

*Dedicated to the memory of
Professor Mircea D. Banciu (1941–2005)*

PHOTOCATALYTIC DEGRADATION OF ACETONE ON ZnO-DOPPED TiO₂ FILMS PREPARED BY SPUTTERING

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ZnO-doped thin films were prepared by reactive dc magnetron sputtering using a metallic titanium target with 1 up to 5 metallic Ni inserts and different compositions of the reactive gas mixture and of the total pressure inside the chamber. Glass, (100) n-type silicon, or glass coated with indium-tin oxide (ITO) were used as carriers. The loading in Zn was smaller than 0.08 wt% as determined from electron probe microanalysis. These materials were characterized by film thickness, XRD patterns, atomic force microscopy, UV-Vis spectra, and by thin films. The photocatalytic behavior of these materials was checked in the degradation of acetone. The doping with Zn ions resulted in a different behavior as a function of the conditions the films were prepared. For each preparation conditions, an optimum of the Zn loadings was found to provide an optimum activity.

INTRODUCTION

Titanium dioxide is the photocatalytic active material most utilized for water and air depollution. Its electronic properties and the redox potential of the electron/hole pairs allow the degradation of a wide range of organic compounds.¹⁻¹⁴ Both electrons and holes are implied in the photocatalytic transformations, each type of charge carrier acting in a specific manner. Electrons are trapped at the surface by Ti(IV) sites, where, due to their reductive potential, are captured by O₂ molecules. The resulted peroxide species are very effective in the decomposition of organic substrates. On the other hand the holes, once reaching the surface, are either directly implied in the oxidation of organics, or react with OH species covalently bound at the titania surface, transforming them in very reactive radical species.¹⁵ The improvement of the photocatalytic activity is consequently directly correlated with the increase of the lifetime of the electron/hole pairs.

There have been many attempts to increase the charge separation. The TiO₂ coupling with another semiconductor possessing different redox energy levels for the conduction and valence bands can be successfully used to achieve more efficient charge separation.¹⁶ From this point of view, the couple CdS/TiO₂ is very efficient, but the application of this system to a larger scale is not possible due to the cadmium toxicity. Another way to act over the lifetime of the charge carriers is the titania doping with metallic ions. The doping ions can act as electron traps, resulting in an efficient separation of the electrons and holes,¹⁵ or as recombination centers for the electron/hole pairs, in this latter case leading to a decrease in the lifetime of the charge carriers.¹⁷ The factors deciding between these two behavior types are not completely understood, requesting further investigations.

The aim of this study was to prepare and to study the properties of several Zn-doped titania thin films photocatalysts. The technique used for the preparation was the dc reactive sputtering. By this technique, atoms from a target (cathode) connected to a voltage source are sputtered off by positively charged ions existing in the plasma created between the cathode and the anode (substrate holder). These atoms react further with the particles of the reactive gas and deposit on the substrate under an oxidized form. This

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technique has been used because is a very versatile deposition method, allowing the preparation of thin films with controlled crystallinity, composition (including ion doping) and thickness.¹⁸⁻²³

The photocatalytic behavior of the thin films was checked in the acetone photooxidation. Acetone was chosen because is a model pollutant molecule, which is responsible for the air quality lowering in the insufficiently aerated indoor spaces. Data concerning the adsorption and photocatalytic degradation of acetone on pure TiO₂ have been previously reported.²⁴⁻²⁵ The titania catalysts utilized in these studies were either those available on the market (as Degussa P25) or prepared via titanium precursors precipitation.²⁴⁻²⁵ Kinetic studies²⁵ indicated that the gas-phase photocatalytic oxidation of acetone is thermally activated up to 100 °C, and the reaction rate obeys a Langmuir-Hinshelwood rate expression.

EXPERIMENTAL

Photocatalysts preparation

Thin films deposition was carried out by reactive dc magnetron sputtering using a Sputtron II, Balzers equipment. The titanium source was a metallic titanium target (99.7%, from Lesker, 10 cm diameter), which was modified with 1 up to 5 metallic Ni inserts (99.98 % purity), each insert having a surface area of about 0.2 % from the total area of the target. The Ti target was connected to a negative dc bias source, so as to be bombarded by positively charged ions present in the plasma. For each deposition, various carrier materials were introduced in the deposition chamber: glass (microscope slides, RE-WA Lehmann-Schmidt), (100) n-type silicon (Siltronix), or glass coated with indium-tin oxide (18 ohm per square ITO, Merck Balzers).

