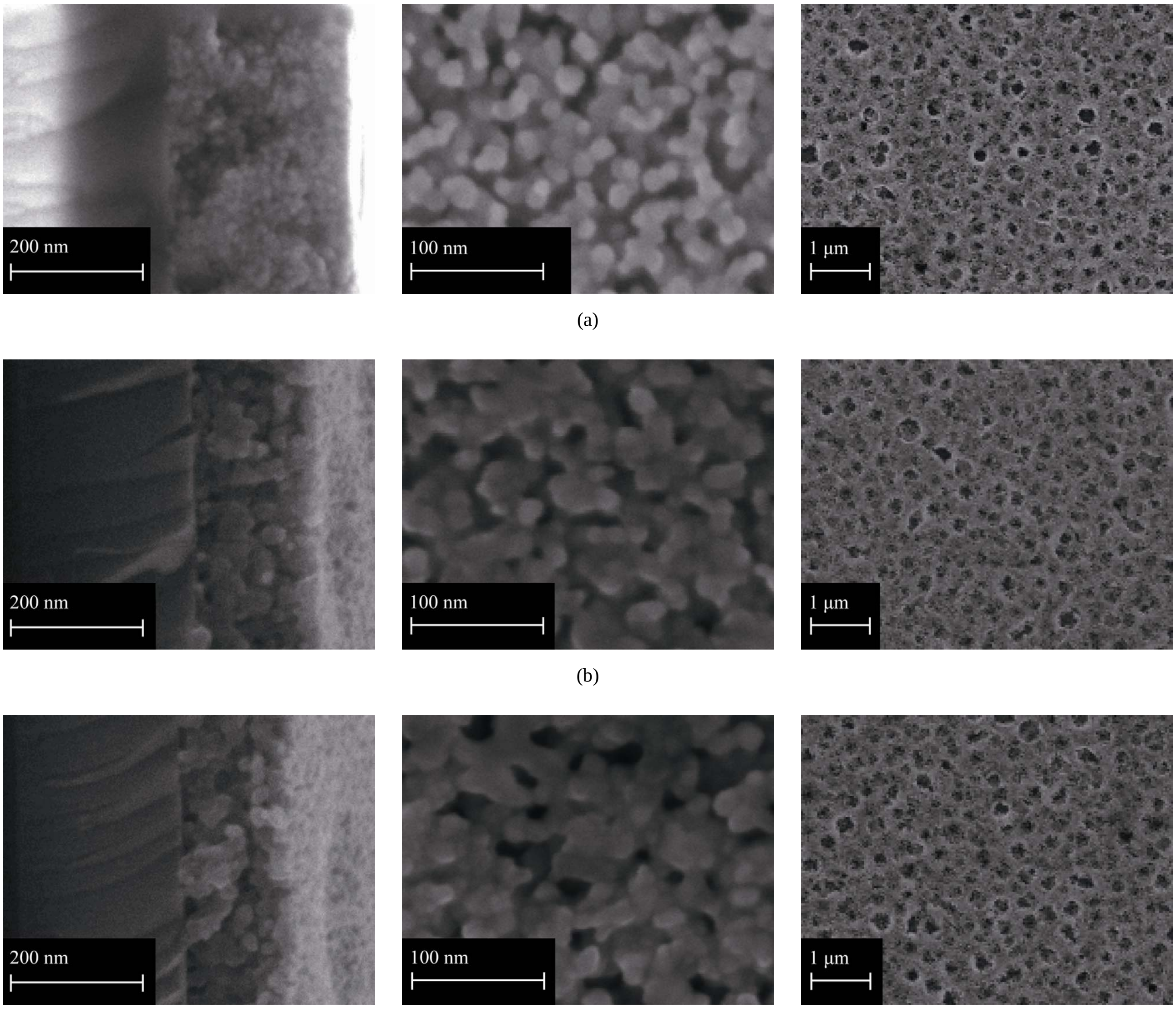


Figure 2. X-ray diffractograms of TiO_2-films doped with Cu.



(a)

(b)

(c)

Figure 3. Micrographs of FEG-SEM of TiO_2-films obtained by citrate precursor method: (a) Pure TiO_2 films; (b) TiO_2-CuO 5 mol%; (c) TiO_2-CuO 10 mol%.

