

Effect of the In_2O_3 content on the photodegradation of the alizarin dye using TiO_2 - In_2O_3 nanostructured semiconductors

V. Rodríguez-González^{a,*}, F. Paraguay-Delgado^b, X. García-Montelongo^a, L.M. Torres-Martínez^a and R. Gómez^c

^aUniversidad Autónoma de Nuevo León, Facultad de Ingeniería Civil, Instituto de Ingeniería Civil, Depto. Ecomateriales y Energía, Ave. Universidad S/N, San Nicolás de los Garza, Nuevo León, C.P. 66451, México

^bCentro de Investigación en Materiales Avanzados S. C., Miguel de Cervantes 120, Complejo Industrial Chihuahua, C. P. 31109. Chihuahua, México

^cNational Institute for Nanotechnology, 11421 Saskatchewan Drive, Edmonton, T6G 2M9, Canada

^cUniversidad Autónoma Metropolitana-Iztapalapa, Departamento de Química/Av. San Rafael Atlixco No 186, Col. Vicentina, México 09340, D.F. México

The photocatalytic degradation of the synthetic red mordant dye alizarin on TiO_2 - In_2O_3 semiconductors as a function of the In_2O_3 content (1–12 wt%) was studied. High specific surface areas varying from 122 to 178 $\text{m}^2 \text{g}^{-1}$, depending on the In_2O_3 content, were obtained. A modification of the Eg band gap from 3.12 to 3.50 eV was obtained for low and high In_2O_3 contents. The XRD spectral patterns of the solids showed that anatase is the main crystalline titania phase. STEM-EDX chemical maps show that the In_2O_3 was found highly dispersed on the surface of the TiO_2 - In_2O_3 mixed oxide. By means of TEM images, nanostructured materials with crystallite sizes between 8 and 12 nm were identified. The photocatalytic activity for the alizarin degradation showed a maximum with the catalyst with 3.0 wt% of In_2O_3 . The role of the In_2O_3 developing an optimal alizarin adsorption on the TiO_2 - In_2O_3 semiconductors is discussed.

Key words: Alizarin photodegradation, TiO_2 - In_2O_3 nanosized semiconductors, Titania-indium STEM-EDX chemical map, Titania-indium sol-gel doping.

Introduction

The photo-oxidation of organic pollutants in aqueous media is one of the main applications of photocatalytic processes [1, 2]. Nowadays, all the research groups are focusing on preparing photocatalysts to work under visible light conditions [3]; however, in most cases, the visible light is not useful to degrade various dye intermediates formed during the photodegradation due to the fact that these intermediates do not absorb the actinic visible light radiation. In order to obtain the total decomposition of organic dye compounds, a simultaneous displacement of electrons and holes between the semiconductor and the metallic nanoparticles deposited on its surface was recommended [2, 4]. The doping effect by metals or metal oxides on semiconductors improving their photoactivity has been extensively reported [5, 6]. The enhanced activity of the doped semiconductors was explained by the electron-hole separation retarding their recombination as well as by the band gap shift to the visible spectrum range [7, 8]. However, a lack of information about the doping effects produced by an extended occupation of the doping agent of the semiconductor surface persists. The amount of the

doping compound on the semiconductor surface certainly became an important factor, which induced important changes on the adsorption of the organic compound on the semiconductor surface. Organic molecules such as alizarin red are molecules that remain strongly adsorbed on the semiconductor surface; and hence, their photo-oxidation is limited. A dilution of the adsorption sites can be induced when the doping agent is found highly dispersed on the semiconductor surface.

In the present study, the effect of variable amounts of In_2O_3 (1 to 12 wt%) as a doping agent on TiO_2 was analyzed. The semiconductors were prepared by the sol-gel method and characterized by nitrogen adsorption, XRD; and STEM-TEM and UV-Vis spectroscopies. The effect of the dopant concentration on the photoactivity was evaluated in the photodegradation of the alizarin red (1,2-dihydroxy-9-10-anthraquinone sulfonic acid); which is an important dye used in the textile industry.

