Shifting to the red the absorption edge in TiO_2 films: a photoacoustic study

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When Titanium dioxide in contact with a polluted water sample is irradiated with ultraviolet light, electron-hole pairs can be generated, which can react with oxygen and water producing free radicals that can degrade the pollutants, changing them into harmless compounds for the environment. The ultraviolet component of the solar radiation is around 7%. Therefore, it is convenient to modify the TiO_2 films crystalline structure for obtaining photocatalytical processes with visible light. In this work we report on the growth of TiO_2 thin films by the Sol-gel technique considering the incorporation of $AgNO_3$ in the initial solution containing the precursor. The concentration of the $AgNO_3$ saline solution was changed between 5 and 30% to control the grain size of the grown TiO_2 nanocrystals, impregnating 6 layers over glass slide substrates and using a sintering temperature of 600 °C. The obtained films were characterized structurally by means of X-ray diffraction. The shift in the forbidden energy bandwidth value to the red part of the optical absorption spectrum was evidenced by Photoacoustic Spectroscopy. The photocatalytic activity was tested on a solution of methylene blue using also the Photoacoustic technique.

Keywords: Titanium dioxide; Thin films; Sol-gel; Photocatalysis; Photoacoustic

1. Introduction

Heterogeneous photocatalysis has become an alternative method for air and water purification as a very efficient process for removing organic pollutants in the environment. This catalytic effect has shown a high potential in applications related to gas and liquid phase pollution control processes, and renewable hydrogen production [1, 2]. One of the most common photocatalyst is titanium dioxide (TiO_2), a wide-gap, cheap, reusable, nontoxic, photocorrosion resistant, and high oxidant power semiconductor. However, the efficient use of sunlight for photocatalysis with this material needs that the photoexcitation energy threshold become lower than the corresponding to the bulk material. One way to do that is by doping the TiO_2 with transition metals and non-metallic impurities [3].

The photocatalytic efficiency evaluation has been frequently measured by spectrophotometric methods using the methylene blue (MB) blanching as a function of time when this is placed in contact with the photocatalyzer radiated with light. However, this technique does not allow observing gases generation in the process and it is affected by light dispersion problems.

In this work, in-situ evaluation of the photocatalytic effect of TiO_2 films was done using the Photoacoustic (PA) Technique. This technique is based in measuring the pressure changes in a thin layer of gas adjacent to a body radiated with intensity modulated light, which are due to heating by non-radiative de-excitation process [4]. This effect can be detected as sound with a microphone placed inside a cell that also encloses the sample. If in addition, the sample presents photochemical activity, the production of gases contributes to the PA signal too. Then, when PA measurements are resolved in time it is possible to study, for instance, the photocatalytic activity.

2. Experimental

The TiO_2 films were grown by the sol-gel technique using titanium tetraisopropoxide as alcoxide precursor and nitride acid as catalytic acid. Silver was incorporated from an $AgNO_3$ dissolution, with concentration changing from 5 to

Table 1. Size grain (S) and band gap energy (E_g) estimated for TiO_2 films using Scherrer equation and indirect transitions model (equation (1)), respectively.

Sample	**S** (nm)	$\mathbf{E_g}$ (eV)
Ag 5%	18	2,3
Ag 10%	23	2,1
Ag 15%	24	2,0
Ag 20%	25	2,0
Ag 25%	29	2.0
Ag 30%	30	2.0

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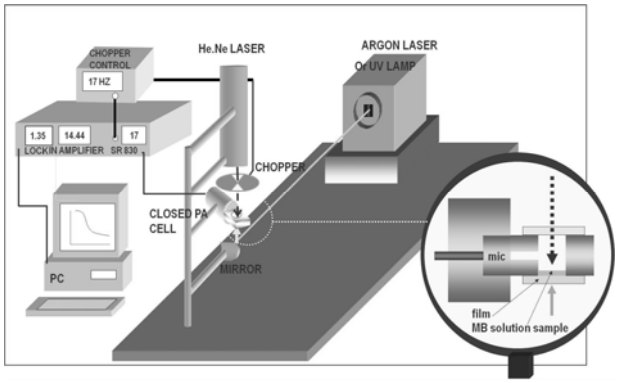

Figure 1. PA system arrangement used for photocatalytical evaluation.

