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Electrodeposited Mesoporous ZnO Thin Films as Efficient Photocatalysts for the Degradation of Dye Pollutants

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Thin mesoporous films of ZnO were prepared by electrochemical deposition using eosin Y as a structure-directing agent. After removal of the eosin from the structure, transparent porous ZnO films were obtained. The porosity and surface area of these films were determined by performing krypton BET measurements. Electrochemical deposition parameters, such as the deposition time and the eosin concentration in the plating bath, were optimized to prepare films with large internal surface areas and good mechanical properties. Eosin concentrations of 50–60 μM were found to give the best-quality mesoporous zinc oxide films with film thicknesses ranging from 2 to 3 μm . The photodegradations of a heteropolyaromatic dye (methylene blue) and a diazo dye (congo red) served as model reactions to assess the photocatalytic activity of the zinc oxide films. For both dyes, the photodegradation rate reached its maximum for mesoporous films that were prepared with eosin concentrations above 40 μM . As the photodegradation was found to occur preferentially in the larger-diameter pores of the films, the development of a very large surface area owing to a fine network of mesopores narrower than 8 nm did not significantly enhance the photocatalytic performance of ZnO films.

1. Introduction

In recent years, major attention has been devoted to the preparation of mesoporous transition metal oxides thin films. These materials are promising candidates for applications in photocatalysis, solar cells, sensors, displays, etc., because of their high internal surface areas, which have been shown to be both chemically and electrochemically accessible. Two of the most commonly employed routes for their preparation include sol–gel methods¹ and electrochemical deposition.^{2–5} These methods involve the use of structure-directing agents (SDAs) to create mesoporosity that have to be removed in a final step to allow pore accessibility.

Mesoporous metal oxide films with large pore diameters can be prepared by the sol–gel method using evaporation-induced block copolymer self-assembly (EISA) in combination with complexation of the molecular inorganic species. This has resulted in high-quality mesoporous films with good mechanical, optical, and transport properties. In comparison to sol–gel methods, electrodeposition has the advantage that it represents a low-cost and low-temperature method that enables the use of plastic conductive supports. For this reason, the electrodeposition of zinc oxide (ZnO) has been studied in detail in the presence of various structure-directing agents, such as dyes,^{6,7} surfactants,⁴ and different organic molecules,⁵ in particular for dye-sensitized solar cells² and luminescent thin film applications.³

Oxide semiconductors, such as TiO_2 ^{8–13} and ZnO,^{13–15} are very promising photocatalysts, especially for the mineralization of organic pollutants dissolved in solution. Although they both exhibit the same band gap of about 3.3 eV, ZnO has been shown

to be more efficient in the photodegradation of organic compounds under UV-light illumination.^{9–11} For instance, Sakthivel et al.¹¹ compared the efficiency of different semiconductor photocatalysts, such as TiO_2 , ZnO, SnO_2 , ZrO_2 , $\alpha\text{-Fe}_2\text{O}_3$, WO_3 , and CdS, in the photodegradation of an azo dye (acid brown 14) in aqueous solution under identical experimental conditions using sunlight as the energy source. From this comparative study, ZnO emerged as the most active photocatalyst. Lizama et al.⁸ optimized the photodegradation of reactive blue 19 on ZnO and TiO_2 by using a factorial design method and showed that ZnO is the most efficient photocatalyst. Although most of the studies investigating the photocatalytic behavior of ZnO have been carried out with powder materials, it would be preferable to use porous zinc oxide films that exhibit very large internal surface areas instead because they would not require a final separation operation. The photodegradation properties of nanostructured^{16–18} or macroporous¹⁴ ZnO films have been studied, although, to the best of our knowledge, no study has reported the photodegradation properties of well-characterized mesoporous ZnO films. Electrochemically prepared mesoporous ZnO films are highly promising photocatalysts because of their facile and low-cost preparation yielding materials with large internal surface areas that are highly accessible.