Before each deposition, the deposition chamber was evacuated to a vacuum of 10⁻⁷ mbar, and the target was cleaned by sputtering in Ar atmosphere for 30 min. Subsequently, the composition of the reactive gas mixture and the total pressure inside the chamber were fixed. For all the samples, the depositions were carried out in an Ar + H₂O (vapors) gas mixture. The total pressure and the composition of the gas mixture varied from 3 · 10⁻³ mbar and 33% H₂O for samples #1^b - #5^b to 6 · 10⁻³ mbar and 16% H₂O for samples #1^a - #4^a. Substrates temperature during depositions was kept constant at 573K.

Catalysts characterization

Films thickness was measured with an Alphastep 500 Surface profiler (Tencor Instruments) coupled to a computer. XRD patterns were obtained using a Rigaku diffractometer, the Cu K α radiation ($\lambda=1.5418$ Å) being provided by a Philips X-ray source. The measurements were realized in grazing incidence geometry, with an angle of 5° between the X-ray direction and the film surface. Atomic force microscopy (AFM) observations were provided by a Topometrix Explorer AFM in the non-contact mode. UV-Vis spectra were collected using a Cary 500 Scan (Varian) spectrometer. Photocatalysts composition was determined by electron probe microanalysis (EPMA). Thin films resistivity was measured in vertical geometry, using gold contacts on the top surface of the films, and contacts on ITO substrates, as previously described.²⁵ Because of the presence of the conducting pinholes, only an approximate value could be deduced for the resistivity of the samples.

Photocatalytic tests

Photocatalytic tests were performed in a flow system, using a water-cooled quartz reactor. The catalysts were irradiated using a medium pressure Philips HPK 125 W UV-lamp. For the catalytic tests we utilized only the samples deposited on glass. Catalyst platelets of 1.60-2.30 cm² surface area were placed inside the reactor, perpendicular to the light propagation direction, the titania-based film being exposed to the UV radiation.

Purified and dried air, containing 34% acetone, was sent to the reactor with a flow rate of 6.6 cm³ min⁻¹. The gas flow circulation rate was maintained constant during the experiments using a pump. The reactor was on line coupled to a Fisher-Rosemount gas analyzer, equipped with a CO₂ detector. The gas analyzer was calibrated before each test. Analysis of the liquid in the photoreactor was carried out by gas chromatograph analysis using a GC Hewlett-Packard 5890 Series II.

Before UV irradiation, the acetone containing air stream was purged through the reactor over the catalysts for 20 minutes. No catalytic reaction products were detected in the absence of the UV irradiation. The initial moment of each catalytic experiment was considered the moment when the UV lamp was turned on.

The activity was expressed as steady-state conversion % per surface area of platelets. The conversion was calculated as number of moles of acetone transformed in CO₂ reported to the number of moles of acetone present in the gas mixture. The exposure time was at least 200 min.

RESULTS AND DISCUSSION

Photocatalysts preparation

Table 1 presents the Zn amount for each photocatalyst, as provided by EPMA. The titanium to oxygen ratio (not shown) is slightly higher than the stoichiometric value of 2, suggesting that zinc was incorporated in the titania matrix in an oxidized form. The amount of Zn incorporated by sputtering in the titania matrix was lower than 0.1%.

Table 1

Chemical composition of the investigated photocatalysts

Sample	Zn at%
#1 ^a	0
#2 ^a	0.0279
#3 ^a	0.0522
#4 ^a	0.0844
#1 ^b	0
#2 ^b	0.023976
#3 ^b	0.040057
#4 ^b	0.055983
#5 ^b	0.07654

^a – thin films deposited under a total pressure of $6 \cdot 10^{-3}$ mbar (water partial pressure 16%)

^b – thin films deposited under a total pressure of $3 \cdot 10^{-3}$ mbar (water partial pressure 33%)

Photocatalysts characterization

1. Crystalline structure

XRD patterns recorded for the investigated samples exhibit diffraction peaks corresponding to the anatase and rutile allotropic forms of titania. The anatase-to-rutile ratios calculated with the formula given in²⁶ show that the anatase phase is predominant (the percent in anatase was higher than 98%). Crystallites size was calculated by using the Scherrer equation.²⁷ Fig. 1 presents the crystallite size versus Zn content, for samples #1^b - #5^b. Crystallites dimensions varied between 11 and 16 nm, the highest value corresponding to the undoped sample.