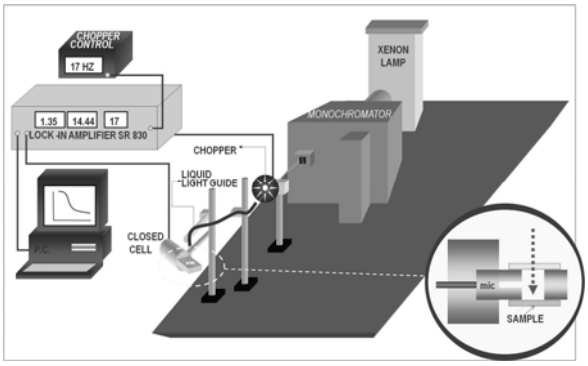

Figure 2. PAS system using a closed PA cell. The thin film grown on glass slide was used as cover of the cell cavity.

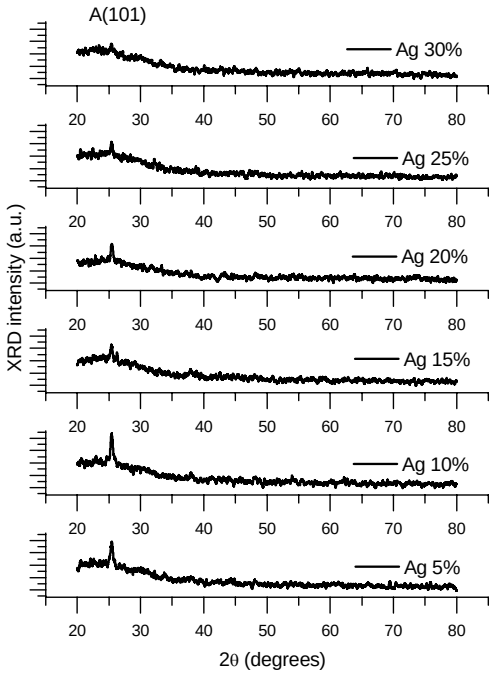

Figure 3. Difractograms for all TiO_2 grown films show a peak related to (101) anatase phase. Samples were called according to $AgNO_3$ dissolution concentration in growth process which was changing from 5 to 30 %.

Modulated light from He-Ne laser is absorbed by MB solution. Non-modulated Light from Argón laser or Xe lamp is turned on after 200 seconds of this radiation. It generates a photocatalytic process.30 %. In this process nitric acid was used as a catalyzador. The water/alcoxide ratio was fixed in 3 and the films were deposited on glass slide substrates by a dip-coating method. After drying at 210 ^oC for 15 minutes, the films with six impregnation layers were treated in air at temperatures of 600 ^oC during one hour. Phase identification of the nanocomposite thin films was conducted with an X-ray diffractometer (XRD) using Cu-K_α radiation (D8 Advance Bruker).

The PA effect was used for analyzing the transformation of methylene blue (MB) solution due to TiO_2 films photocatalytic activity using a system like that shown in figure 1. The bottom opening of the PA cell is closed by the samples in such a manner that the film, with a drop of the MB solution, faces the cell´s cavity. The top opening is closed with a quartz window through which the mechanically chopped light from a Helium-Neon laser

(JDS Uniphase) impinges on the solution-sample system. After 200 s approximately, light of 514 nm wavelength from an Argon ion laser (Omnichrome 543-BS-A02) or from a Xe lamp (ORIEL 66924) irradiated the system from above. A conventional electret microphone located inside the cell detected the PA signal, which is fed to a SR850 lock-in amplifier synchronized at the chopped light frequency. The PA signal is produced by the photothermal effect due to the chopped light absorption and by the photocatalytic effect when the Argon laser beam or the Xe lamp is turned on.

Photoacoustic spectra of the films were measured using a system showed schematically in figure 2. The sample is cyclically heated by chopped light from the Xenon arc lamp (ORIEL 66924) using 700 W power. A monochromator (ORIEL Cornerstone 130 1/8 m) was used for selecting the light wavelength. The monochromatic modulated light beam is focused on the sample using a liquid light guide. The light energy absorbed by the sample excites electrons to higher levels; the non-radiative de-excitation processes heats periodically the sample and thus its surrounding gas within the closed PA cell. The oscillatory motion of this gas layer produces an acoustic signal detected in the cell by the electret microphone, and the intensity of this signal has a direct correspondence with the amount of light energy absorbed by the sample [5]. A lock-in amplifier was also used for reading and amplifying the signal from the transducer.

