

Characterization of the catalytic activity and of luminescence in Ag/TiO₂ films

Caracterización de la actividad catalítica y de la luminiscencia en films de Ag / TiO₂

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Abstract

Ag/TiO₂ thin films are synthesized on soda-calcium glass substrates, using the sol-gel chemical route and repeated immersion. Series of TiO₂ films at a certain thickness, were modified superficially with several layers of Ag nanoparticles and thus obtaining the Ag/TiO₂ catalysts. The physical-chemical properties of the films are studied. The Ag/TiO₂ films were characterized by XRD and Raman spectroscopy, SEM morphology, chemical composition by EDS, the topography was recorded with AFM, its optical properties with UV-Vis and the ionic states of the surface components by XPS. The film thickness was 173.0 nm, a crystallite size of the order of 20 nm, a transmittance of 80%, a refractive index between 2.046-1.599, and E_g between 3.67-3.52 eV, depending on the surface modification with Ag. The catalytic activity was recorded evaluating the degradation of aqueous solution, depending on the concentration and time of irradiation with UV-Vis. The photoluminescence of the films was recorded when excited with photons of 325 nm. From the results of the study of Ag/TiO₂ films, they have the potential to be applied as catalysts in the treatment of contaminated water, and in radiation dosimetry.

Ag/TiO₂, Photocatalysis, Photoluminescence.

Resumen

Se sintetizan películas delgadas Ag/TiO₂ sobre sustratos de vidrio sodo-cálcico, usando la ruta química sol-gel e inmersión repetida. Series de películas TiO₂ a determinado espesor, se modifican superficialmente con varias capas de nanopartículas de Ag y se obtienen así los catalizadores Ag/TiO₂. Se estudian las propiedades físico-químicas de las películas. Las películas Ag/TiO₂ se caracterizaron por DRX y espectroscopia Raman, morfología por MEB, composición química por EDS, se registró la topografía con MFA, sus propiedades ópticas con UV-Vis y los estados iónicos de los componentes superficiales por XPS. El espesor de película resultó de 173.0 nm, un tamaño de cristalito del orden de 20 nm, una transmitancia del 80%, un índice de refracción entre 2.046-1.599 y el E_g entre 3.67-3.52 eV, dependiendo de la modificación superficial con Ag. Se registró la actividad catalítica evaluando la degradación de solución acuosa, en función de la concentración y el tiempo de irradiación con UV-Vis. Se registró la fotoluminiscencia de las películas al ser excitadas con fotones de 325 nm. De los resultados del estudio de las películas Ag/TiO₂, las mismas tienen posibilidades de poder aplicarse como catalizadores en el tratamiento de aguas contaminadas, y en dosimetría de radiaciones.

Ag/TiO₂, Fotocatálisis, Fotoluminiscencia

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Introduction

Among the metal oxides that may be employed to solve problems such as environmental pollution, both in air and in water, are TiO₂, ZnO and SnO₂, among others. But is the TiO₂ the most contested for its properties such as photosensitivity, is non-toxic, economical, inexpensive (Liu, H., et al, 2013, Malagutti, A.R., et al., 2009). Given their electronic, optical, photocatalytic, and as film or powder, present various phases such as anatase (orthorhombic or tetragonal) or rutile (tetragonal), to mention the most common and of interest. Both are semiconducting broad band, with values between 3.1 to 3.3 eV (Chae, Y.K., et al, (2013), Castrejón-Sánchez, V.H., et al, (2014)); but is the anatase the most widely applied as photocatalyst by its various properties (Cruz-González, N., et al, (2013), Ochoa, Y., et al., (2010), Nada, A., et al., (2014), Yu, J., et al., (2000)). The band gap of the anatase phase allows photons interact with both the visible and UV electromagnetic spectrum. When irradiated with UV, the film of TiO₂ anatase is a source of pairs of e⁻ and h⁺ charges, that when migrate to the surface, can interact with species of oxygen or hydroxyl ions (OH⁻), the latter being produced by ionization of H₂O in the aqueous solution (Yu J. et al., 2000) or by irradiation (Malagutti, A.R., et al., (2009), Yu, J., et al., (2000)) and thus participate in redox reactions that may degrade contaminating molecules found in the environment (Chae, Y.K., et al., (2013), Yu, J., et al., (2000), Malagutti, A.R., et al., (2009)). The properties of TiO₂ films grown on substrates soda-lime exhibit good adhesion and nanostructures are fixed, as produced either by chemical spraying, by sol-gel route, precursor physical technique methods, or laser ablation, between others (Maldonado, A., et al., (2010), Tirado-Guerra, S., (2010), Yu, J., et al., (2000), Malagutti, A.R., et al., (2009), Jongnavakit P., et al., (2012), Pérez-Álvarez J., et al., (2007)).

The semiconductor films TiO₂ were prepared using the sol-gel chemistry and repeated immersion route, using precursors in solution of metal alkoxides, in equipment and technique implemented in the laboratory, controlling specific area, structure and morphology, temperature and air as well as the composition of the precursors used.

