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Efficient photodecoloration catalysts, based on ZnO nanoparticles coated in two steps on glass substrates

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***Abstract*—ZnO, ZnO:Ag and ZnO:Cu thin coatings were prepared on glass substrates by an innovative dip–coating technique coupled with the addition of ZnO nanoparticles and their structural, morphological and optical properties were investigated. X-ray Diffraction (XRD) analysis revealed the coating´s hexagonal wurtzite phase with a preferred (002) plane orientation. The mean crystallite size calculated on the basis of the Debye-Scherrer model was 31 nm and a small dislocation density of 1.04×10^{-3} nm^{-2} was obtained, indicating the existence of few lattice defects and good crystallinity. The atomic force microscopy (AFM) observation showed the coating´s granular nature composed of spherical nanoparticles with almost homogeneous distribution. The average transmittance in the visible región is around 75–80% and optical bandgap, 3.25 eV, respectively were obtained for our coatings indicating their suitability in photocatalytic applications. UV–vis spectrometry reveals a methylene blue (MB) dye decoloration efficiency of 96% after 180 min using ZnO:Ag (3:3 layers) film.**

Keywords—photocatalysis, ZnO thin coatings, methylene blue, dip–coating

I. Introduction

Global pollution around the whole world is a thread to human health and peace. Water pollution is now a serious issue in countries with emergent economy and permissive laws. First world economies are not free from this cathastrophic situation [1,2]. As a matter of fact large scale production of factories, open minery, toxic wastes from pharmaceuticals, farms, etc. pollute more and more water resources and air [3]. The conventional sewage treatment plants are part of the solution to water pollution involving physical and chemical techniques, such as filtration, adsorption, biodegradation, coagulation and ion exchange but are not high efficiency enough in removing the synthetic organic dyes like methylene blue (MB) because they are expensive and non-environmentally friendly processes for complete conversion of the pollutants [4,5].

The Advanced Oxidative Processes have emerged as an ecofriendly decontamination techniques for water reciclyng. The photocatalityc process (PP), based on UV or visible light with stable catalysts are now a well stablised and reliable technique.

Oxide semiconductors such as TiO_2, ZnO, have shown relevance in dye degradation, hydrogen production, carbon dioxide reduction and antimicrobial activity [1,2,3,4,5]. The relative abundance in nature, harmless and low cost makes ZnO a good candidate for catalyst manufacturing by low cost techniques.

The physical and chemical techniques have consolidated in the manufacturing of quality catalysts for water reciclyng. ZnO versatility concerning the deposition method could be very appealing. Pulsed laser deposition (PLD), molecular beam deposition (MBD), atomic layer deposition (ALD), chemical synthesis and magnetron sputtering have been significantly applied in optoelectronic research fieds [6,7].

The manufacturing of catalyst with increased efficiency has received a new impulse with the nanotechnology innovations. Low cost, energy saving and less contamination are the characteristics of new processing. In this regard, there are antecedents about the incorporation of Ag and Cu in semiconductors lattice aiming to boost the photocatalytic performance [8,9]. The addition of this metals to ZnO results in enhanced photocatalytic activity in the visible spectral range through the surface plasmon resonance (SPR), increasing visible light absorption [8]. Besides, the electron-hole pair recombination rate is diminished via the formation of a Schottky barrier [8,9,10]. The selection of the most appropriated ZnO:M growth method and the comprehension of the metal (M) incorporation mechanism in the ZnO lattice (both as a dopant, or forming aggregates, or combined oxide form), continues to be under debate.

The preparation of ZnO nanoparticles by low cost techniques followed by deposition on glass substrates by simple dip coating technique prevents the contamination usually observed with traditional film processing. In fact, by RBS studies the presence up to 10 at% of alkaline ions can be detected on the surface of ZnO films deposited on sodalime glass substrates [11]. A solution to this undesirable situation is by manufacturing the

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metal oxide powders at high temperatures of processing, followed by adding the obtained nanoparticles in a gel and then coating a cheap glass substrate by dippings at the required application or optimum thickness. In this work, the manufacturing of ZnO as more efficient cataliyst for decoloration of MB dissolved in water is showed.