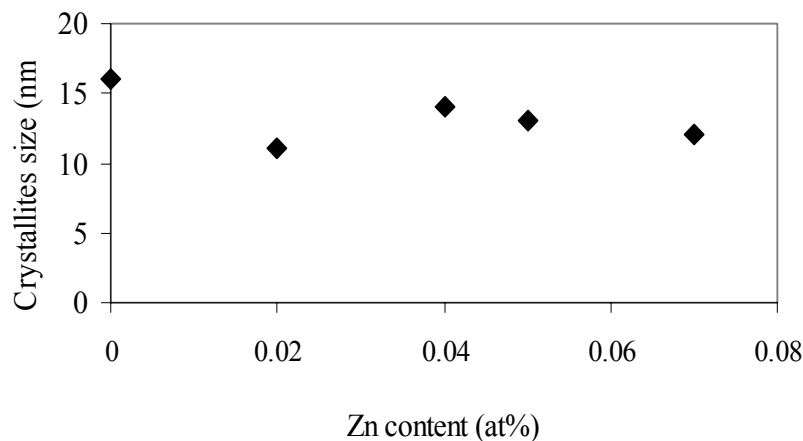


Fig. 1 – Crystallite size versus Zn content, for the samples #1^b - #5^b.

2. Surface morphology

AFM analyses revealed a polycrystalline structure for the investigated catalysts. The top view image for all the samples corresponds to a superposition of round- and oval-shape grains. The morphology does not seem to depend neither on the deposition conditions nor on the Zn content. Fig. 2 shows a typical AFM top view picture, obtained for sample #3^a, scanning a surface of 10^6 nm². For this sample, the analysis of the surface led to a roughness value of 28 nm. For the other samples, the roughness varied around this value within a narrow range (28 ± 8 nm).

3. Electric properties

Resistivity measurements showed that the samples exhibit a high resistance to the transport of charge carriers, irrespective to the Zn content. Fig. 3 presents the conductivities exhibited by the samples #1^b - #5^b, as

function of the Zn content. The conductivity seems to not be influenced by Zn doping. For this catalysts series, the highest conductivity is shown by the sample #4^b ($42 \cdot 10^{-7} \text{ Sm}^{-1}$), but this value is still in the range of a resistive behavior. The repetition of these measurements confirmed the fact that the values given in Fig. 3 are not an artifact. Under these conditions the value measured for the sample #4 can be assigned to the doping effect of Zn.

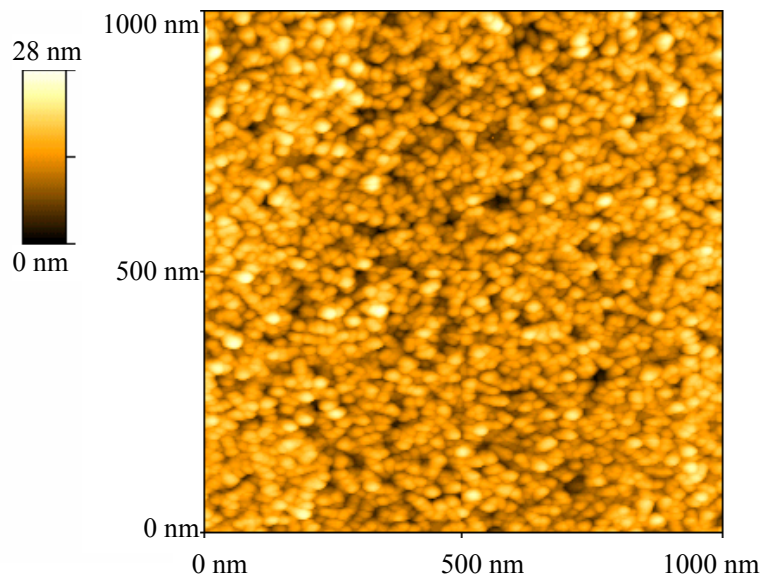


Fig. 2 – AFM picture of sample #3^a.