The aim of the present study was twofold: First, the mesoporosity of electrodeposited ZnO films prepared in the presence of eosin Y (EY)^{2,19–21} was studied in detail by employing krypton adsorption measurements. The effects of deposition parameters, such as the deposition time and EY concentration, were also investigated. Second, the photodegradations of heteropolyaromatic (methylene blue) and diazo (congo red) dyes in solution were used as model reactions for studying the photocatalytic activity of the mesoporous zinc oxide films. This provides insights into how the morphological properties

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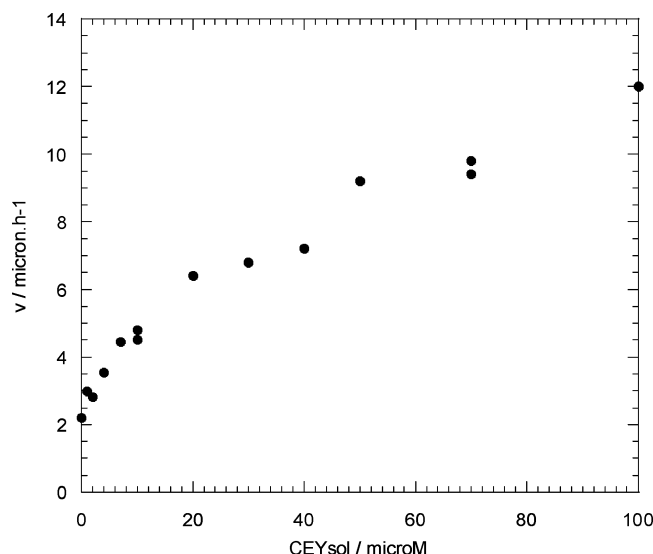


Figure 1. Variation of the film growth rate with the concentration of eosin Y in the deposition bath.

of ZnO films, such as the porosity and film thickness, can be correlated with their photodecomposition efficiency.

2. Experimental Section

2.1. Preparation and Characterization of Mesoporous Films. Mesoporous films of zinc oxide with diameters of 12 mm (for photodegradation) and 20 mm (for the adsorption study) (with geometric areas of 1.13 and 3.14 cm², respectively) were electrodeposited from oxygen-saturated electroplating baths containing 5 mM ZnCl₂ (Merck) and 0.1 KCl (Merck). Electrochemical deposition was carried out at a temperature of 70 °C and a potential of −1 V vs a saturated calomel electrode (SCE). Eosin Y (Kanto) was added at concentrations ranging from 10 to 100 μM. A zinc wire was used as a counter electrode. Fluorine-doped SnO₂-coated glass slides were used as working electrodes and fixed to a rotating-disk electrode, with a rotational speed of 300 rpm. Figure 1 shows the increase in the film deposition rate with increasing EY concentration. The as-deposited films were transparent but turned red after exposure to air. Eosin Y incorporated within the film was subsequently removed by dipping the films into a KOH solution at pH 10.5, according to the procedure described earlier.²

The optical specular transmission spectra of the films were measured with a Cary 100 UV/visible spectrophotometer with a bare conducting substrate as a reference. A typical absorption spectrum is shown in Figure 2a. The layer exhibits a well-defined absorption edge and good transparency. Mesoporous films prepared from solutions more concentrated than 20 μM were transparent, with eosin being almost fully extracted by the desorption treatment. The porosities of the films were determined by comparing the equivalent thickness of ZnO and the total thickness of the films. The equivalent thickness was calculated from the amount of ZnO present in the film, which was determined by ICP-AES titration of zinc after the complete dissolution of ZnO in 1 mL of 10% HCl (Merck, suprapur). The total thickness was measured with a profiler (Veeco, Dektak 3). The accessible surface areas of the films were determined from adsorption isotherms of Kr at the boiling point of liquid nitrogen (approximately 77 K) using an ASAP 2010 apparatus (Micromeritics). The molecular area of krypton was taken as 0.21 nm² as recommended by the equipment producer. Prior