II. Experimental

A. Synthesis of ZnO NPs

Chemical homogeneous precipitation method was applied to synthesis of ZnO NPs. Here, 2.1 g of [$Zn(CH_3COO)_2$*$2H_2O$] was dissolved in 60 mL dH_2O under stirring. Then, 1.6 g of NaOH was dissolved in 100 mL CH_3OH and was deposited drop by drop to [$Zn(CH_3COO)2$*$2H_2O$] solution and continued the stirring (1.5 h, 60 °C). The white precipitate formed was obtained by centrifugation (4,500 rpm) followed by CH_3OH wash. The NPs were kept for drying (100 °C) and calcinated (800 °C, 2 h).

B. Coatings deposition

ZnO, AgO and CuO precursor solutions were prepared independently at room temperature (RT) by the following procedure: for ZnO sol-gel 16.46 g of [$Zn(CH_3COO)_2$*$2H_2O$] was dissolved in 125 mL of methoxyethanol, which was maintained in constant magnetic stirring for 30 min. After that, 16.20 mL monoethanolamine(MEA) was slowly added to allow complete dissolution of the solid salt, then solution was left aging for 7 days, and 0.5 g of ZnO NPs was added later. AgO solution was prepared by dissolution 0.5 g of $AgNO_3$ in 100 mL of CH_3OH. Finally, CuO solution was prepared by dissolution 0.32 g of $CuCl_2$*$2H_2O$ in 100 mL of CH_3OH. Transparent solutions without precipitates were obtained in all cases. Each solution was kept separated.

The ZnO, ZnO:Ag and ZnO:Cu films were deposited by the dip-coating method at a withdrawal speed of 5 cm/min. Each layer was dried for 5 min at 250 °C, cooled to RT, and coated again to obtain a thickness of ~200 nm for all films. Different number of coatings were necessary (3–6). The final films were sintered in a conventional oven under an open atmosphere at 450 °C for 1 h. Two sets of samples were prepared, the first set of samples consisting on ZnO, ZnO:Ag and ZnO:Cu with 3 layers of ZnO coatings and 3 layers of metal oxyde (MO) coatings for the doped ones, and the second set consisting on ZnO, ZnO:Ag and ZnO:Cu with 6 layers of ZnO coatings and 3 layers of (MO) coatings for the doped ones.

C. Structural characterization

The resulting nanomaterials were characterized by X-Ray Diffraction on a PANalytical X'Pert PRO Diffractometer using Cu Kα radiation of 1.5406 Å operating at 45 kV and 20 mA, in a scanning range of 10-80° (2θ). Crystallite sizes were estimated from Scherrer's equation (1), where D_{hkl} is the average crystallite size (nm), λ is the wavelength of Cu-Kα radiation, θ is the Bragg's angle of diffraction, β is the full-width at half maximum intensity of the peak in radians, and K is a constant, usually 0.9.

$$D_{hkl} = K\lambda/\beta \cos\theta \quad (1)$$

The dislocation density (δ) was calculated from D (2):

$$\delta = 1/D^2 \quad (2)$$

D. Optical properties

Optical properties were characterized with a Jasco V-670 UV–Vis spectrophotometer in the 300–900 nm spectral range. The band gap values were calculated from the Tauc´s formula equation (3), where, α is the absorption coefficient, A is a constant, hν is the photon energy (eV), Eg is the energy band gap (eV), and n= 2, since ZnO is a direct band gap semiconductor.

$$\alpha h\nu = A(h\nu - Eg)^n \quad (3)$$

The film thicknesses were also measured using a mechanical stylus profilometer (KLA-Tencor P-15) with a vertical resolution of 0.15 nm.