Table 1. Thickness and particle size of TiO_2 films obtained by citrate precursor method.

Material	Thickness (nm)	Average Particle Size (nm)
TiO_2	269 ± 7	15 ± 2
TiO_2 CuO 5%	180 ± 7	20 ± 2
TiO_2 CuO 10%	183 ± 7	20 ± 2

using different photocatalytic systems. It can be observed that after 48 hours, the decrease in the absorbance of the irradiated solutions using pure TiO_2 films reached about 38%. This result confirms the film activity, considering that the direct photolysis of Rhodamine B reached only 17% within the same irradiation time (data not shown). When TiO_2/CuO films were employed as catalysts, it was observed a decrease of nearly 50% of Rhodamine B concentration after 12 and 10 hours of irradiation, using 5 and 10% of copper on TiO_2 films, respectively. In addition, after 48 hours of irradiation, there was a decrease in absorption of 90% and 94% in 550 nm for TiO_2 films containing 5 and 10% of copper, respectively. However, the increase of CuO from 5 to 10% in the TiO_2 film did not lead to any significant increase in the film photoactivity to the degradation of Rhodamine B.

Nonetheless, analyzing the obtained results in the absorption spectrum and taking into account the low flow

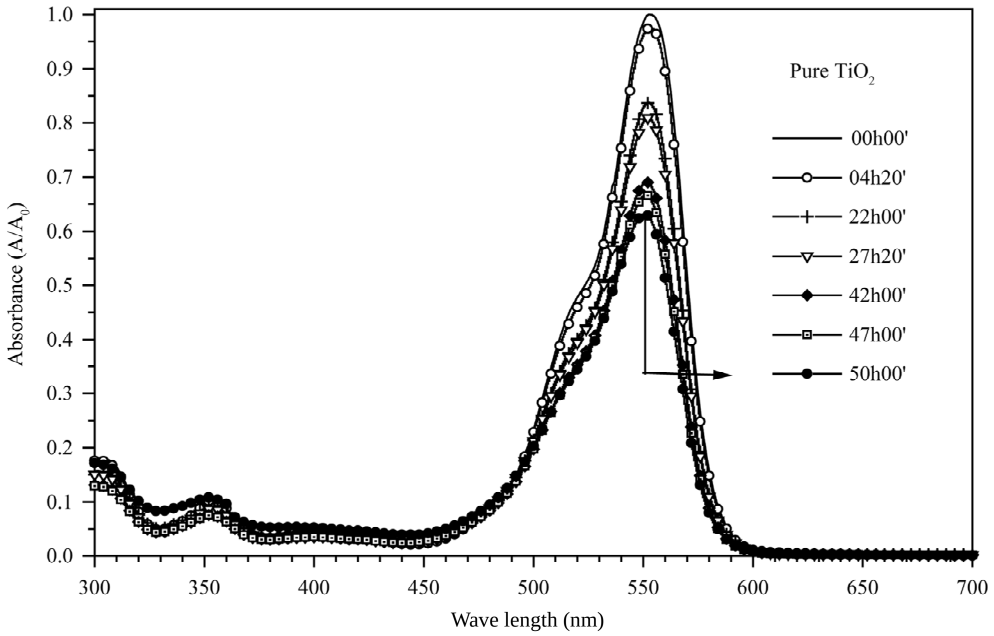


Figure 4. Absorption spectrum obtained for Rhodamine B solutions considering the exposition time under ultraviolet light within the interval of 300 to 700 nm using pure TiO$_2$-films.

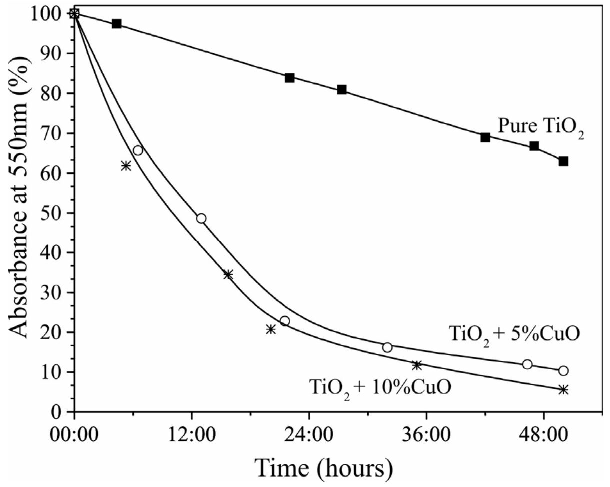


Figure 5. Comparison between the decrease in absorption values of Rhodamine B in λ = 550 nm as a function of time under ultraviolet light for pure TiO$_2$-films, TiO$_2$ + 5% and + 10% CuO.