The catalytic activity of TiO₂ catalyst by itself is limited, and to improve it, it can be contaminated with precious metals or transition elements, or also complexing with other semiconductors (Liu, H., et al., (2013), Yu, J., et al., (2000)), or well a surface modification with Cu, Ti, Pd and Ag, which modifies the band gap Eg of film TiO₂, and promotes the formation of oxygen vacancies V₀ (Chae, Y.K., et al., (2013), Liu, H., et al., (2013), Yu, J., et al., (2000); Malagutti, A.R., et al., (2009)).

A semiconductor such as TiO₂ or similar systems can be excited with UV radiation and from the absorbed photons, charge carriers are generated as e⁻ and h⁺, where the electron is ejected from the valence band (VB) leaving a hole, and transferred to the conduction band (CB), generating electron-hole pairs (Nejand, B.A., et al., (2010)). The pairs produced can participate in reactions that decompose contaminating molecules found in the environment. Catalytic semiconductor response to UV irradiation, depends on various factors: the catalyst structure, radiation, the preparation method, etc. (Xin, B., et al., (2008), Nejand, B.A., et al., (2010), Malagutti, A.R., et al., (2009), Jongnavakit P., et al., (2012)).

In this work, semiconductor Ag/TiO₂ films are synthesized and are characterized in their structure, morphology, chemical composition (EDS), topography, its optical properties, its potential photocatalytic in degradation of methyl orange (MO) under UV radiation, as well as properties of photoluminescence and emission under UV excitation, of a set of semiconductor films Ag/TiO₂ prepared by sol-gel.

The work is presented in the order: introduction-justification, experimental method, synthesis and preparation of films, film growth, characterization techniques, results, XRD, SEM and EDS, AFM, UV-Vis, X-rays photoelectron spectroscopy (XPS), photocatalysis and photoluminescence, discussion, conclusions, acknowledgments and references.

Methodology experimental

Synthesis and films preparation

Oxy-acetylacetonate titanium (IV) ((C₅H₇O₂)TiO) (Aldrich) was dissolved in 2-methoxyethanol (Aldrich, 99.3+ reagent grade) (CH₃OCH₂CH₂OH) (Aldrich) and monoethanolamine (CH₂CH₂OH)NH₂ (Aldrich) (MEA), the salt of titanium (IV) was dissolved at a 0.2 M concentration, then it was slowly added the MEA to stabilize and prevent precipitation of titanium, the solution was left under constant stirring for about 2 h at room temperature. In the preparation process, the solution was stirred until obtain a complete dissolution of the salt and achieve, a transparent solution without precipitates.

After the preparation a pH of 7 was measured and then allowed to age in a dark and cool room and from this, TiO₂ films were grown up to five layers. From a solution of silver nitrate (AgNO₃) films of titanium were surface modified, using the silver salt dissolved in ethanol (CH₃CH₂OH) at a low concentration, such solution was stirring for 2 h until to obtain a pH 5; the series of TiO₂ films was modified with the method already described, to obtain the Ag/TiO₂ series.

Film growth

From the prepared sol, the TiO₂ films were grown on substrates of soda-lime glass, introducing and removing the substrate from the sol repeated times, with a thickness of the films, proportional to the repetition of the process performed at room temperature. At each step the solvent and moisture were evaporated, while takes place the formation and growth of the film on the substrate in an oven at 250 °C in an air atmosphere. Finally, a heat treatment is given at 400 °C for one hour and evaporating solvents and moisture from to the film involved, while stabilizes and improves its properties. Films were grown in an oven with air, at five dives and at fixed velocity. Similarly, films of Ag/TiO₂ series were obtained with the procedure outlined, by modifying the respective surfaces with several layers of the Ag solution.

Characterization

XRD patterns of Ag/TiO₂ films were recorded with θ -2 θ symmetric geometry and grade beam sample position at 0.5° in a PANalytical diffractometer X'pert PRO using the K α line of Cu (λ = 0.15406 nm) with line focus, at 45 kV and 40 mA. Spectra were recorded from 3 to 60° with 0.05° step and accumulation time 150 s, but only spectra 20 to 60 degrees are presented. The Raman spectra were recorded on a LabRam spectrometer, model HR 800 and Horiba Jobin Yvon brand (400-4000 cm⁻¹).

SEM micrographs were recorded on a QUANTA 3D FEG SEM microscope (FEI) and EDS (EBSD detector EDAX). Topography was recorded by atomic force microscopy (AFM) on microscope PARK AutoProbe Equipment (Veeco) with a tip of 10 microns of silicon intermittently. The optical properties of thin films were recorded by a UV-Vis spectrophotometer Perkin Elmer, Lambda 2 UV-Vis double beam in 200-900 nm range and the glass substrate as a reference. Test photo-degradation of an aqueous solution of methyl orange (MO), was conducted to determine the absorbance of the solution when irradiated with UV-Vis light, using a reactor equipped with eight fluorescent blue lamps G8T5, 8 watts, once the film-solution, is irradiated for 10 min in a spectrometer GBC Cintra 20 model in absorbance mode and in the range of 190-600 nm. The main absorption band at 464 nm was screened during the irradiation process. Ionization states of the components O, Ti and Ag of films, were determined by X-ray photoelectron spectroscopy (XPS) in a Thermo Scientific K Alfa, dual source Mg and Al, equipment. The photoluminescence properties of Ag/TiO₂ films were recorded at room temperature in a RF-5301 Spectrofluorophotometer Shimadzu mark.