E. Morphology

The surface morphology of the ZnO coatings was analyzed by atomic force microscope (Solver next NT-MDT) operating in tapping mode. Particle size was directly estimated by using the image software.

F. Photocatalytic activity

The photocatalytic properties of the ZnO coatings were assessed by the decoloration of an aqueous solution of methylene blue (1.2×10^{-5} M). The process consisted in immersing the deposited coatings into a quartz cell containing 3 ml of MB solution. Then, cells were put into an isolated chamber and where irradiated with a central UV lamp (G15T8 germicidal 15 W with major emission at 232 nm). The sample to lamp distance was kept at 4 cm. The optical absorbance was continuously monitored with a Jasco V-670 UV–Vis spectrophotometer in intervals of 0.5 h, during 3 h. The residual concentration of MB was calculated from the absorption peak located at 664 nm which corresponds to the MB maximum absorption peak. A dark room test was performed prior to the photocatalytic tests.

III. Results

A. Structural properties

The X-ray diffraction spectra of ZnO coatings, undoped, Ag and Cu doped, are shown in Fig. 1. According to the JCPDS card No. 01–074–0534, all samples fit well to hexagonal ZnO wurtzite structure and no extra phases of Cu and Ag compounds were detected above the 2 at. % detection limit of the technique. The peaks corresponding to (002) and (102) planes are observed, with a small contribution of (103) planes in all the cases. The peak associated to (102) planes increases its height when coatings were doped by Cu or Ag. This can be due to the annealing process after inmersing coatings in the solution containing the dopant. The slight shift observed in (002) peak position can be considered as an indicator of the incorporation of Cu or Ag dopant in the ZnO host lattice by the substitution of Zn^{2+} ions.

The crystals growth direction seems to be affected by the incorporation of the MO since the preferred orientation along (002) plane is no longer observed in ZnO:Ag (3:3 layers) and ZnO:Cu (3:3 layers) samples. The rise in intensity of the (102) plane signal might indicate an increase in the lateral growth of ZnO wurtzite structure, which was initially dominated by orientation of *c*-axis growth.

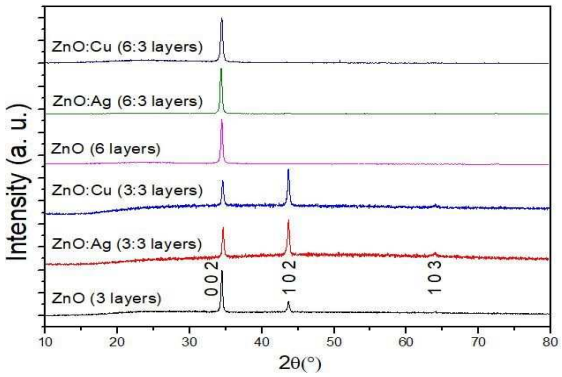


Fig. 1. X-ray diffractograms of samples.

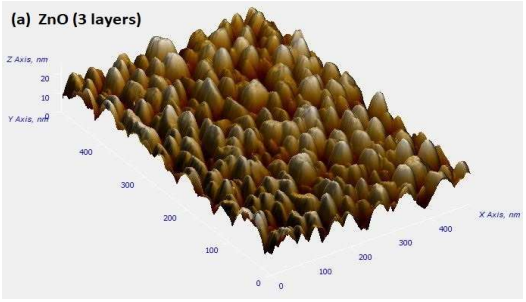
Crystallite size calculations from (002) plane is summarized for each film in Table 1. The dislocation density (δ) was found to be 1.04×10^{-3} nm^{-2}.