Experimental

Preparation of Photocatalysts

The sol-gel In_2O_3 - TiO_2 mixed oxides were prepared using titanium (IV) butoxide (Aldrich 97%) and indium acetylacetonate (Chemat 98%) as precursors. To a solution containing distilled water and n-butanol, titanium butoxide and a solution containing indium acetylacetonate were

*Corresponding author:
Tel : 00 52 81 83 52 19 83 ext. 221
Fax: 00 52 83 76 04 77
E-mail: vicenrg@hotmail.com

simultaneously added. The quantity of co-gelled indium acetylacetonate was calculated to provide 1, 3, 5, 10 and 12 wt% of indium oxide in the titanium dioxide. The solution was maintained under reflux for 48 h until gelling. After gelling, the sample was dried in air at 70 °C for 12 h; and then calcined at 500 °C for 4 h using a heating rate of 2 K minute^{-1} . The samples were identified as TI X, where X denotes the indium oxide content.

Characterization of the $\text{TiO}_2\text{-In}_2\text{O}_3$ semiconductors

The physical adsorption of N_2 at -196°C using a Quantachrome 3B automatic instrument was used to measure the specific surface area. Before the nitrogen adsorption, the catalyst was out-gassed at 350 °C for 12 h to remove the adsorbed impurities. The Brunauer-Emmett-Teller method (BET method) was applied to calculate the specific surface area, while the Barrett-Joiner-Halenda method (BJH method) was used for the pore size distribution evaluation.

The titanium dioxide microstructure and the mean particle size were determined by transmission electron microscopy (TEM); and the chemical elemental distribution mapping by the scanning transmission electron microscopy-energy dispersive X ray spectroscopy (STEM-EDS) mode using a CM200 Philips microscope with an LaB_6 emission gun, and an accelerating voltage of 200 keV. The elemental composition was determined by EDS with an EDAX prime model fitted to the TEM. In order to prepare the materials for observation, the powdered samples were dispersed in ethanol and supported on holey-carbon-coated copper grids. The ultraviolet-visible (UV-Vis) spectra were obtained with a Varian Cary 100 UV-Vis spectrophotometer equipped with an integrating sphere. The reflectance spectra for the prepared catalysts were analyzed in the wavelength range of 200–800 nm. The band gap of the solids was calculated by linearization of the slope to the X axis (wavelength, nm) with the Y axis (absorbance) equal to zero. The XRD powder patterns of the calcined samples were recorded on a Brucker D8 Advance diffractometer using $\text{CuK}\alpha$ radiation (within the 2θ range going from 10° to 70°).

Photocatalytic decomposition of alizarin

The photocatalytic degradation of alizarin (Alizarin Red S, Aldrich 98%) was performed with a standard Pen-Ray UV lamp (UVP Products) with a typical λ intensity of 254 of 4,400 $\mu\text{W}/\text{cm}^2$. The photocatalytic tests were performed in a slurry reactor at room temperature. The quartz lamp was immersed in a cooled vessel containing the reactant solution consisting of 200 mL with 20 ppm of alizarin acid and 200 mg of catalyst. In order to achieve the saturation of dissolved oxygen; and to assure the adsorption of the alizarin molecule on the semiconductor, a flux of dry air was bubbled for 60 minutes (1 mL s^{-1}) before turning on the light source. The photoactivity degradation rate of the alizarin dye was performed by following the intensity of the main absorption band at

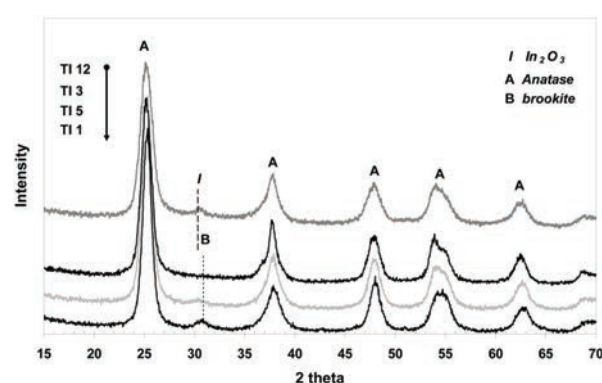


Fig. 1. XRD patterns of the $\text{TiO}_2\text{-In}_2\text{O}_3$ mixed oxides.