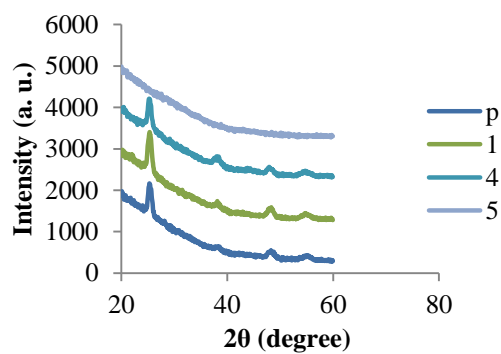
Results

X-ray diffraction

X-rays of Ag/TiO₂ films (Ag/TiO₂-p,1,4,5) (Graphic 1) were poly-crystalline (except Ag/TiO₂-5) with peaks at 25,335°, 37,780°, 38,565° and 48,022°, associated with the planes (1 0 1), (0 0 4), (1 1 2), (2 0 0), respectively (coding 00-021-1272) and correspond to the anatase TiO₂ phase of tetragonal space group 141/amd, density 3,89 g/cm³.

Diffraction peaks were also recorded at $31,508^\circ$, $42,821^\circ$ and $51,354^\circ$, with Miller indices (1 1 0), (1 0 1) and (2 1 0) of rutile phase (coding 00-021-1276) tetragonal, space group P42/mnm, with density $4,23 \text{ g/cm}^3$.

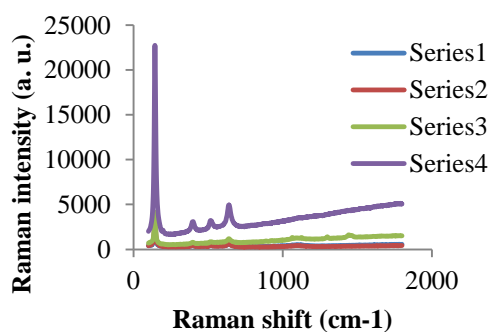
The anatase phase of TiO_2 was the majority one and no silver was recorded. From Scherrer's formula, $D = 0.9\lambda/\beta\cos\theta$ (meaning of known parameters), the crystallite size D in the 18-24 nm range of the samples was estimated.



Graphic 1 XRD spectra for Ag/TiO_2 films, (p) pure, (1) one layer of Ag, (4) four and (5) five layers of Ag samples

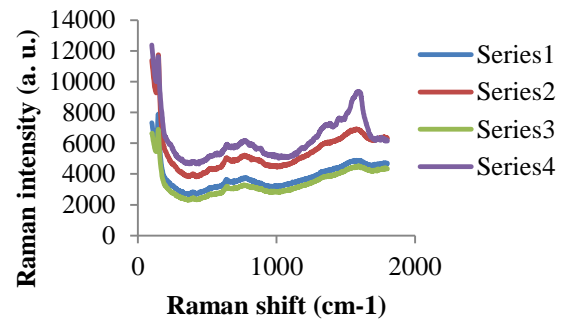
Raman spectroscopy

The Raman spectra of Ag/TiO_2 samples prepared at 250°C and 400°C of treatment, were recorded in equipment already indicated. The Graphic 2a arrangement with Raman spectra of the pure sample ($\text{Ag/TiO}_2\text{-p}$) is shown: they are four different points and whose data are, among others: 143.206 (Eg) , 198.373 (Eg) , 396.655 (B1g) , 516.546 (A1g) and $639,512 \text{ (Eg)}$, vibrational modes in cm^{-1} , the data are typical modes of the anatase phase of TiO_2 systems.



Graphic 2 Raman spectra of the pure sample TiO_2 , in four different points

The Raman spectra for samples with four Ag catalyst layers ($\text{Ag/TiO}_2\text{-4}$) at four different points are given in Graphic 2b, the data among others: 143.206 (Eg) , 256.468 , 397.05 (B1g) , 518.368 (A1g) and 638.547 (Eg) , all in cm^{-1} , resulted; modes assigned in the literature to the anatase phase of TiO_2 (Cruz-González, N., et al., (2013)). It is observed the presence of broad bands around 1500 cm^{-1} , which do not appear in the spectra of the pure sample (Graphic 2).



Graphic 3 Raman spectra of the sample with four Ag layers, Ag/TiO_2 , at four different points

Scanning electron microscopy

SEM micrographs of Ag/TiO_2 films representative x20000 magnification are shown in Figures 1(a) and 1(b). The micrograph of the Ag/TiO_2 pure films (Figure 1a) has an uneven and porous morphology, however for micrograph in Figure 1b of the Ag/TiO_2 films with a surface deposited with Ag can be observed a morphology more uniform with fine grains and growth in areas (lights) corresponding to nanoparticles of Ag, with EDS analysis the presence of silver nanoparticles was detected, the surface distribution of the growth of the nanoparticles was uniform, making more evident the surface distribution and increased grain size (image not shown).