rate of the solution over the film surface, combined with the small area of exposition used in the experimental studies, it can be observed that TiO$_2$ films doped with 5 and 10% of copper presented a relatively good photocatalytic performance.

The increase observed in the photoactivity is probably due to the coupled structures, in which the illumination of one of the semiconductors produces a response in the other, or at the interface between the two, as observed for the CdS/TiO$_2$ coupled structure particles [31,37]. This mechanism can probably be used to explain the photocatalytic increase of the TiO$_2$/CuO system. Given the difference between band gap energy of the TiO$_2$ (3.2 eV) and of the CuO (2.8 eV) [38], it can be suggested a reduction in the band gap energy of the coupled structure TiO$_2$/CuO, which could lead to an increase in the quantity of the electron/hole formation and recombination.

3.3. Band Gap Energy Calculation

The band gap energy of the obtained powders was calculated by the remission function of Kubelka-Munk [39]. After analyzing **Figure 6**, that present the diffuse reflective absorption spectra acquired in the remission function of Kubelka-Munk mode, and extrapolating its results with the Tauc [40] graphic, the following results were attained for the powders; 3.18 eV and 2.80 eV for TiO$_2$/CuO 5 mol% and TiO$_2$/CuO 10 mol%, respectively, and from literature 3.28 eV for pure TiO$_2$ [38]. These results indicate the reduction of the band gap energy with the addition of CuO to TiO$_2$.

The formation of this structure can be a result of the low sintering temperature that was used during thermal treatment of the films (600˚C). The Cu loading presented here suggest a different coupling of the Cu in the TiO$_2$ matrix for this particular synthesis compared with the one present in the previous publications where the maximizing efficiency were 2% or lower of Cu loading [29,30]. The integration of Cu into the TiO$_2$ matrix is critical for this photocatalytic behavior. Diffusion of Cu cations on the surface of TiO$_2$ particles can be suggest

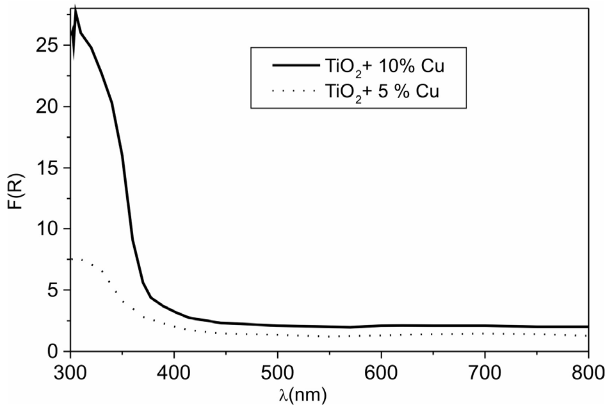


Figure 6. Remission function of Kubelka-Munk [39] of the TiO_2/CuO powders obtained by citrate precursor method.

due to the likely slight narrowing on (011) reflection of anatase phase observed when Cu content increases (**Figure 2**). The solid solution formed can stress the crystallites on the particle surface, and resulting in the changes of (001) peak. In addition, since there is a difference of two electrons between Ti and Cu on the valence band, there is a possibility of the formation of two electronic holes with a typical behavior of a type P semiconductor (Equation (1)). It can lead to increase the photoactivity of the coupled structure CuO/TiO_2.

$$\mathrm{CuO} \xrightarrow{\mathrm{TiO_2}} \mathrm{Cu}''_{\mathrm{Ti}} + V_O^{\bullet\bullet} + O_O^x \qquad (1)$$