TABLE I. CRYSTALLITE SIZE

Sample	*Crystallite size (nm)*	*FWMH(°) from (002)*
ZnO (3 layers)	31	0.2560
ZnO:Ag (3:3 layers)	30	0.2360
ZnO:Cu (3:3 layers)	24	0.2760
ZnO (6 layers)	33	0.2560
ZnO:Ag (6:3 layers)	33	0.2760
ZnO:Cu (6:3 layers)	36	0.3420

B. Morphology. Thickness and roughness measurements.

The thickness of coatings deposited on glass substrates ranged between 115–207 nm. Fig. 2. Displays AFM micrographs in tapping mode of ZnO thin coatings deposited. It reveals that all films have a smooth granular surface morphology composed of grains with uniform average diameter of 40 nm, free of cracks and other surface defects, in good agreement with (δ). For scanning area of 10×10 μm^2, the root-mean square (RMS) of average surface roughness for all samples was determined obtaining close values of RMS for all samples. The measured roughness parameters were summarized in Table 2.



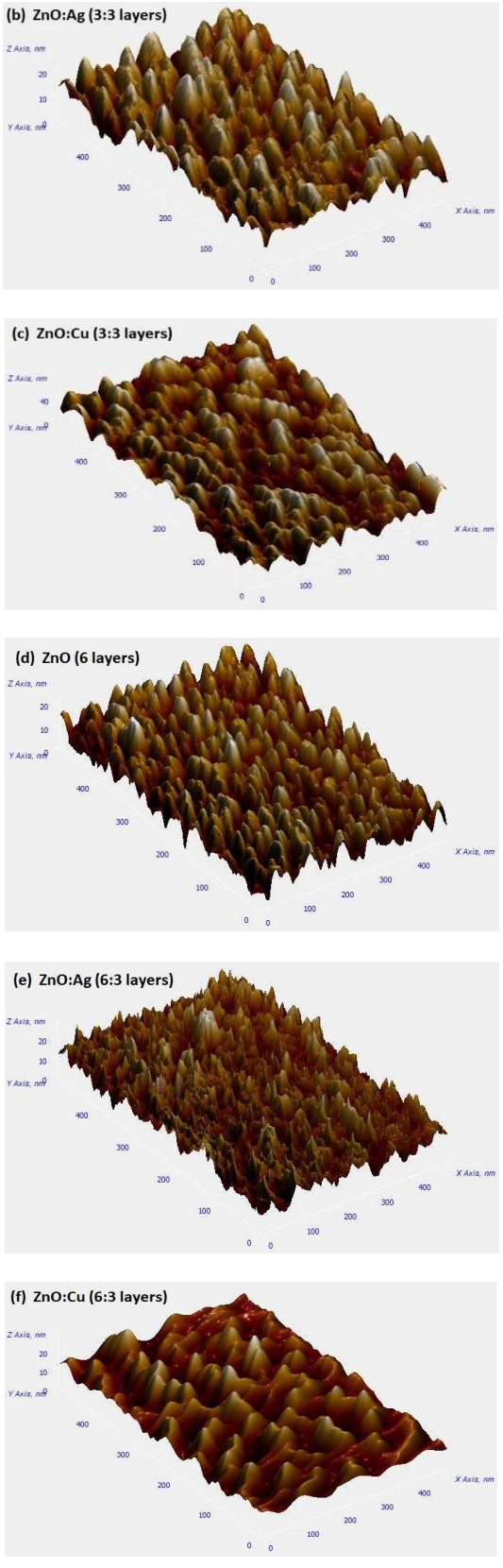


Fig. 2. AFM surface morphology images of the ZnO thin films.

TABLE II. RMS ROUGHNESS AND THICKNESS MEASUREMENTS

Sample	*RMS (nm)*	*Thickness (nm)*
ZnO (3 layers)	13.562	154
ZnO:Ag (3:3 layers)	5.445	115
ZnO:Cu (3:3 layers)	7.375	124
ZnO (6 layers)	9.190	175
ZnO:Ag (6:3 layers)	9.049	156
ZnO:Cu (6:3 layers)	12.263	207

C. *Transmittance spectra and band gap calculations*

Fig. 3 shows the transmittance spectrum of the ZnO thin films. Fluctuations and wave like patterns appeared on the transmittance spectrum due to the interference of light reflected between the air-film and film-glass interfaces, indicating the film's low surface roughness and good uniformity. The film had an average transparency of about 75–80% in the visible region which may be associated with the film's good structural homogeneity and crystallinity [12].