3. Results and discussion

The X-ray diffractograms in figure 3 showed that the crystalline structure of TiO_2 films does not depend of the used parameters. A peak around $2\theta=25^0$ in these patterns revealed preference for anatase phase in agreement with reports for TiO_2 films grown by the same technique [6]. From the peak full width at half maximum (FWHM), the

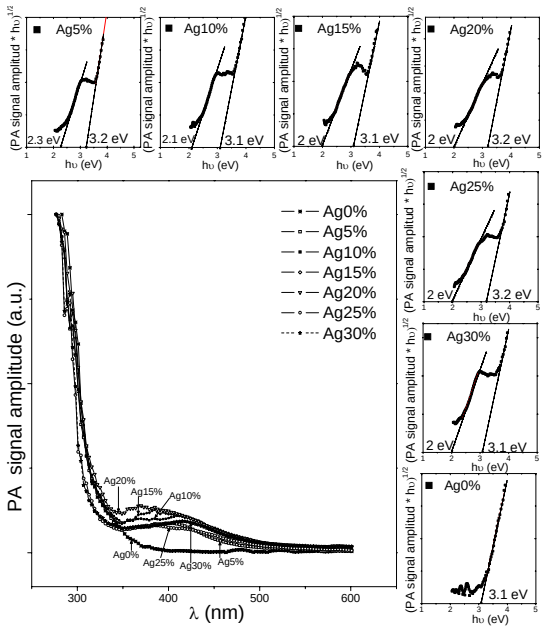

Figure 4. Photoacoustic spectra of the films. The insets plots illustrates the (PA signal amplitude *hν)$^{1/2}$ vs. hν graphs. The values of the corresponding optical band gap were estimated by extrapolation of an apparently narrow linear region according to equation (1).

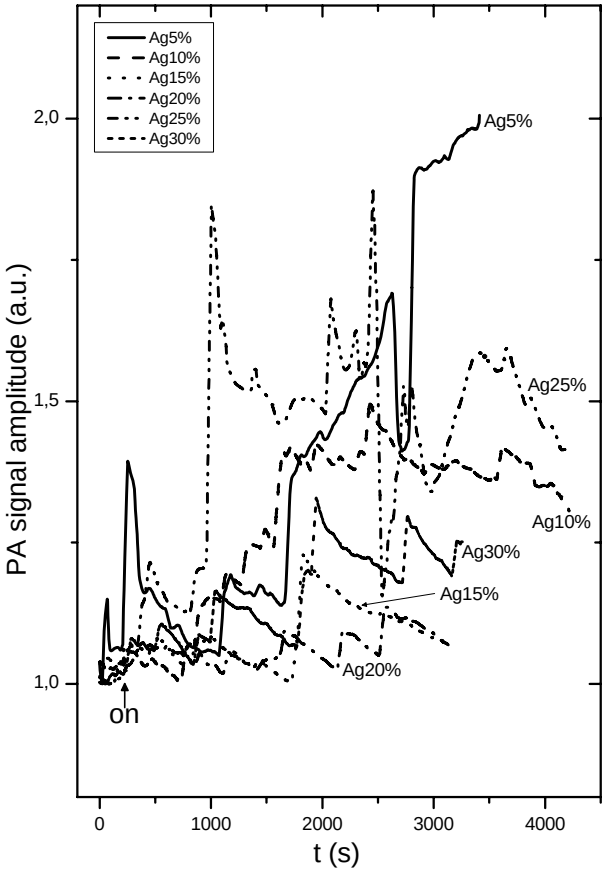

Figure 5. Photocatalytic activity curves measured using time- resolved PA technique. In this case, 25% Ag sample and light from an Argon laser were used for the photo-activation.