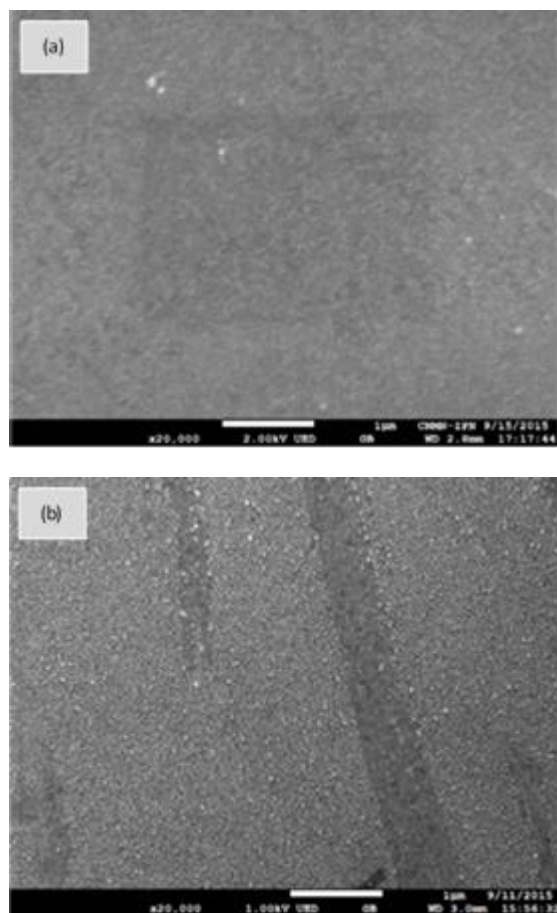


Figure 1 (a) and (b) SEM micrographs increased x20000, (a) Ag/TiO₂ pure and (b) Ag/TiO₂ samples with one layer of silver

Atomic force microscopy

From topographical images shown in the figures (Figures 2a and 2b) and (Figures 3a and 3b) of the samples, pure and that with one layer of Ag, roughness parameters Rq, Ra and Rmax were evaluated, among others, for the samples Ag/TiO₂, which are shown for three samples in Table 1. The parameters are higher in the pure sample compared to that of samples with one and four layers of Ag. The density in grains/μm², 3.80 and 6.32, resulted, respectively.