3.4. Kinetics Studies of Rhodamine B Degradation

In the study of the reaction kinetics for the discoloration of Rhodamine B, the Langmuir-Hinshelwood (L-H) kinetics model [41] was adopted:

$$r = -\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{kKC}{1+KC} \qquad (2)$$

where C is the Rhodamine B concentration at time t, k is the constant rate of reaction ($\mathrm{ppm \cdot min^{-1}}$), and K the absorption coefficient. Integrating the Equation (2) it results in Equation (3):

$$t = \frac{1}{Kk}\ln\left(\frac{C_0}{C}\right) + \frac{1}{k}\left(C_0 - C\right) \qquad (3)$$

Considering that the concentrations obtained were small, the second term of the Equation (3) can be withdrawn, hence we have Equation (4):

$$\ln\left(\frac{C_0}{C}\right) \cong kKt = k't \qquad (4)$$

k' is the constant rate of the apparent reaction ($\mathrm{min^{-1}}$).

The k' values obtained were: 0.22; 1.07; and 1.45 $\mathrm{min^{-1}}$ for the experiments in the following sequence: control; pure TiO_2; TiO_2/CuO 5 mol%; and TiO_2/CuO 10 mol%. The increase in the k' values was attributed to an increase in the photochemical activity of the films, indicating that CuO is enhancing the photoactivity of the TiO_2 according to the L-H model [41].

Also, the higher degradation activity of TiO_2/CuO films than pure TiO_2 can be attributed to the morphological structure of films, since it is clear analyzing the FEG micrographs (**Figure 3**) that TiO_2-CuO films shows biggest and irregular particles when compared with particles on the pure TiO_2 films, that present more regular, compacted and higher thickness than TiO_2/CuO films (**Table 1**). Then, the Rodhamine solution probably remains in contact with TiO_2/CuO films for extend time when compared with dense TiO_2 films. This fact based on structure of films and supported by the band gap energy differences can be explain the higher photocatalytic activity of TiO_2/CuO films.

One of the advantages in the development of photoactive films is the possibility to manufacture fixed bed photochemical reactors eliminating the inconvenience of post filtration procedure that is needed when the photocatalyst is used in the powder form.

4. Conclusions

In this study, TiO_2 films containing about 10% of CuO were obtained using Pechini method. The photocatalytic activity of these films was studied during the photodegradation of Rhodamine B solutions. It was observed that the photocatalytic activity of TiO_2 films increased with the addition of CuO, resulting in Rhodamine B removal up to 90% after 48 hours of irradiation. This increase in photoactivity can be attributed to the activity of CuO, reducing the band gap energy value of the hybrid system TiO_2/CuO on the surface and the morphology of this film that allows a better contact of the Rhodamine solutions with the catalyst. Furthermore, it can also due to the generation of electronic holes, with formation of solid CuO solution on the surface of TiO_2 particles. The increase in the photoactivity of TiO_2 film when doped with CuO is promising and thus allows further studies on the development of photoactive films for the production of fixed bed reactors.

5. Acknowledgements

The authors would like to thank FAPESP, FAPEMIG, CAPES and CNPq for the financial support.

REFERENCES

[1] T. da S. Pereira, J. A. V. Rocha, A. Duccatti, G. A. Silveira, T. F. Pastoriza, L. Bringuenti and V. M. F. Vargas, "Evaluation of Mutagenic Activity in Supply Water

at Three Sites in the State of Rio Grande do Sul, Brazil," *Mutation Research*, Vol. 629, No. 2, 2007, pp. 71-80. doi:10.1016/j.mrgentox.2006.12.008

[2] I. Arslan, A. I. Balcioglu and D. W. Bahneman, "Advanced Chemical Oxidation of Reactive Dyes in Simulated Dyehouse Effluents by Ferrioxalate-Fenton/UV-A and TiO_2/ UV-A Processes," *Dyes and Pigments*, Vol. 47, No. 3, 2000, pp. 207-218. doi:10.1016/S0143-7208(00)00082-6

[3] P. V. Vandeviver, R. Bianch and W. Verstraete, "Review: Treatment and Reuse of Wastewater from the Textile Wet-Processing Industry: Review of Emerging Technologies," *Journal of Chemical Technology and Biotechnology*, Vol. 72, No. 4, 1998, pp. 289-302. doi:10.1002/(SICI)1097-4660(199808)72:4<289::AID-JCTB905>3.0.CO;2-#