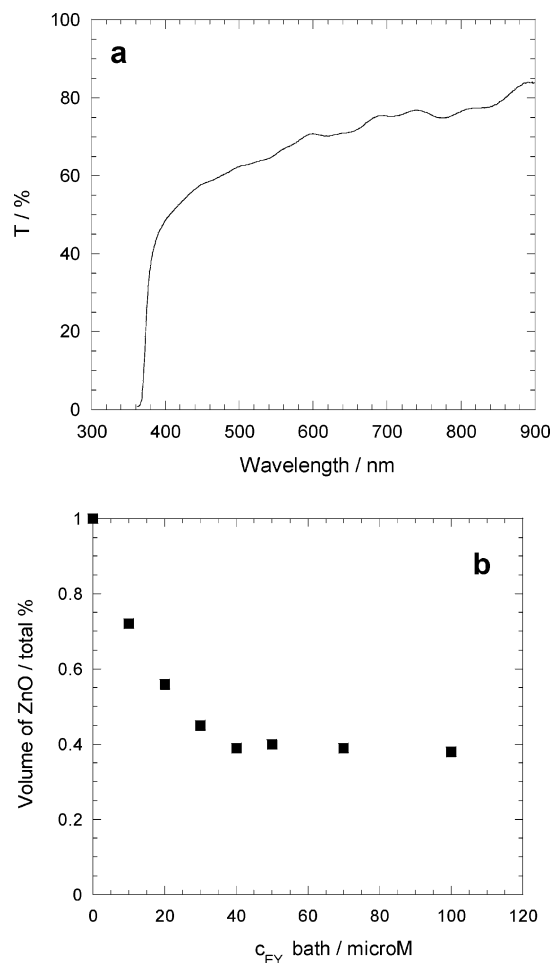


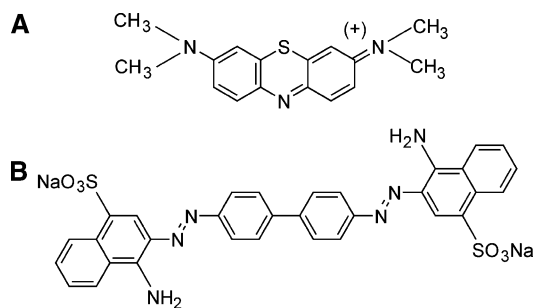
Figure 2. (a) Specular transmission spectrum of a film deposited with 50 μM EY for 15 min after dye desorption. (b) Effect of the concentration of eosin Y in the deposition bath on the volume occupied by ZnO in the film.

to each adsorption measurement, samples were outgassed at 150 °C overnight.

2.2. Photodegradation Measurements. The samples were covered with a 6.3-mm-thick layer of a 28 μM solution of either methylene blue (corresponding to 10 mg L⁻¹) or congo red (18.6 mg L⁻¹) in equilibrium with air. All of the films were placed in the test dye solution for 5 min in the dark in order to soak their pores with the solution and to bring the films into equilibrium with the dissolved dye. An equilibration time of 5 min was found to be sufficient, as no significant adsorption of the dye occurred at longer times. The films were illuminated with a 300-W Oriel lamp that was placed at a distance of 70 cm from the sample, the beam being focused by a converging mirror and the illumination power being 25 mW cm⁻² for wavelengths shorter than 390 nm. Changes in dye concentration were determined by measuring the absorption spectrum of 1 mL aliquots using a UV/vis spectrometer (Varian, Cary 100), which were returned to the samples after the measurement. The typical duration of an experiment was 60–75 min.

Photocatalytic experiments were carried out at pH 8 to avoid dissolution of ZnO. Furthermore, the acid–base properties of the metal oxide surface were found to have a considerable effect on their photocatalytic activity. Previously published experimental data report higher photocatalytic degradation efficiencies of ZnO at pH values of 8–10,^{11,15} at which the adsorption of dye molecules is low and the photooxidation is not directed by

CHART 1: Molecular Structures of (A) Methylene Blue Dye, 3,7-Bis(dimethylamino)phenazathionium Chloride Tetramethylthionine Chloride, and (B) Congo Red Dye, [(1,1-Biphenyl)-4,4-diyl(azo)]bis(4-aminonaphthalenesulfonate)



holes (h^+) photogenerated in the valence band but indirectly induced by hydroxyl radicals (OH^\bullet) generated by the reaction of h^+ with water. Alkaline pH values favor the formation of hydroxyl radicals, which are extremely strong nonselective oxidants. Additionally, as the point of zero charge of ZnO is about 9,²² the surface is neither positively nor negatively charged at the pH chosen, and the preferential adsorption of either positively or negatively charged dye ions is prevented. Therefore, the decomposition rates of cationic methylene blue (Chart 1A) and anionic congo red (Chart 1B) can be directly compared without the masking effects of the adsorption.

3. Results and Discussion

3.1. Effects of Electrochemical Deposition Parameters on ZnO Film Mesoporosity. For embedding mesoporous ZnO films as photoanodes in solar cells or photocatalysts in practical devices, it is desirable to fabricate films with the highest possible porosity and accessible surface area, as well as sufficient mechanical strength. In the present study, two key deposition parameters were investigated in this context, namely, the concentration of EY in the deposition bath and the deposition time. The former parameter was studied by keeping the deposition time constant at 15 min. The results are shown in Figure 2b as the percentage of the volume in the film occupied by ZnO. The minimum volume of ZnO obtained at eosin concentrations of 40 μ M or more corresponds to the maximum achievable void fraction of about 60%.

