

ZnO ELECTRODEPOSITION ONTO GOLD FROM RECORDABLE COMPACT DISCS AND ITS USE AS PHOTOCATALYST UNDER SOLAR IRRADIATION

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Abstract - A ZnO film was electrodeposited onto a gold substrate obtained from a recordable compact disc and tested as photocatalyst in degradation of dye in aqueous solution. X-ray diffractometry and atomic force microscopic analysis showed a pure ZnO phase with particle sizes in the nanometric scale. The results showed that the photocatalytic activity of the film is significant, with more than 90 % degradation of the dye in under 6 h sunlight irradiation. The photocatalytic process in sunlight follows first-order kinetics.

Keywords: ZnO Film; Electrodeposition; Recordable compact discs; Photocatalysis.

INTRODUCTION

Zinc oxide is an important semiconductor material for applications in batteries, biosensors, photovoltaic devices and solar cells (Wang, 2004). ZnO powder has been used as photocatalyst in the degradation of organic pollutants in aqueous solution (Gaya *et al.*, 2009). The use of a conventional powder catalyst has the disadvantage of requiring separation of the powder after the reaction process. An alternative to solve this problem of separation and recovery of the powder photocatalyst is to use the photocatalyst in an immobilized form, such as a thin film. Different techniques have been used to prepare ZnO films such as thermal evaporation, oxidation and anodizing, chemical vapor deposition, sputtering, pulsed laser deposition, sol-gel, spray pyrolysis and electrodeposition (Niesen and Guire,

2002; Triboulet and Perrière, 2003). Compared to other methods, electrodeposition is a simple, low cost, and low temperature method suitable for large-scale production (Xu *et al.*, 2005). Recent research demonstrates the possibilities of using ZnO films, obtained by different methods, as photocatalyst for the degradation of different organic compounds under UV and visible irradiation (Flores *et al.*, 2011). However, studies of azo-dye photodegradation by ZnO films immobilized onto gold substrates obtained by electrodeposition, using solar energy as the source of UV irradiation, are nonexistent in the literature.

In this work we present a simple use for recycled recordable compact discs (CD-R), using the gold contained in them as a substrate for the ZnO film used in the photocatalytic process. The electrodeposition technique was used for the formation of the film on the gold substrate. The structure and

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morphology of the film formed was analyzed by X-ray diffractometry (XRD) and atomic force microscopy (AFM).

EXPERIMENTAL

Deposition of the Film

The electrolyte used was composed of 0.1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, at pH 5.0. The ZnO film was electrodeposited at - 0.9 V for 2 min under agitation, with the bath temperature maintained at 70 °C. The deposit was controlled by means of a potentiostat-galvanostat (G 3901 model), using a three electrode configuration: Ag/AgCl electrode (-0.1988 V vs. normal hydrogen electrode) as a reference electrode, platinum wire as a counter electrode and the Au (111) substrate (film area: 9 cm²) as the working electrode. The voltammetric analysis was performed in the voltage range from - 0.1 to - 1.0 V versus Ag/AgCl, at a scan rate of 10 mV.s⁻¹. After electrodeposition, the sample was dried under ambient conditions at room temperature for subsequent analyses. The gold (111) substrate was obtained from a recordable compact disc (commercial CD-R). The CD-R is composed of different layers as shown in Fig. 1(a). The CD-R was subjected to the action of concentrated nitric acid (HNO_3) (Sawyer, 1974) in order to expose the Au metallic layer.

Characterization of the Film

The film was characterized with a X-ray diffractometer (Bruker D8 Advance). The X-ray source was Cu-K α radiation, powered at 40 kV and 40 mA. Data were collected from 30 to 65° (2 θ) with

a step size of 0.05° and a count time of 35s. The average nanocrystal size was determined using the Debye-Sherrer equation: $D = K \cdot \lambda / (\beta \cdot \cos\theta)$, where D is the average crystallite size, K is the Sherrer constant (0.90), λ is the wavelength of the X-ray radiation (0.15425 nm for Cu-K α), β is the peak width at half height and θ corresponds to the peak position (in the current study, $2\theta = 34.33$). The morphology of the film was examined in an atomic force microscope (Agilent Technologies 5500).