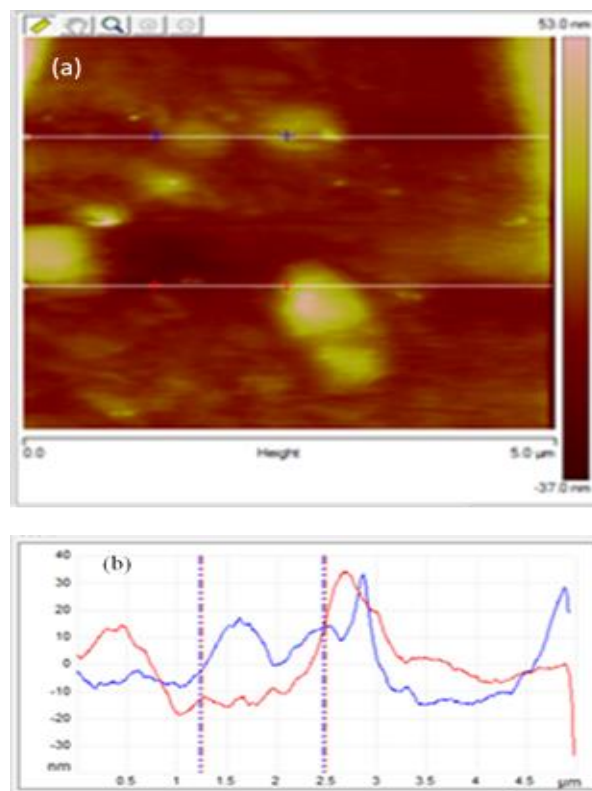


Figure 2 (a) AFM topography of Ag/TiO₂ pure sample, and (b) marked profiles

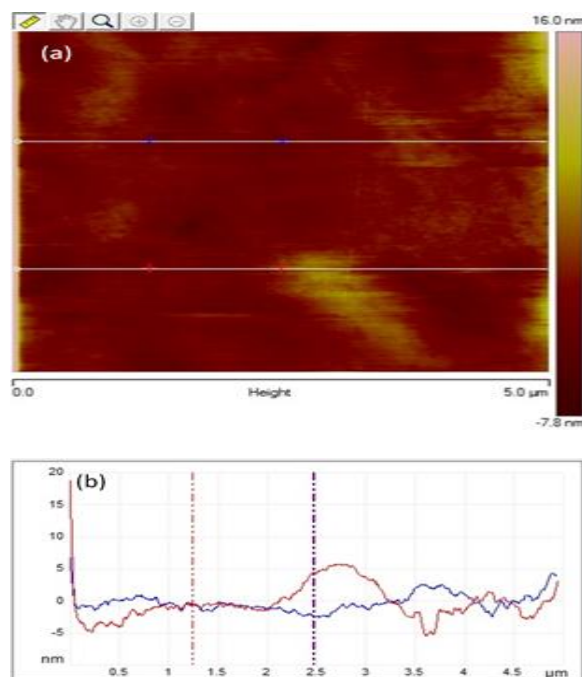


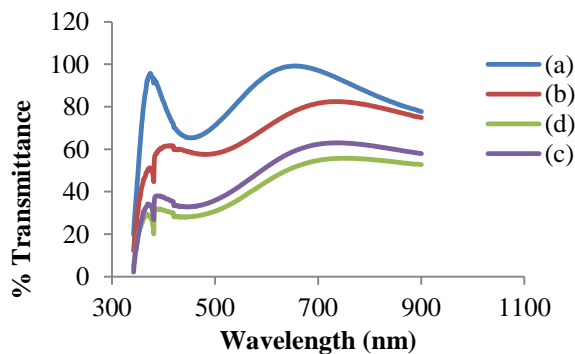
Figure 3 (a) AFM topography of Ag/TiO₂ sample with one Ag layer, and (b) marked profiles

Samples	Rms (nm)	Ra (nm)	Rmax (nm)	Av. grain (nm)	Density (g/μm ²)
Ag/TiO ₂ -p	6.03	8.5	26.2	82	3.812
Ag/TiO ₂ -1	1.69	0.83	4.21	47	6.32
Ag/TiO ₂ -4	1.226	0.626	18.776	22.5	9.849

Table 1 Roughness parameters for samples Ag/TiO₂, pure, one and four layers of Ag

UV-Vis microscopy

The optical properties of Ag/TiO₂ films were recorded by UV-Vis in the 190-900 nm range, using glass substrate as a reference; spectra of the sample without deposits Ag (pure) were highly transparent (Graphic 4), with increased transmittance to 90% in the visible range (400-700 nm), and the absorption band at 382 nm; from the interference effects, the thickness of pure and for samples with Ag layers, between 87-65 nm, respectively, were estimated. The transmittance of Ag/TiO₂ films decreased with the increasing of the silver layers and the absorption edge has a slight redshift. The refractive index of pure film turned between 1.149-1.550 and 1.902-2.723 for the sample with one Ag layer, in the visible range. The wide band gap E_g was evaluated for the anatase phase of TiO₂, an indirect band, from the graph $(\alpha h\nu)^{1/2} = A(h\nu - E_g)$ (Jongnaavakit, P., et al., (2012)). The values for the films were between 3.67-3.62 eV, decreasing with the Ag layers, and thus the possible improvement in film optical properties.

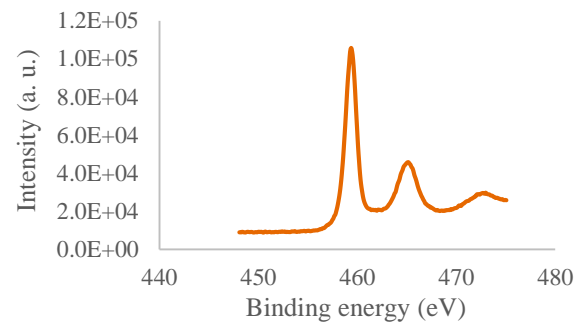


Graphic 4 UV-Vis spectra for Ag/TiO₂ films, (a) pure, (b) one layer, and (c) four and (d) layers of Ag samples

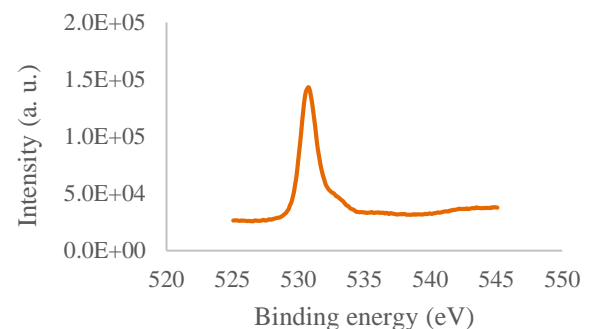
Photoelectron spectroscopy

Using photoelectron spectroscopy (XPS), the orbitals of, O1s, Ti2p, Ag3d, and ionization states of O, Ti and Ag, as well as the binding energies of the respective orbitals were evaluated; in the high-resolution spectrum of Ti2p, the spin-orbital values of 458.38 and 464.48 eV, ($2p_{3/2}$, $2p_{1/2}$), respectively, quite symmetrical, with $\Delta E = 5.9$ eV, and also the broad band with a value of 472.48 eV, were recorded (Graphic 5). For the orbital O1s the data 529.78, 531.96 and 532.18 eV and also the higher energy value of 535.48 eV were recorded (Graphic 5). For the orbital Ag3d of the metallic state of Ag, the values were, 367.48 and 373.58 eV ($3d_{5/2}$, $3d_{3/2}$) respectively (Graphic 7).