260 nm as a function of the irradiation time. Each sample was filtered through a 0.45 μm nylon filter; and monitored with a UV-Vis spectrophotometer. For the photocatalytic evaluation, rate drops of the solution were taken every 15 minutes.

Results and Discussion

The XRD patterns obtained for the various samples show the formation of anatase as the main crystalline phase (Fig. 1). It must be noted that no peaks identifying the presence of indium oxide, even in the samples containing 12 wt% of In_2O_3 , can be seen. The absence of indium oxide reflections can be taken as evidence for the formation of indium oxide with nanometric size, which is not detectable by XRD. In Fig. 1, a widening of the anatase peaks in the semiconductors with high indium oxide content can also be seen. This behavior indicates a diminution in the anatase crystallite size. By using the Scherrer equation, the anatase crystallite size was calculated from the (101) peak; and the values obtained are reported in Table 1. The average of the TiO_2 crystallite size ranged from 9 to 12 nm; where the small crystallite size corresponds to the samples containing the highest In_2O_3 content. We also observe analogous behavior by TEM as is shown in Fig. 2, where the grain size is on average 20 nm. By XRD calculations and TEM grain size determination there is accord. In the Fig. 2, we also show a high resolution image of the anatase titania crystalline phase. To confirm that the In_2O_3 particles are found as highly dispersed oxide particles on the titania surface, two-dimensional elemental distribution maps were

Table 1. Physicochemical characterization of the mixed oxide semiconductors

Semiconductor	BET (m^2/g)	Pore Size (nm)	Band-gap (eV)	Crystallite size (nm)
TI 1	178	3.10	3.16	12
TI 3	166	2.30	3.12	10
TI 5	122	3.10	3.16	12
TI 10	153	4.55	3.40	13
TI 12	174	2.70	3.50	9

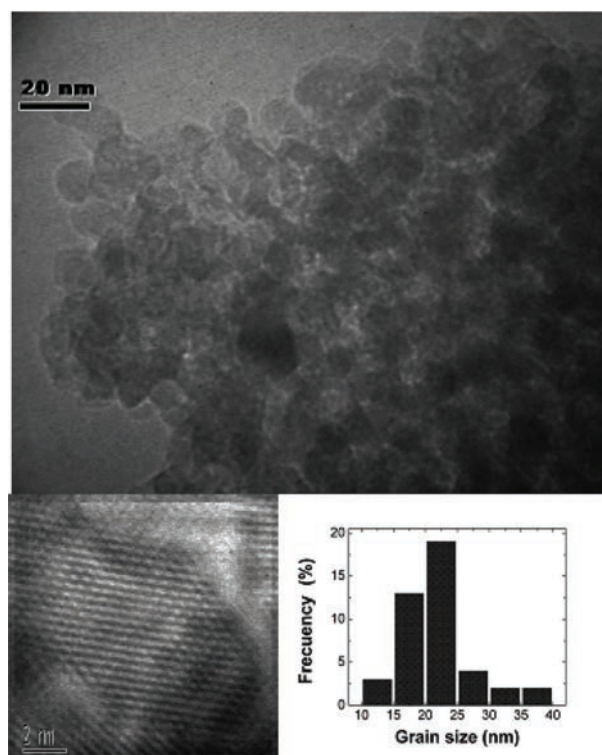


Fig. 2. TEM and HRTEM images for the TI 3 mixed oxide and grain size distribution.

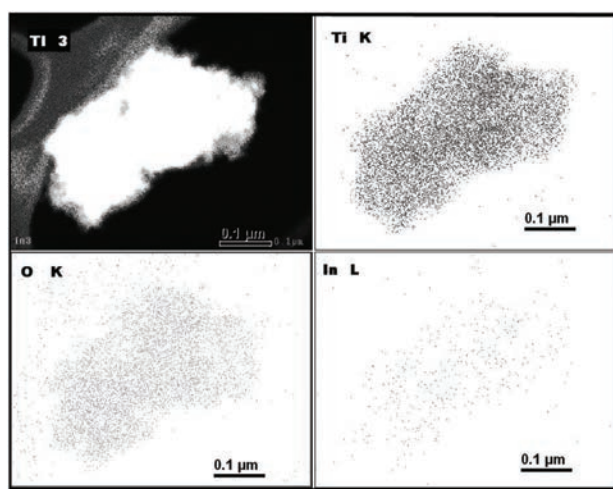


Fig. 3. Two-dimensional elemental distribution maps (STEM-EDS) for the TI 3 sol-gel semiconductor.