Photocatalytic Activity Measurements

The sunlight experiments were carried out in a glass vessel ($\varnothing_{\text{int.}} = 5$ cm) (Fig. 1(b)) between 10.00 am and 4.00 pm during the month of August, 2011 (winter season), in Santa Maria City (29° 43' 23" S and 53° 43' 15" W), Brazil. The intensity of sunlight was measured using a Brewer spectrophotometer (Canada) (~160 W m⁻²). The photocatalytic degradation of Direct Black 38 (DB38) dye was studied at a dye concentration of 10 mg.L⁻¹, at a solution pH = 6.0. Direct Black 38 (C.I. 30235; CAS number 1937-37-7; chemical formula $\text{C}_{34}\text{H}_{25}\text{N}_9\text{Na}_2\text{O}_7\text{S}_2$; molecular weight = 781.7 g.mol⁻¹) is a triazo dye extensively used in the leather industry. During the course of the reaction, the temperature of the dye solution ranged from 19 to 25 °C.

The ZnO film was immersed about 4 cm below the liquid surface. The solution (40 mL) was stirred with a magnetic stirrer under sunlight and aliquots were taken at certain periods of time. These aliquots were centrifuged before the analysis of colour. The concentration of dye in the aqueous solution was determined by spectrometry (Spectro vision T6-UV model), at $\lambda_{\text{máx}}$ 590 nm.

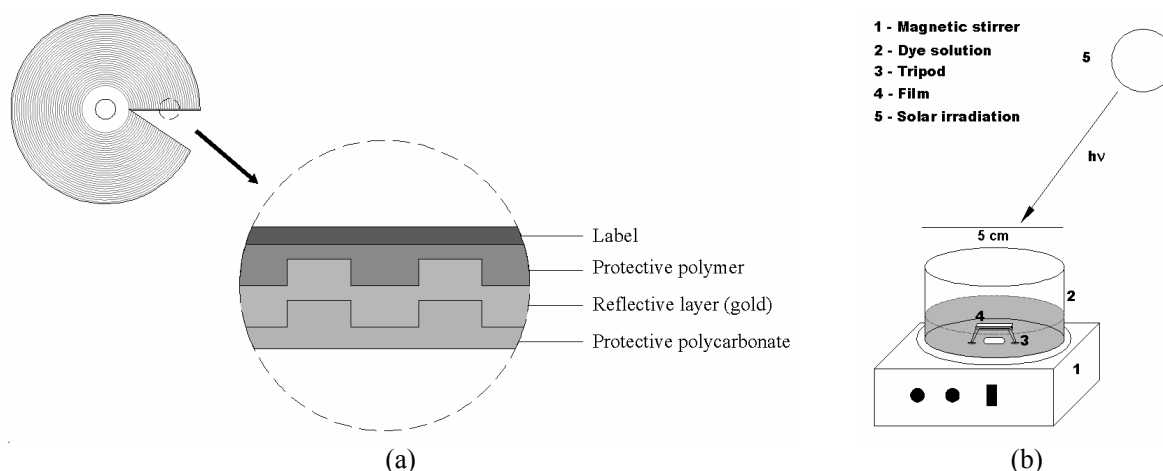


Figure 1: (a) Scheme of the structure of a CD-R, and (b) apparatus used in the photocatalytic tests.

RESULTS AND DISCUSSION

Characterization of the Film

The electrochemical behavior of ZnO was investigated through a voltammetric study (Fig. 2(a)), revealing the potential adequate for deposition and growth of the film. Fig. 2(a) shows that, above the cathodic potential -0.8 V, a sharp rise in current is observed, attributed to zinc deposition (Yoshida *et al.*, 2002). So, in this work, the optimum potential selected for the electrodeposition of ZnO film was -0.9 V, with the range between -0.8V and -1.2 V being suitable for ZnO formation (Lupan *et al.*, 2011). The XRD pattern (Fig. 2(b)) indicates that the ZnO is a wurtzite type hexagonal structure by comparison with that in JCPDS 01-070-8070 card. Six peaks appear in the diffraction spectrum in the 2θ interval of $30\text{--}65^\circ$, and correspond to (100), (002), (101), (102), (110) and (103) orientations of the ZnO hexagonal structure. The film formed is polycrystalline with a preferential orientation

of the (002) diffraction peak, showing that the film is preferentially oriented in the c-axis direction, which indicates that this axis in the ZnO film tends to grow perpendicular to the substrate surface (Ahmed *et al.*, 2010). In the XRD pattern, characteristic peaks of the (111) Au substrate also appears by comparison with JCPDS 065-2870 card. The average crystallite size, based on the peak located at $2\theta = 34.33$, of the ZnO powder deposited on the substrate was about 50 nm. In addition, the thickness of the electrodeposited ZnO film was found to be about 70 nm.