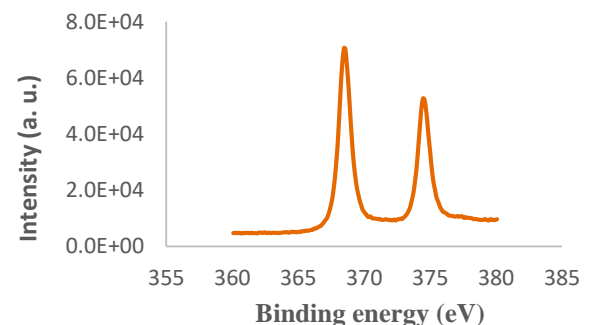
The above data for Ti2p, O1s and Ag3d correspond to the Ag/TiO₂ systems. The energy values of the orbitals of the components of the Ag/TiO₂ films are referred to the energy of carbon C1s (284.48 eV).



Graphic 5 High resolution XPS spectra of Ag/TiO₂ films, for Ti2p with double 458.38 and 464.48 eV, besides the signal at 472.48 eV



Graphic 6 High resolution XPS spectrum of Ag/TiO₂ films, for species O1s, at 529.78, 531.96, 532.18 and in 535.48 eV



Graphic 7 For the orbital Ag3d of the metallic state of Ag, the values were, 367.48 and 373.58 eV ($3d_{5/2}$, $3d_{3/2}$) respectively

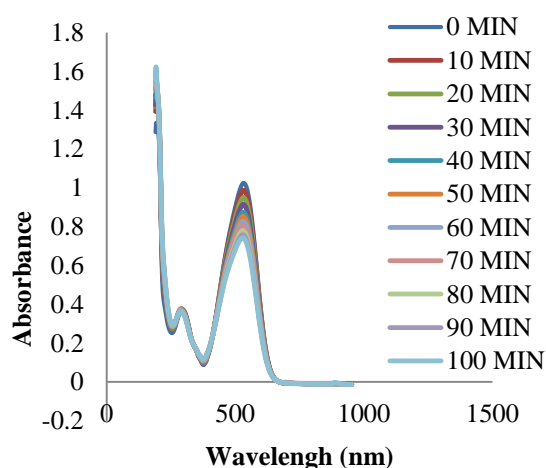
Catalytic activity

Spectra MO degradation to first cycle to 14 ppm registered for Ag/TiO₂, of pure sample, and those with one layer of Ag catalyst, are given in Graphics 7 and 8 (for the four layers arrangement of Ag, is not shown).

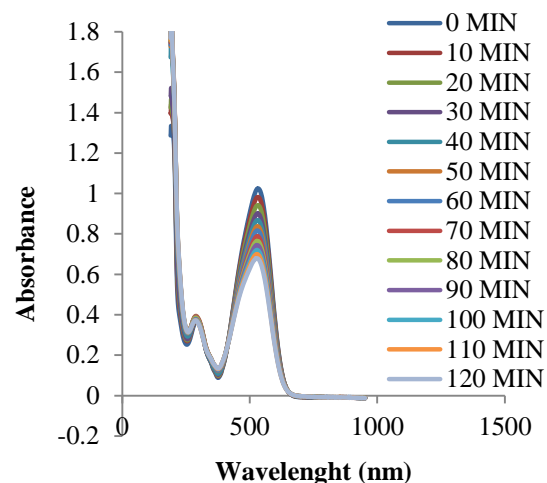
The absorption spectrum of the aqueous solution of MO and their intensity were recorded; the intensity of the band at 464 nm is proportional to the initial concentration C_0 , was monitored.

Subsequently, the film-aqueous solution, (film with area 1 cm^2 , both sides), the system was irradiated each 10 min with UV light in a rectangular reactor and the absorbance of the solution is recorded, thus obtaining the concentration C of MO corresponding to time t ; the process is repeated until 120 min.

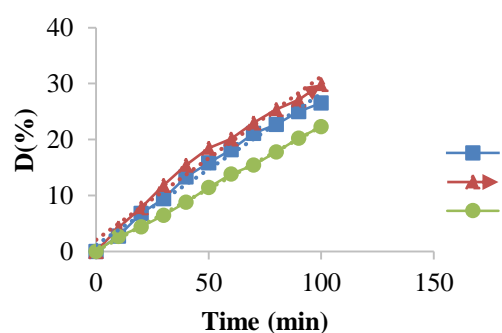
The ratio of the concentration C of MO at time t , with the starting C_0 concentration, can be modeled with a kinetic equation of first order, $C = C_0 e^{-kt}$, where k is the pseudo constant of reaction, C is the concentration for time t , the irradiation time of the system. From Graphic 9 and the respective slopes of the systems, the better catalytic performance corresponds to that with one deposit of Ag catalyst, relative to Ag/TiO_2 pure system; Ag/TiO_2 system with four Ag layers catalyst, was the lowest performance among the three systems presented.