developed by means of the STEM-EDS analysis. The three elements present in the material can be visualized using inner-shell ionization edges In (3.29 eV), O (0.28 eV) and Ti (4.28 eV). Selected elemental maps were chosen to identify well dispersed indium oxide particles (Fig. 3). The elemental distribution maps for the TI 3 sample showed that In_2O_3 was found to be highly dispersed on the titania surface. The two-dimensional elemental distribution maps are also reported for the TI 12 mixed oxide (Fig. 4). The elemental distribution maps confirm that the indium oxide is highly dispersed even at contents as high as

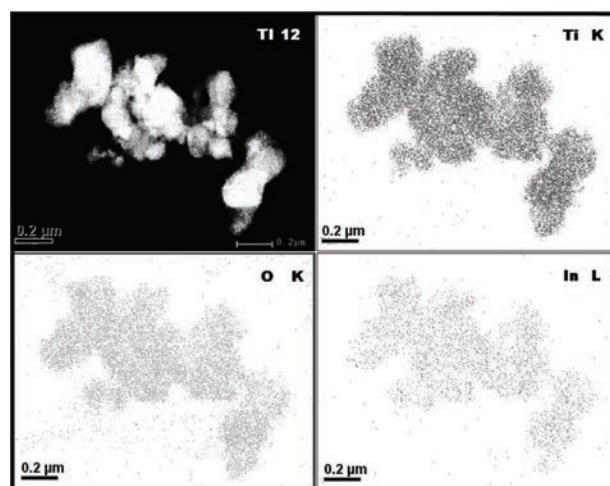


Fig. 4. Two-dimensional elemental distribution maps (STEM-EDS) for the TI 12 sol-gel semiconductor.

12 wt%. These results are in good agreement with the XRD patterns, where the indium oxide diffraction peaks cannot be seen. On the other hand, it has been reported that on indium-doped titania, some insertion of In^{3+} cations into the titania network can also occur [9, 10].

The specific surface area and the semiconductor properties were determined for the mixed oxides; and the calculated values for these materials are reported in Table 1, where high specific surface areas (122–178 m^2/g) for all the solids can be seen. High specific surface areas on In_2O_3 -doped titania has also been reported by Chandra Babu et al., when preparing the oxides by solid state sintering [11]. For the sol-gel indium-doped TiO_2 preparations, mesoporous materials with pore sizes ranging from 2.7 to 4.5 nm were obtained. On the other hand, the energy band gap, determined from the UV-Vis spectra of the semiconductors, showed a blue shift from 3.12 to 3.5 eV for the lowest and highest indium oxide content, respectively [12].

Photocatalytic decomposition of alizarin

The photocatalytic degradation in aqueous medium of the anthraquinone dye (Alizarin Red S) was investigated. The activity of the mixed oxides under UV-Vis light for the photodegradation of alizarin is reported in Table 2 as half life ($t_{1/2}$). All the semiconductors present a better performance than photolysis. In Fig. 5, the

Table 2. Kinetic parameters for alizarin photodegradation

Semiconductor	%C*	$t_{1/2}$ * (minute)
TI 1	81.82	15.00
TI 3	99.00	10.76
TI 5	90.20	19.97
TI 10	88.62	22.30
TI 12	81.82	26.35

* At $t = 75$ min 99% with TI 3

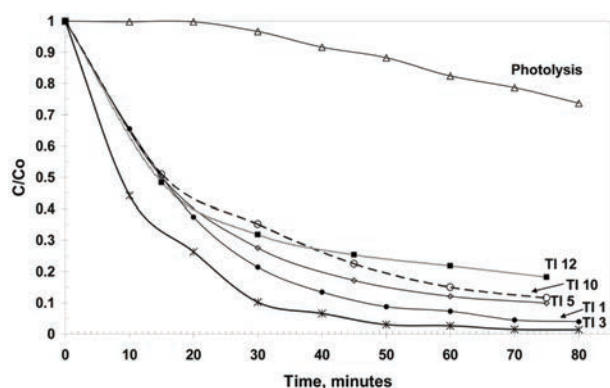


Fig. 5. Alizarin conversion as a function of time for the sol-gel indium-doped materials.