[4] V. S. Houk, "The Genotoxicity of Industrial-Wastes and Effluents: A Review," *Mutation Research*, Vol. 277, No. 2, 1992, pp. 91-138. doi:10.1016/0165-1110(92)90001-P

[5] M. A. Brown and S. C. Devito, "Predicting Azo Dye Toxicity," *Critical Reviews in Environmeantal Science and Technology*, Vol. 23, No. 3, 1993, pp. 249-324. doi:10.1080/10643389309388453

[6] N. Daneshvar, D. Salari and A. R. Khataee, "Photocatalytic Degradation of Azo Dye Acid Red 14 in Water: Investigation of the Effect of Operational Parameters," *Journal of Photochemistry and Photobiology A*, Vol. 157, No. 1, 2003, pp. 111-116. doi:10.1016/S1010-6030(03)00015-7

[7] F. P. van der Zee and S. Villaverde, "Combined Anaerobic-Aerobic Treatment of Azo Dyes—A Short Review of Bioreactor Studies," *Water Research*, Vol. 39, No. 8, 2005, pp. 1425-1440. doi:10.1016/j.watres.2005.03.007

[8] B. Y. Chen, "Understanding Decolorization Characteristics of Reactive Azo Dyes by Pseudomonas Luteola: Toxicity and Kinetics," *Process Biochemistry*, Vol. 38, No. 3, 2002, pp. 437-446. doi:10.1016/S0032-9592(02)00151-6

[9] R. Andreozzi, V. Caprio, A. Insola and R. Marotta, "Advanced Oxidation Process (AOP) for Water Purification and Recovery," *Catalysis Today*, Vol. 53, No. 1, 1999, pp. 51-59. doi:10.1016/S0920-5861(99)00102-9

[10] P. Wardman, "Reduction Potentials of One Electron Couples involving Free Radicals in Aqueous Solution," *Journal of Physical Chemical Reference Data*, Vol. 18, No. 4, 1989, pp. 1637-1723. doi:10.1063/1.555843

[11] R. F. P. Nogueira and W. G. Jardim, "Heterogeneous Photocatalysis and Its Environmental Applications," *Química Nova*, Vol. 21, No. 1, 1998, pp. 69-72. doi:10.1590/S0100-40421998000100011

[12] A. Mills, R. H. Davies and D.Worsley, "Water Purification by Semiconductor Photocatalysis," *Chemical Society Reviews*, Vol. 22, No. 6, 1993, pp. 417-425. doi:10.1039/cs9932200417

[13] K. Rajeshwara, M. E. Osugi, W. Chanmanee, C. R. Chenthamarakshana, M. V. B. Zanoni, P. Kajitvichyanukul and R. Krishnan-Ayera, "Heterogeneous Photocatalytic Treatment of Organic Dyes in Air and Aqueous Media," *Journal of Photochemistry and Photobiology C*, Vol. 9, No. 4, 2008, pp. 171-192. doi:10.1016/j.jphotochemrev.2008.09.001

[14] W. A. Jacoby, P. C. Maness, E. J. Wolfrum, D. M. Blake and J. A. Fennel, "Mineralization of Bacterial Cell Mass on a Photocatalytic Surface in Air," *Environmental Science and Technology*, Vol. 32, No. 17, 1998, pp. 2650-2653. doi:10.1021/es980036f

[15] A. L. Pruden and D. F. Ollis, "Photoassisted heterogeneous Catalysis—The Degradation of Trichloroethylene in Water," *Journal of Catalysis*, Vol. 82, No. 2, 1983, pp. 404-417. doi:10.1016/0021-9517(83)90207-5

[16] A. L. Pruden and D. F. Ollis, "Degradation of Chloroform by Photoassisted Heterogeneous Catalysis in dilute Aqueous Suspensions of Titanium-Dioxide," *Environmental Science and Technology*, Vol. 17, No. 10, 1983, pp. 628-631. doi:10.1021/es00116a013

[17] A. Fujishima and K. Honda, "Electrochemical Photolysis of Water at a Semiconductor Electrode," *Nature*, Vol. 238, 1972, pp. 37-38. doi:10.1038/238037a0