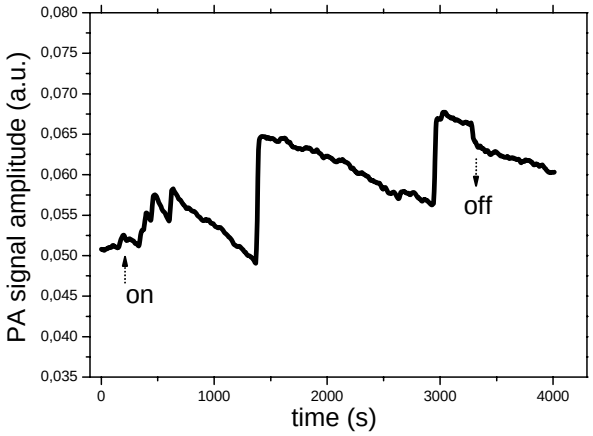

Figure 6. Photocatalytic activity curves measured using time- resolved PA technique. In this case white light from Xenon lamp was used for the photo-activation.

average nanometer grain size was estimated using Scherrer equation to be in the range 17-30 nm [7].

The forbidden band gap energy was calculated from absorption spectrum assuming indirect allowed transitions close to the fundamental absorption, using the following relationship for the absorption coefficient, α:

$$\alpha h\nu \sim A_i (h\nu - E_g)^2, \qquad (1)$$

where hν is the photon energy, A_i is a photon energy independent parameter and E_g is the optical bandgap energy [8]. The calculated values are shown in Table 1. One of them corresponds to the anatase phase, reported as 3.2 eV [9], while the other one is probably due to shifting by impurities. These values, obtained from the fitting of the experimental data showed in figure 4 to equation (1) are highly dependent on the experimental absorbance range, and so they give a rough approximation to the true bandgap values. However, it is possible to see that the addition of $AgNO_3$ caused a shifting of the band gap value in a range between 2 and 2.3 eV.

The time-resolved PA signal curves indicated the photocatalytic activity measured through the methylene blue solution changes due to degraded molecules, water cleavage and possible generation of other gases.

The figure 5 shows the PA signal as a function of the time when chopped light is absorbed by the MB solution and non-modulated light from the Argon laser is irradiated on the MB solution-film system after first 200 s. The Photocatalytic effect can be observed from these curves for all grown TiO_2 films. The curves in figure 5 were normalized respect to the minimal value data for comparison purposes. It is possible to see that the signal intensity increases with time, so real blanching did not happen in this observed period, but other degradation process with gas generation. The curve in figure 6 presents a similar behavior for the 25% Ag sample as measured with the same arrangement when the MB solution-film

system was radiated with non-modulated light from a Xe lamp. In this case the PA signal corresponding to photochemical effect is an evidence of photocatalytic activity using white light.

4. Conclusions

The in-situ analysis using the PA technique of Ag doped TiO_2 films photocatalytical action, showed high efficiency for monitoring this activity. Thin films PA spectra show than inclusion of Ag in the growth process of these films produces a shifting of the forbidden band energy values, which stimulates films photoactivity with white light. The obtained PA signal for photocatalytic activity is related to other effects different to MB blanching that could be studied with more deep.

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References

[1]. M. Bertelli, E. Selli. Journal of Hazardous Materials B, **138**, 46 (2006).
[2]. W. Shangguana, A. Yoshida, M. Chen. Solar Energy Materials & Solar Cells, **80**, 433 (2003).
[3]. Akira Fujishima, Xintong Zhang, Donald A. Tryk. Surface Science Reports **63**, 515 (2008).
[4]. S. Banerjee, J. Gopal, P. Muraleedharan, A. K. Tyagi and B. Raj. Current Science, **90**, 10, 1378 (2006).
[5]. A.Rosencwaig and A.Gersho. J. Appl. Phys. **47**, 64 (1976).
[6]. P. Zeman, S. Takabayashi. Surfaces and Coatings Technology **153**, 93 (2002).
[7]. H.G. Jiang, M. Ruhle, E. J. Lavernia. Journal of materials research, **14**, 2, 549 (1999).
[8]. J.I. Pankove. Optical Processes in Semiconductors. Dover publications Inc., New Jersey, 37 (1971).
[9]. H. Tang, H. Berger, P.E. Schmid, F. Levy, V. T. Gritsyna, and D. A. Shirley, Solid State Commun. **87**, 847 (1993).