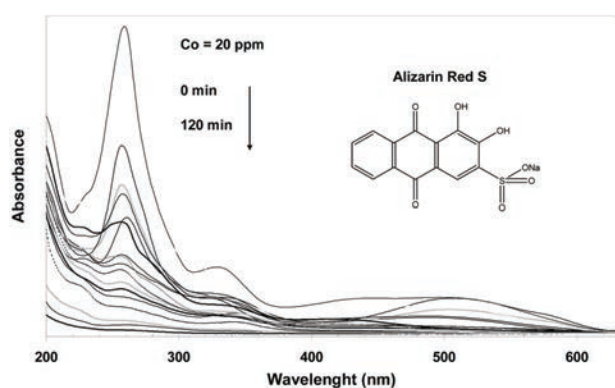


Fig. 6. UV-Vis spectra for the alizarin photodecomposition as a function of time on the $\text{TiO}_2\text{-In}_2\text{O}_3$ semiconductors.

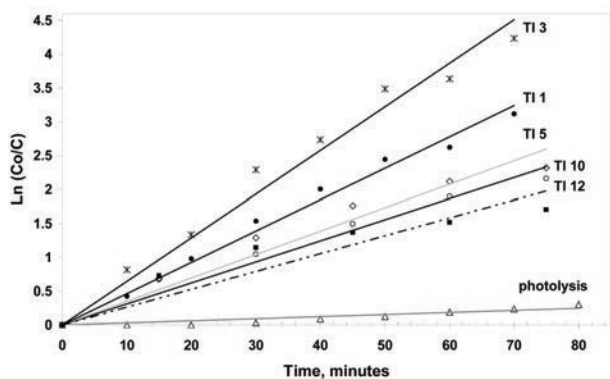


Fig. 7. Representation of the pseudo-first-order kinetics ($C_0 = 5.84 \times 10^{-5} \text{ mol L}^{-1}$) for the $\text{TiO}_2\text{-In}_2\text{O}_3$ semiconductors.

photodecomposition evolution of alizarin as a function of the time is shown. The chemical structure of the ARS dye and the principal band absorption are reported for illustration purposes in Fig. 6. The photodegradation of the organic dye molecule follows, approximately, a pseudo-first kinetic order, according to the Langmuir-Hinshelwood model, Fig. 7. The kinetic $t_{1/2}$ (half life) parameters for the photodegradation of alizarin red show a maximum in photoactivity. The sample with 3 wt% of In_2O_3 is the most active of all (Fig. 8). The indium oxide effect increasing the photoactivity of doped TiO_2 has also been reported on the aqueous UV photodecomposition

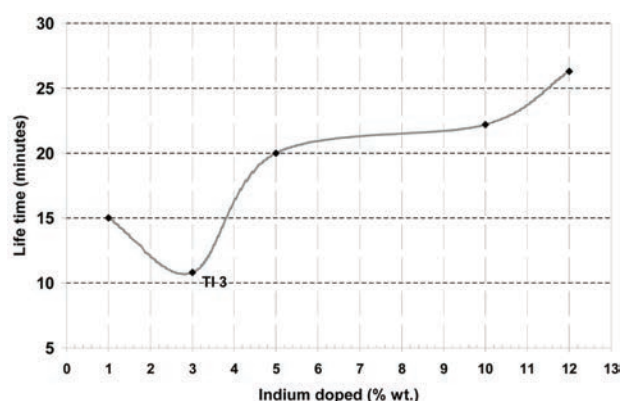


Fig. 8. Indium dope effect on the life time in the photodecomposition of alizarin.

of 2-chlorophenol [13] and for the herbicide 2,4-D [9].