To obtain information about the morphology of the ZnO film formed on the gold substrate, atomic force microscopy (AFM) was carried out. As can be seen in Fig. 3(b), the film is composed of small ZnO nanograins, covering all the surface of the gold substrate. The average nanograins size is about 50 nm, comparable to the size estimated from XRD analysis. The film morphology presents tracks, accompanying the original shape of the gold layer of the CD-R (see Fig. 1(a) and Fig. 3(a)).

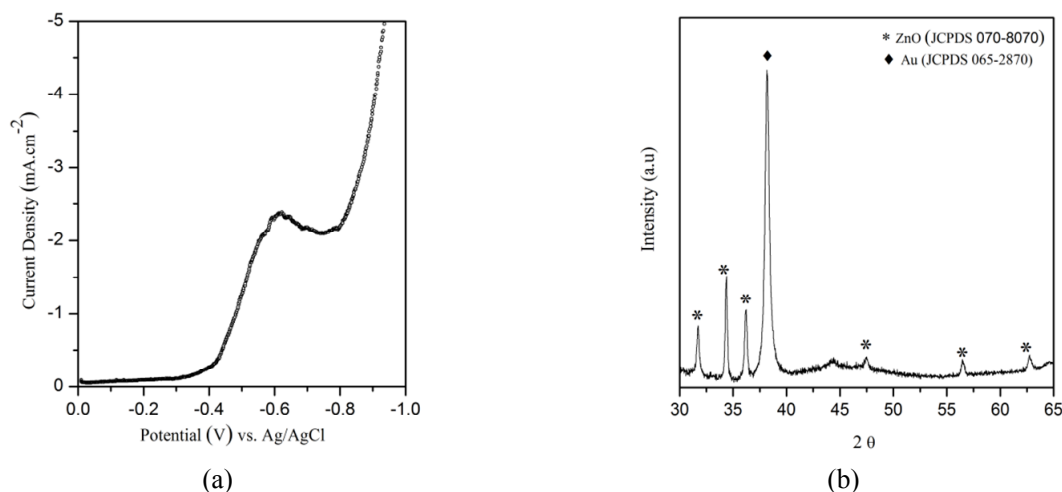


Figure 2: (a) Voltammogram of ZnO on the Au (111) substrate from a CR-R (experimental conditions = 0.1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; scan rate = $10 \text{ mV} \cdot \text{s}^{-1}$) and (b) XRD pattern of the ZnO film electrodeposited at -0.9 V.

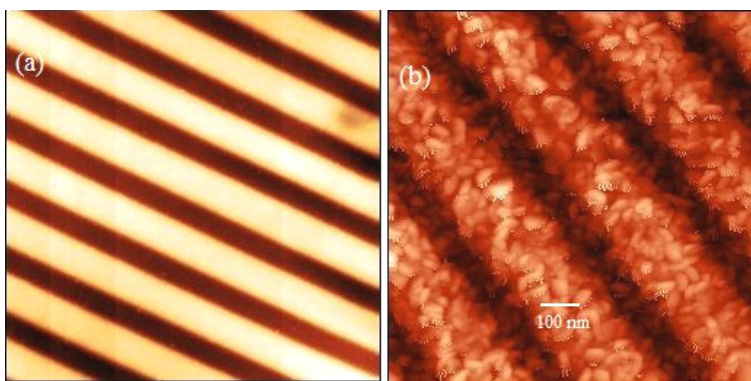


Figure 3: AFM images of (a) the gold substrate and (b) the ZnO film prepared by electrodeposition.

Photocatalytic Activity

Prior to photoirradiation, the suspension of the DB38 dye and ZnO film was magnetically stirred for 60 min to establish the adsorption equilibrium. The degradation of the dye molecules was negligible upon direct photolysis (with sunlight only) with the gold substrate alone (without the ZnO film). Degradation of the dye was only observed with the simultaneous presence of the photocatalyst and sunlight. The experimental results are shown in Fig. 4. The ZnO film exhibited the highest degradation efficiency, with 92 % of DB38 being degraded in 6h. The photocatalytic process in sunlight follows first-order kinetics according to the equation $\ln(C/C_0) = -k.t$ (Wei *et al.*, 2009), where C_0 is the initial concentration of the dye solution, C is the concentration at time t , and k is the apparent rate constant of photocatalysis. The straight line (see insert in Fig. 4) indicates a first-order process and the slope of this line corresponds to the apparent rate constant (k), which was found to be $k = 6.9 \times 10^{-3} \text{ min}^{-1}$. Other researchers have reported the efficiency of ZnO films as photocatalysts for the degradation of organic dyes. Bizarro (2010) obtained rate of reaction of the order of $7.0 \times 10^{-3} \text{ min}^{-1}$ for ZnO:Al film, while Wei *et al.* (2009) obtained rates of reaction ranging from 4×10^{-3} to $1.14 \times 10^{-2} \text{ min}^{-1}$ for ITO/CdS/ZnO composite films.