[18] A. Fujishima, X. Zhang and D. A. Tryk, "TiO_2 Photocatalysis and Related Surface Phenomena," *Surface Science Reports*, Vol. 63, No. 12, 2008, pp. 515-582. doi:10.1016/j.surfrep.2008.10.001

[19] S. Sakthivel, M. V. Shankar, M. Palanichamy, B. Arabindoo, D. W. Bahnemann and V. Murugesan, "Enhancement of Photocatalytic Activity by Metal Deposition: Characterization and Photonic Efficiency of Pt, Au and Pd Deposited on TiO_2 Catalyst," *Water Research*, Vol. 38, No. 13, 2004, pp. 3001-3008. doi:10.1016/j.watres.2004.04.046

[20] C. Guillard, B. Beaugiraud, J. Herrmann, H. Jaffrezic, N. Jaffrezic-Reault and M. Lacroix, "Physicochemical Properties and Photocatalytic Activities of TiO_2-Films Prepared by Sol-Gel Methods," *Applied Catalysis B*, Vol. 39, No. 4, 2002, pp. 331-342. doi:10.1016/S0926-3373(02)00120-0

[21] I. Kazuya; R. Sun, M. Toki, K. Hirota and O. Yamaguchi, "Sol-Gel-Derived TiO_2/Poly(Dimethylsiloxane) Hybrid Films and Their Photocatalytic Activities," *Journal of Physics and Chemistry of Solids*, Vol. 64, No. 3, 2003, pp. 507-513. doi:10.1016/S0022-3697(02)00357-8

[22] M. P. Pechini, US Patent, No. 3330697, 1967.

[23] N. Serpone, P. Maruthamuthu, E. Pelizzetti and H. Hidaka, "Exploiting the Interparticle Electron Transfer Process in the Photocatalysed Oxidation of Phenol, 2-Chlorophenol and Pentachlorophenol: Chemical Evidence for Electron and Hole Transfer between Coupled Semiconductors," *Journal of Photochemistry and Photobiology A*, Vol. 85, No. 3, 1995, pp. 247-255. doi:10.1016/1010-6030(94)03906-B

[24] K. Y. Song, M. K. Park, Y. T. Kwon, H. W. Lee, W. J. Chung and W. I. Lee, "Preparation of Transparent Particulate MoO_3/TiO_2 and WO_3/TiO_2 films and Their Photocatalytic Properties," *Chemistry of Materials*, Vol. 13, No. 7, 2001, pp. 2349-2355. doi:10.1021/cm000858n

[25] A. A. Ismail, I. A. Ibrahim, R. M. Mohamed and H. El-Shall, “Sol-Gel Synthesis of Titania-Silica Photocatalyst for Cyanide Photodegradation,” *Journal of Photochemistry and Photobiology A*, Vol. 63, No. 3, 2004, pp. 445-451. doi:10.1016/j.jphotochem.2004.01.017

[26] B. Pal, T. Hata, K. Goto and G. Nogami, “Photocatalytic Degradation of O-Cresol Sensitized by Iron-Titania Binary Photocatalysts,” *Journal of Molecular Catalysis A*: *Chemical*, Vol. 169, No. 1-2, 2001, pp. 147-155. doi:10.1016/S1381-1169(00)00549-5

[27] A. A. Ismail, “Synthesis and Characterization of Y_2O_3/Fe_2O_3/TiO_2 Nanoparticles by Sol-Gel Method,” *Applied Catalysis B*: *Environmental*, Vol. 58, No. 1-2, 2005, pp. 115-121. doi:10.1016/j.apcatb.2004.11.022

[28] Y. Wang, H. Cheng, L. Zhang, Y. Hao, J. Ma, B. Xu and W. Li, “The Preparation, Characterization, Photoelectrochemical and Photocatalytic Properties of Lanthanide Metal-Ion-Doped TiO_2 Nanoparticles,” *Journal of Molecular Catalysis A*: *Chemical*, Vol. 151, No. 1-2, 2000, pp. 205-216. doi:10.1016/S1381-1169(99)00245-9

[29] I.-H. Tseng, W. C. Chang and J. C. S. Wu, “Photoreduction of CO_2 Using Sol-Gel Derived Titania and Titania-Supported Copper Catalysts,” *Applied Catalysis B*: *Environmental*, Vol. 37, No. 1, 2002, pp. 37-48. doi:10.1016/S0926-3373(01)00322-8