The effect of the indium oxide content on the behavior of the $\text{TiO}_2\text{-In}_2\text{O}_3$ sol-gel prepared photocatalysts could be related to the alizarin adsorption on the surface of the solids. It has been reported that on P25 commercial titania, alizarin is adsorbed because of coulombic forces; and the adsorption of the dye on the surface was around 38% [14, 15]. As a consequence of the high concentration of alizarin on the P25 surface, the photodegradation was disturbed. Shchukin et al., [13] reported that the incorporation of indium oxide into titania allows a better separation of the photogenerated charge carriers, improving the oxygen radical formation; and hence, the photodegradation. In our $\text{TiO}_2\text{-In}_2\text{O}_3$ sol-gel photocatalysts, the adsorbed alizarin was spread over the titania surface avoiding a high concentration of the dye on the titania surface. This phenomenon occurs because the indium oxide was found on the titania surface as a highly dispersed nanostructured material; as has been shown by TEM-EDS. The agglomeration of adsorbed alizarin on the titania surface was then strongly diminished and the photogeneration of the OH free radicals initiates the photooxidation of the dye in the aqueous medium. The optimal concentration of In_2O_3 at which the best equilibrium between the alizarin adsorption and the OH radical formation is reached, seems to occur at around 3 wt%. These results show the major role that the indium oxide content in the doped titania plays in the photodegradation of organic compounds.

Conclusions

In the preparation of the $\text{TiO}_2\text{-In}_2\text{O}_3$ semiconductors by the sol-gel method, the main emerging conclusions are: i) anatase was the main crystalline titania phase; ii) indium oxide was found as highly dispersed conglomerates on the titania surface; iii) the co-gelling of titanium alkoxide and indium acetylacetonate produces $\text{TiO}_2\text{-In}_2\text{O}_3$ semiconductors with high specific surface areas; iv) the band gap values show a shift to the blue region of the UV-Vis spectra in the solids with high In_2O_3 content; v) the photoactivity for the alizarin degradation as a function of the In_2O_3

content showed a maximum at 3.0 wt%. A role of the indium oxide in inhibiting the absorption of the dye on the large extension of the surface area of the TiO₂-In₂O₃ sol-gel catalysts is suggested.

Acknowledgements

V.R.G. acknowledges Dr. Albino Moreno Rodríguez for his synthesis help. The authors want to thank M. Ruiz Gómez (XRD), W. Antunez (STEM-EDS), and J. Sergio Ramos Garza (BET-BJH) for their technical assistance.

References

1. K. Hashimoto, H. Irie and A. Fujishima, *J. Appl. Phys.* 44 (2005) 8269-8285.
2. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science* 293 (2001) 269-271.
3. S-C. Lee, C-W. Lee, S.C. Lee and J-S. Lee, *Materials Letters* 62 (2008) 564- 566.
4. V. Rodríguez, R. Zanella, G. del Angel and Ricardo Gómez, *J. Mol. Catal. A: Chemical* 281 (2008) 93-98.
5. K.Y. Jung, S.B. Park and S.-K. Ihm, *Appl. Catal. B: Environmental* 51 (2004) 239-245.
6. A. Orlov, D.A. Jefferson, M. Tikhov and R.M. Lambert, *Catal. Commun.* 8 (2007) 821-824.
7. V. Keller and F. Garin, *Catal. Commun.* 4 (2003) 377-383.
8. S-M. Chiu, Z-S. Chen, K.-Y. Yang, Y.-L. Hsu and D. Gan, *J. Matls Processing Techn.* 192-193 (2007) 60-67.
9. V. Rodríguez, A. Rodríguez, F. Tzompantzi, M. May and R. Gómez, and J. Photochem. Photobiol. 193 (2008) 266-270.
10. M.A. Debeila, R.P. Wells and J.A. Anderson, *J. Catal.* 239 (2006) 162-172.
11. K.S. Chandra Babu, D. Singh and O.N. Srivastava, *Int. J. Hydrogen Energy* 16 (1991) 387-391.
12. W.A. Badawy, *J. Mater. Sci.* 32 (1997) 4979-4984.
13. D. Shchukin, S. Poznyak, A. Kulak and P. Pichat, *J. Photochem. Photobiol. A* 162 (2004) 423-430.
14. G. Liu, X. Li, J. Zhao, S. Horikoshi and H. Hidaka, *J. Mol. Catal.A: Chemical* 153 (200) 221-229.
15. G. Lui, T. Wu, J. Zhao, H. Hidaka and N. Serpone, *Environ. Sc. Technol.* 33 (1999) 2081-2087.