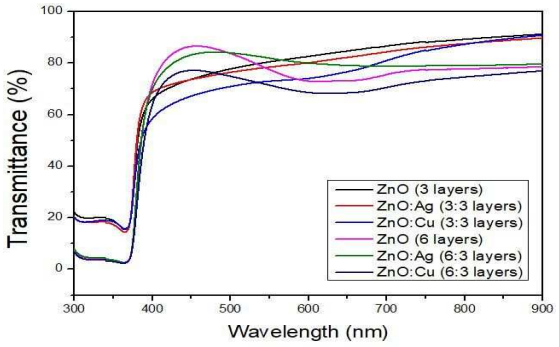


Fig. 3. Optical transmission spectrum of ZnO thin films.

Eg was found to be 3.25 eV for all simples, from the Tauc plot $(\alpha h\nu)^2$ versus $h\nu$, shown in Fig. 4, by extrapolating the linear portion of the absorption edge to $\alpha h\nu$=0. This was slightly less than 3.37 eV for bulk ZnO.

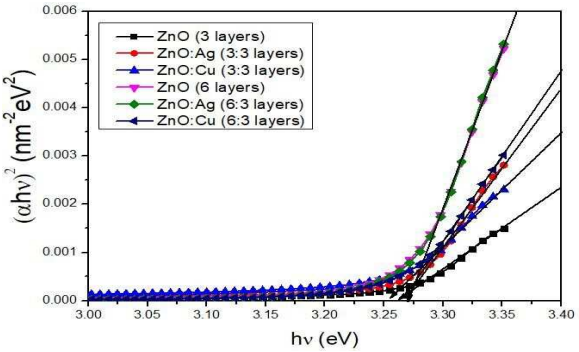


Fig. 4. Tauc plot of ZnO thin films.

D. *Photocatalytic activity measurements*

The change in MB dye concentration C/C_o as a function of exposure time to the UV illumination for undoped, Cu and Ag doped ZnO coatings are presented in Fig. 5. Since the MB dye is decolored with exposure to UV light, a control test, namely photolysis, without catalyst or sample was also performed for this purpose, and it is identified in the plots as blank, also a dark room test was made before each sample measurement for the purpose of reaching adsorption-desorption equilibrium. The MB concentration [MB] = C was calculated from the absorption spectra of the degraded MB solution contained in a quartz cell, following the Beer–Lambert's law for a wavelength of 664 nm. Each photocatalytic test was performed 4 times, so that each experimental point in Fig. 5. represents the average of 4 measurements made with the same film.

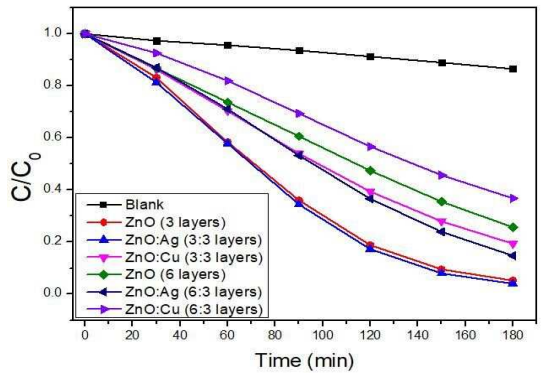


Fig. 5. Photocatalytic decoloration rate of ZnO thin films.

Even though the photocatalytic activity of pure ZnO (3 layers) film was higher tan most of the doped ones in this work, only bested by ZnO:Ag (3:3 layers), it is thought that the lower activity of the doped films was caused by a detriment on the crystalline quality of ZnO. This results indicate that the use of ZnO nanoparticles in the dip-coating process favors the obtention of a more efficient catalyst.