Graphic 8 Degradation process of MO by the Ag/TiO_2 pure film as a function of irradiation time



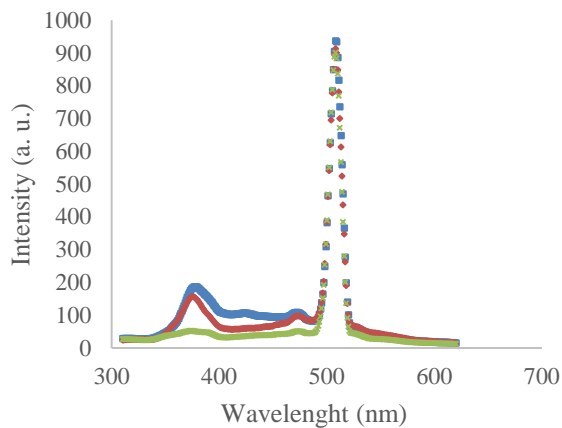
Graphic 9 Degradation process of MO by the Ag/TiO_2 film with one Ag layer, depending on the irradiation time



Graphic 10 Charts of the catalytic activity of Ag/TiO_2 samples corresponding to pure (p), for one (1) and four Ag layers (4)

Photoluminescence properties

The photoluminescence spectra (PL) of the Ag/TiO_2 films were recorded at room temperature in the 310 to 620 nm range with excitation energy corresponding to 325 nm. The emission spectrum of the pure sample, for the UV region in 375 nm (3.31 eV), in the intermediate region at 425 nm (2.9 eV), a wide and complex band, while in the visible region a band at 473 nm (2.62 eV) of low intensity, and the intense band at 509 nm (2.436 eV) were resolved. From the 520 nm the spectra are fading at 600 nm. The arrangement of PL spectra of three samples is given in Graph 11. By fixing the position of the main peak at 509 nm, the intensities of the Ag/TiO_2 samples are: 933.992, 899.691 and 883.056 (a.u.) of the pure, for one and four Ag deposits samples, respectively.



Graphic 11 Arrangement of PL spectra of Ag/TiO₂ films, for pure, one, and four Ag layers with a broadband emission at 375 nm, another around 425 nm, and the band at 473 nm, and the principal one in 509 nm

Discussion

XRD patterns of Ag/TiO₂ films were polycrystalline with the TiO₂ anatase phase and density of 3.89 g/cm³, where also peaks of tetragonal rutile as minority phase and density of 4.23 g/cm³ were detected. The estimated grain size for the anatase phase was between 18 to 24 nm. No silver was detected by X-rays, given the low concentration used. Grain density was higher in films with layers of silver, smaller pore size, less roughness; in general the roughness parameters evaluated in the series Ag/TiO₂ films, could explain both the optical properties and also the photocatalytic and photoluminescence ones. The Ag catalyst at low concentration incorporated superficial in the films should play an important role in such properties. The pure films were highly transparent (>90%) and also thin, and films with silver layers resulted more opaque than pure ones, such that the Eg values were affected, which could improve the catalytic activity. The band width of the Ag/TiO₂ systems were lower than those found in systems composed as ZnO/TiO₂ (Liu G., et al., (2009)).

The transmittance is greater in the pure film than those with deposits of Ag catalyst. For films Ag/TiO₂ more opaque, less light penetrates and thus become less active.

From the study by XPS, to the right of the orbital O1s intense peak, one has values: 529.78, 531.96 and 532.18 eV, and another with more energy at 535.48 eV. Within the experimental resolution, the first two values, which when adjusted, could be associated with the species O²⁻ on the network that is linked to the titanium dioxide or to the Ti-O bond, while the peak at 532.18 eV, to surface hydroxyl groups, i.e., Ti-OH or also links like C-O and C=O, because the signals overlap, the H₂O molecules are associated with the energy 535.48 eV (Malagutti, A.R., et al., (2009), Fusi, M., et al., (2011), Liu, H., et al., (2013)). The orbital Ti2p at 458.38 eV (2p_{3/2}) is associated with Ti⁴⁺ in the formula TiO₂ anatase, and the peak at 472.48 eV could be associated with a state of hybridization between orbital O2p and Ti3d; peaks at 367.48 and 373.58 eV of Ag3d correspond to the metallic state of Ag.

From Graphics 7, 8 and 9, the results of the catalytic activity of the films of pure TiO₂ systems, and those with one Ag layer in the photodegradation of MO and with four layers Ag, are shown (included in Graphic 9). The catalytic activity of the sample with one layer of Ag was better than the pure one and the sample with lowest activity corresponded to four layers of Ag, also shown; activity of pure sample is due to own surface defects because the synthesis and of the sample with one layer of Ag, that is, less transparent and less roughness than pure sample, but the silver grain size in the growth, it is felt its effect on the catalytic activity, which does not happen with the film with four layers of Ag, which is more opaque and less catalytically active.

The growth procedure was similar for all systems and if something is changed, only was the number of insertions in the process and therefore a different thickness and thus a longer exposure to the drying and to treatment temperature. By the technique of sol-gel and dipping the films are obtained with surface states, defects, surface area, pore, stresses and strains, which are characteristics and very active such as the oxygen species are, or hydroxyl groups and water molecule adsorbed, that can to react with MO and degrade it (Yu, J., et al., (2000), Fusi, M., et al., (2013)), among other pollutants (Tripathi, A., et al., (2014)), with all they, the phenomenon of photoluminescence of Ag/TiO₂ could be explained, also in thin TiO₂ films, among other nanostructures as TNTs (Yu, J., et al., (2000), Fusi, M., et al., (2013), Lei, Y., et al., (2001)), oxygen vacancies and other defects are used to explain the phenomenon. Intrinsic or structural defects and impurities in metal oxide thin film and the properties thereof, are those of the synthesis, the precursor methods, the atmosphere and the heat treatment temperature (El Hichou, A., et al., (2004) and refs., De-Wei, M., et al., (2003), Lin, B., et al., (2001), Yu, J., et al., (2000), Nada, A., et al., (2014)).