4. Optic properties

All the samples exhibit total light absorption at wavelengths around 330 nm, value resembling to that obtained for the powder anatase (350 nm).²⁸ Fig. 4 shows the UV-Vis spectra of the samples #1^a - #5^a. The bands between 400 and 600 nm are most probably light interference bands, the interference phenomenon appearing when the light is transmitted through thin films. The shift of the band position followed the content of Zn, proving again the structural effect of doping titania.

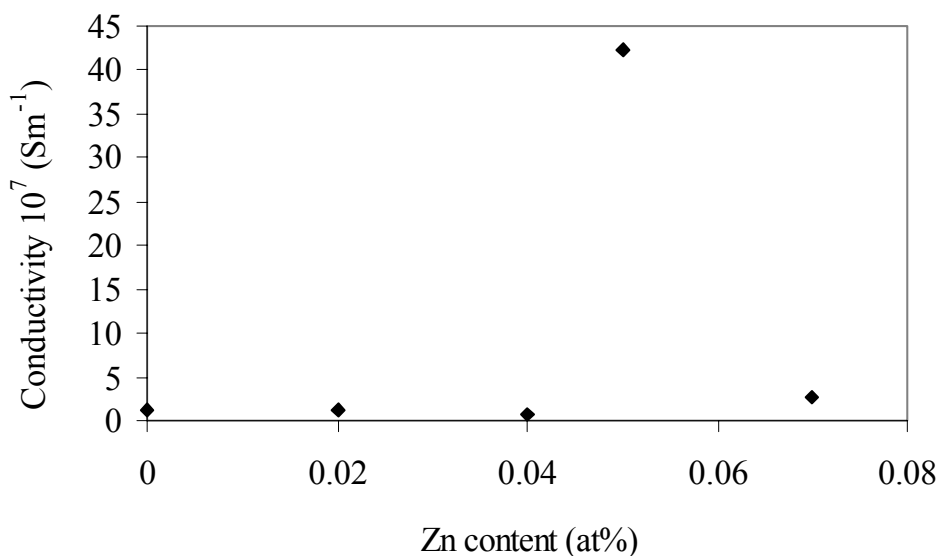


Fig. 3 – Electric conductivity of samples #1^b - #5^b.

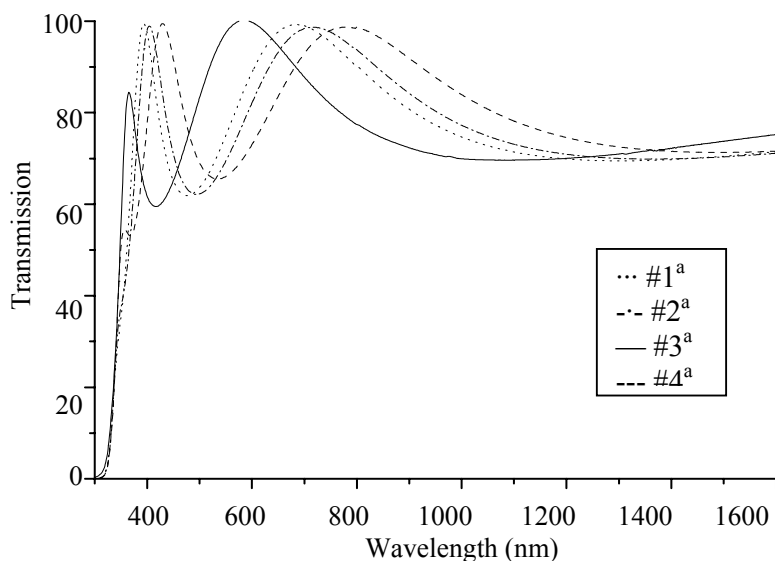
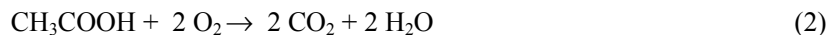


Fig. 4 – UV-Vis spectra of the samples #1^a - #5^a.