[30] I.-H. Tseng and J. C.-S. Wu, “Chemical States of Metal-Loaded Titania in the Photoreduction of CO_2,” *Catalysis Today*, Vol. 97, No. 2-3, 2004, pp. 113-119. doi:10.1016/j.cattod.2004.03.063

[31] G. H. Li, N. M. Dimitrijevic, L. Chen, T. Rajh and K. A. Gray, “Role of Surface/Interfacial Cu_2 Sites in the Photocatalytic Activity of Coupled CuO TiO_2 Nanocomposites,” *The Journal of Physical Chemistry C*, Vol. 112, No, 48, 2008, pp. 19040-19044.

[32] H. Irie, K. Kamiya, T. Shibanuma, S. Miura, D. A. Tryk, T. Yokoyama and K. Hashimoto, “Visible Light-Sensitive Cu(II)-Grafted TiO_2 Photocatalysts: Activities and X-ray Absorption Fine Structure Analyses,” *The Journal of Physical Chemistry C*, Vol. 113, No. 24, 2009, pp. 10761-10766. doi:10.1021/jp903063z

[33] H. Irie, S. Miura, K. Kamiya, K. Hashimoto and K. Hashimo, “Efficient Visible Light-Sensitive Photocatalysts: Grafting Cu(II) Ions onto TiO_2 and WO_3 Photocatalysts,” *Chemical Physics Letters*, Vol. 457, No. 1-3, 2008, pp. 202-205. doi:10.1016/j.cplett.2008.04.006

[34] E. Vigil, F. A. Fernández-Lima, J. A. Ayllón, I. Zumeta, B. González, L. Curbelo, H. D. Fonseca Filho, M. E. H. M. da Costa, C. Domingo, M. Behar and F. C. Zawislak, “TiO_2-CuO Three-Dimensional Heterostructure Obtained Using Short Time Photochemical Deposition of Copper Oxide Inside a Porous Nanocrystalline TiO_2 Layer,” *Microporous and Mesoporous Materials*, Vol. 109, No. 1-3, 2008, pp. 560-566. doi:10.1016/j.micromeso.2007.06.004

[35] E. Vigil, B. González, I. Zumeta, C. Domingo, X. Doménech and J. A. Ayllón, “Preparation of Photoelectrodes with Spectral Response in the Visible without Applied Bias Based on Photochemically Deposited Copper Oxide Inside a Porous Titanium Dioxide Film,” *Thin Solid Films*, Vol. 489, No. 1-2, 2005, pp. 50-55. doi:10.1016/j.tsf.2005.04.098

[36] Z. Zhang, C.-C. Wang, R. Zakaria and J. Y. Ying, “Role of Particle Size in Nanocrystalline TiO_2-Based Photocatalysts,” *The Journal of Physical Chemistry B*, Vol. 102, No. 52, 1998, pp. 10871-10878. doi:10.1021/jp982948+

[37] A. Mills and S. Le Hunte, “An Overview of semiconductor Photocatalysis,” *Journal of Photochemistry and Photobiology A*: *Chemistry*, Vol. 108, No. 1, 1997, pp. 1-35. doi:10.1016/S1010-6030(97)00118-4

[38] A. R. West, “Solid State Chemistry and Its Applications,” Wiley, New Jersey, 1987.

[39] P. kubelka and F. Munk, “An Article on Optics of Paint Layers,” Zeitschrift fur̈ technische Physik, Vol. 12, 1931, pp. 593-609.

[40] J. Tauc and D. L. Wod, “Weak Absorption Tails in Amorphous Semiconductors,” *Physical Review B*, Vol. 5, No. 8, 1972, pp. 3144-3151. doi:10.1103/PhysRevB.5.3144

[41] I. K. Konstantinou and T. A. Albanis, “TiO_2-Assisted Photocatalytic Degradation of Azo Dyes in Aqueous Solution: Kinetic and Mechanistic Investigations: A Review,” *Applied Catalysis B*, Vol. 49, No. 1, 2004, pp. 1-14. doi:10.1016/j.apcatb.2003.11.010