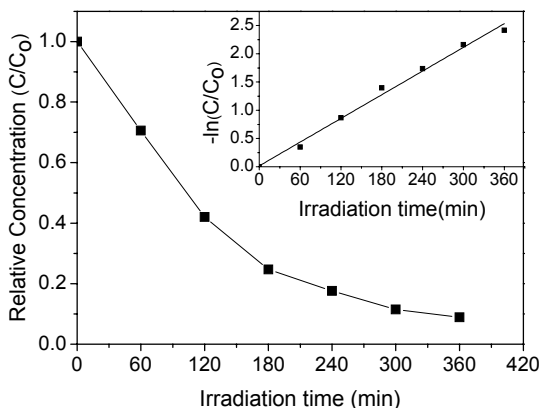


Figure 4: Decrease of the DB38 concentration in aqueous solution during irradiation of the ZnO film under sunlight. The insert shows a first-order plot of the kinetic data.

CONCLUSIONS

A ZnO film was prepared on the gold substrate obtained from a recordable compact disc (CD-R) by an electrodeposition technique. The ZnO film presented a pure phase and a crystal size on the nanometric scale. The ZnO film showed efficient catalytic activity

for degrading an azodye in aqueous solution under sunlight irradiation. The results obtained here for a ZnO film on a gold substrate represent a promising photocatalytic material for water treatment applications.

REFERENCES

- Ahmed, N. A., Fortas, G. and Hammache, H., Structural and morphological study of ZnO thin films electrodeposited on n-type silicon. *Appl. Surf. Sci.*, 256, 7443-7447 (2010).
- Bizarro, M., High photocatalytic activity of ZnO and ZnO:Al nanostructured films deposited by spray pyrolysis. *Appl. Catal. B: Environm.*, 97, 198-203 (2010).
- Flores, N. M., Pal, U. and Mora, E. S., Photocatalytic behavior of ZnO and Pt-incorporated ZnO nanoparticles in phenol degradation. *Appl. Catal. A*, 394, 269-275 (2011).
- Gaya, U. I., Abdullah, A. H., Zainal, Z. and Hussein, M. Z., Photocatalytic treatment of 4-chlorophenol in aqueous ZnO suspensions: Intermediates, influence of dosage and inorganic anions. *J. Hazard. Mater.*, 168, 57-63 (2009).
- Lupan, O., Pauporté, T., Viana, B. and Aschehoug, P., Electrodeposition of Cu-doped ZnO nanowire arrays and heterojunction formation with p-GaN for color tunable light emitting diode applications. *Electrochimica Acta*, 56, 10543-10549 (2011).
- Niesen, T. P. and Guire, M. R. D., Review: deposition of ceramic thin films at low temperatures from aqueous solutions. *Solid State Ionics*, 151, 61-68 (2002).
- Sawyer, D. T., *Experimental Electrochemistry for Chemists*. John Wiley and Sons. New York (1974).
- Triboulet, R. and Perrière, J., Epitaxial growth of ZnO films. *Prog. Cryst. Growth Charact. Mater.*, 47, 65-138 (2003).
- Wang, Z. L., Zinc oxide nanostructures: Growth, properties and applications. *J. Phys. Condens. Matter.*, 16, R829-R858 (2004).
- Wei, S., Shao, Z., Lu, X., Liu, Y., Cao, L. and He, Y., Photocatalytic degradation of methyl orange over ITO/CdS/ZnO interface composite films. *J. Environm. Sci.*, 21, 991-996 (2009).
- Xu, L., Guo, Y., Liao, Q., Zhang, J. and Xu, D., Morphological control of ZnO nanostructures by electrodeposition, *J. Phys. Chem., B*, 109, 1351-1359 (2005).
- Yoshida, T., Oekermann, T., Okabe, K., Schlettwein, D., Funabiki, K. and Minoura, H., Cathodic electrodeposition of ZnO/eosin Y hybrid thin films from dye added zinc nitrate bath and their photoelectrochemical characterizations. *Electrochem.*, 70, 470-487 (2002).