PL spectra are associated with oxygen vacancies and to different types of defects of Ag/TiO₂ samples.

The peak at 375 nm, can be associated with electronic transitions between the CB and VB bands of the semiconductor Ag/TiO₂ and associated to the band gap, where the excited photoelectrons are relaxed to the bottom of the conduction band by the mechanism of phonon (Tripathi, A., et al., (2014)); the broad band at 2.9 eV, close to the board absorption band (NAB) in the pure system, with a redshift of 0.41 eV regarding the value of E_g, emissions that can be given as a recombination of free excitons (Guo, Q.X., et al., (2008), El Hichou, A., et al., (2004) and refs., De-Wei, M., et al., (2003)), the intensity of the band decreases with deposits Ag catalyst and probably decreasing luminescent centers participating in this band; the band at 475 nm (2.62 eV) could be associated with centers such as Ag acceptors or other defects.

The intense emission band in the visible (509 nm) could be associated with radiative transitions between surface or shallow vacancies (Vo⁻), surface defects, commonly-donors, as Ti and deep levels of V_{Ti}, O_i, O_{Ti}, acceptor levels, between levels near the lower board of the CB and acceptor defects located at 2.436 eV below the band. This green band emission at 2.436 eV in our systems, may be sensitive to thermal treatments at different temperatures, such as those used in systems ZnO reported by Lin B., et al., (Lin, B., et al., (2001), Lim J., et al., (2004)) and/or contaminated with Ag ions (Tripathi, A., et al., (2014)); however, in the systems reported here, it shows that the emission intensity is higher in the pure sample (with treatment of one h) in relation to the broadcast of films with one Ag layer (with two h) and compared with the four layers of Ag (with four h), with a longer heat treatment.

However, here there are different samples, where the time treatment of specimens, change by coalescence and crystallite size increase relatively, so that the population of shallow levels as vacancies Vo⁻ or other participants, also other donors and deep levels acceptors contributing to the emission of the green region, are affected by that procedure employed; the presence of Ag⁺ ion must generate an acceptor state in the region of the band gap semiconductor, acceptor level related to the low concentration that was used to modify the surface samples, although unclear the effect on the emission band; on the other hand, in doped ZnO films, the Ag dopant concentration plays an important role in UV emission photoluminescence region (Tripathi, A., et al., (2014)). In nanowires of TiO₂ anatase, Lei, Y., et al., (Lei, Y., et al., (2001) and refs. in) explain the PL spectra in the band at 424 nm, by emissions of excitons self-trapped in the TiO₆ octahedron, and for the bands at 465 and 525 nm, to oxygen vacancies, i.e. emissions from traps shallow of oxygen vacancies at 0.51 eV (band 465 nm) and 0.82 eV (band at 525 nm) below the CB, which were recorded in nanowires.

Conclusions

The Ag/TiO₂ semiconductor films were grown on substrates sodo-calcic using the sol-gel process and repeated dipping. The X-ray diffraction patterns of the Ag/TiO₂ films were polycrystalline, with a majority anatase phase respect to the rutile one.

The grain size was consistent with those obtained with AFM where a higher roughness is obtained in pure films than those with Ag layers, and a grain density 3.812-9.849 (grains/ μm^2). The Ag/TiO₂ films show a high transmittance, T% >90 in pure film, decreasing with Ag layers. The band gap Eg (3.67-3.62 eV) decreases with increasing Ag layers.

The orbital of components of Ag/TiO₂ films were determined, where various oxygen species (orbital O1s) that identify the O²⁻ ion in the network were determined, and associated with titanium dioxide or to the Ti-O bond, and to groups of surface hydroxyls, Ti-OH, and also the presence of H₂O molecules in the surface was identified; similarly the orbital Ti2p (2p_{3/2}) that is associated with Ti⁴⁺ in formula TiO₂ anatase and also the orbital Ag3d of the metallic state of Ag. This allowed proposing possible mechanisms to explain the photocatalytic activity of Ag/TiO₂ films in the decomposition of MO. With the surface composition of the films and the presence of various acceptor defects and also experimental conditions, photoluminescence properties can be explained. The spectra of PL at room temperature showed emission bands in the UV region, intermediate zone and in the visible region, an intense and interesting band, electronic emissions between bands and the band edge close absorption, the last bands are associated with oxygen vacancies and different types of intrinsic defects of Ag/TiO₂ samples.

The results of this study, show the potential application as catalysts and detectors of radiation in the UV-Vis range. Further studies are required with these films as well, varying the thicknesses, significant heat treatments, the MO concentration or other tracers, and higher concentrations of the Ag catalyst.

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