The crystal quality decrease might be chemically caused by the presence of Cu^{2+} ions in the copper precursor solution and further oxidation of the Ag^{+} ions once the film is sintered.

Another possible explanation on the lower photoactivity of doped films is that a clear trend toward the use of MO or an increasing number of ZnO coatings is not observed. This hints that the observed differences in photoactivity can be associated with the surface area of the samples.

The reaction kinetics was obtained by plotting the natural logarithm of concentration ratio versus the exposure time shown in Fig. 6. It was found that photolysis showed a value of 0.05 h^{-1}, whereas measurements with ZnO samples presented reaction rate magnitudes of 1.02, 1.11 and 0.55 h^{-1} for undoped simples, silver and copper doped ZnO coatings, respectively. The highest reaction rate was obtained for the Ag doped ZnO coating (1.11 h^{-1}). These results confirm the enhance in the decoloration catalytic properties of ZnO coatings, as was

expected. The reaction rates of all coatings are presented in Table 3.

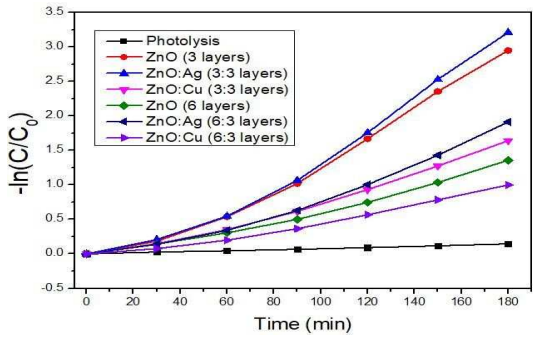


Fig. 6. MB decoloration kinetics for ZnO thin films.

TABLE III. DECOLORATION RATES

Sample	*k (h^{-1})*	*Adj. R^2*
Photolysis	0.05	0.9964
ZnO (3 layers)	1.02	0.9711
ZnO:Ag (3:3 layers)	1.11	0.9656
ZnO:Cu (3:3 layers)	0.55	0.9802
ZnO (6 layers)	0.45	0.9779
ZnO:Ag (6:3 layers)	0.64	0.9638
ZnO:Cu (6:3 layers)	0.34	0.9771

IV. DISCUSSION

The coupling of two techniques, namely nanoparticle synthesis and the dipping techniques for coating processing, in the manufacturing of ZnO coatings, shows enhance in the performance of photocatalityc degradation of MB dissolved in water as compared with films deposited by spray pirolisis published in other works [13,14].

The powder presentation is more efficient in the decoloration of MB than the film sample, due to more exposed active surface area. However, an extra process is required in the first case, regarding the recovery of powder after decoloration process.

The coatings showed a good adhesion to the glass substrates with at least three cicles of operation, this can be assumed because film manipulation does not caused visible coating lose.

V. CONCLUSIONS

The structural, morphological and optical properties of dip–coating deposited ZnO thin films by a innovative dip–coating technique coupled with ZnO nanoparticles were characterized. The films had a hexagonal wurtzite crystal structure with a preferred orientation along the (002) direction. AFM micrographs showed nanoparticles which coalesced to form granular grains on the surface of the film. High average transmittances, around 75–80% were observed in the visible region confirming the high transparency nature of the films. The optical band gap is determined to be 3.25 eV for all samples. indicating the suitability of the ZnO thin films for photocatalytic applications. UV–vis spectrometry reveals a methylene blue (MB) dye decoloration efficiency of 96% after 180 min for ZnO:Ag (3:3 layers) which corresponds to best performance among the studied films, indicating better photocatlytic activities for films with 3 layers of coating, and also indicating that the use of ZnO nanoparticles in the dip-coating process favors the obtention of a more efficient catalyst.

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