5. Photocatalytic tests

Photodecomposition of acetone, as resulted from combined gas and liquid analysis followed the sequence



Figures 5 and 6 present the conversion measured at steady state by the two photocatalysts series, as a function of the Zn content. The steady state was reached after 30 minutes from the beginning of the reaction (see Fig. 6).

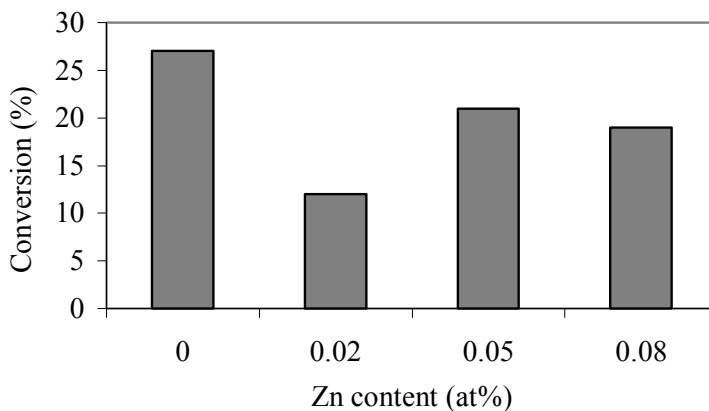


Fig. 5 – Conversion versus Zn content, for the first catalysts series (samples #1^a - #4^a, prepared under a total pressure of $6 \cdot 10^{-3}$ mbar, water partial pressure 16%).

The conversion measured for the undoped samples (#1^a and #1^b) were of 27% and 8%, respectively. Since the photocatalysts compositions was similar, this difference seems to be induced by the use of different preparation conditions. In the first photocatalysts series (samples #1^a - #4^a) the highest activity is exhibited by the undoped sample (#1^a). The doping with Zn ions resulted in a decrease of the catalytic activity. On the contrary, in the second photocatalysts series (samples #1^b - #5^b), the doping with Zn ions had a benefic effect

on the activity, all the doped samples (except for the sample #2^b) exhibiting conversions higher than the undoped sample. However, as a general behavior, the conversions obtained for the second catalysts series were lower than those observed for the catalysts of the first series. These results underline the fact that the deposition conditions play an essential role in establishing the catalytic properties of the titania thin films. For each catalysts series, there is an optimum Zn loadings (#2^a - #4^a and #2^b - #5^b), which provides an optimum activity. These results are in line with data reported previously for Ta- and Ni- doped TiO₂ dc-sputtered catalysts.^{29,30}

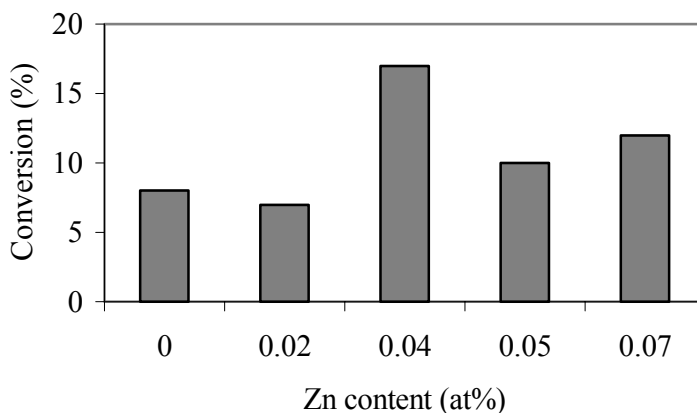


Fig. 6 – Conversion versus Zn content, for the first catalysts series (samples #1^b - #5^b, prepared under a total pressure of $3 \cdot 10^{-3}$ mbar, water partial pressure 33%).

CONCLUSIONS

Using the dc reactive sputtering technique, titania-based thin films of low crystallinity, incorporating Zn ions amounts up to 0.08 at% were synthesized. Although these amounts were far too low to produce in the titania matrix any noticeable XRD transformations, the effect on the catalytic activity was evidenced for each series.

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