The true accessible surface areas of the ZnO films were determined after dye desorption by equilibrium gas adsorption. The most frequently used adsorptives, namely, nitrogen and argon at 77.35 and 87.3 K, respectively, cannot be applied with materials such as thin porous films with very small surface areas in the range of tens of square centimeters. The reason for this is that the saturation pressures of nitrogen and argon at 77 and 87 K, respectively, are very high, reaching ca. 760 Torr, which leads to an extremely large number of molecules being trapped within the void volume of the sample cell. Because of the very small total pore volumes and surface areas of such thin porous films, the pressure changes due to adsorption cannot be measured with sufficient precision. As an alternative, an adsorptive with a substantially lower saturation vapor pressure should be used, such as krypton at the boiling point of liquid nitrogen, whose saturation pressure equals 1.63 Torr as a solid and 2.63 Torr as a supercooled liquid. At 77 K, krypton is well below the bulk triple-point temperature of 115.8 K. The thermodynamic state of krypton confined in narrow pores at temperatures far below the bulk triple-point temperature is not well-defined, and the nature of the experimentally observed

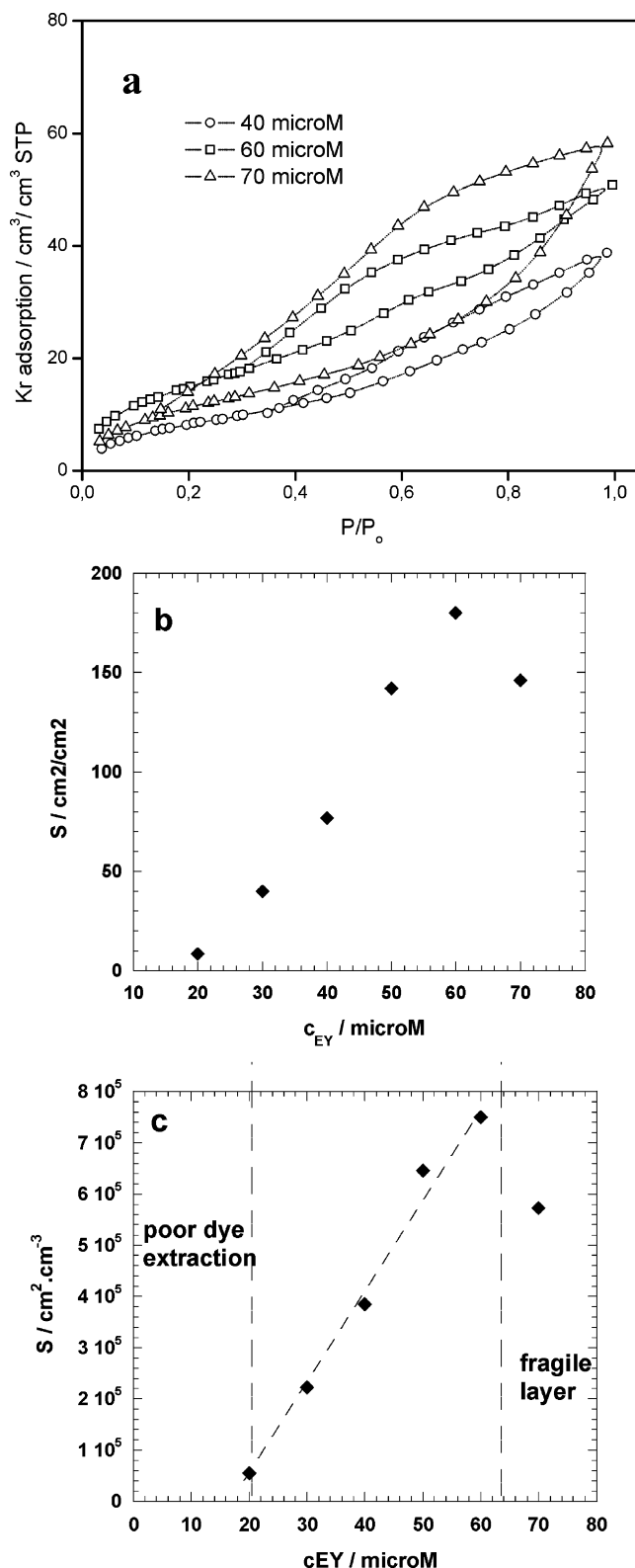


Figure 3. (a) Adsorption isotherms of Kr at 77 K on selected mesoporous ZnO films. (b,c) Specific surface areas of the mesoporous films as a function of (b) eosin bath concentration and (c) film volume.

krypton phase transition depends mainly on temperature and pore size. Confinement influences the phase and sorption behavior of fluids in pores and causes a significant shift in the triple-point temperature. This effect must therefore be taken into account in the interpretation of sorption isotherms.^{23,24} Whereas krypton pore condensation and hysteresis at 77 K occur in

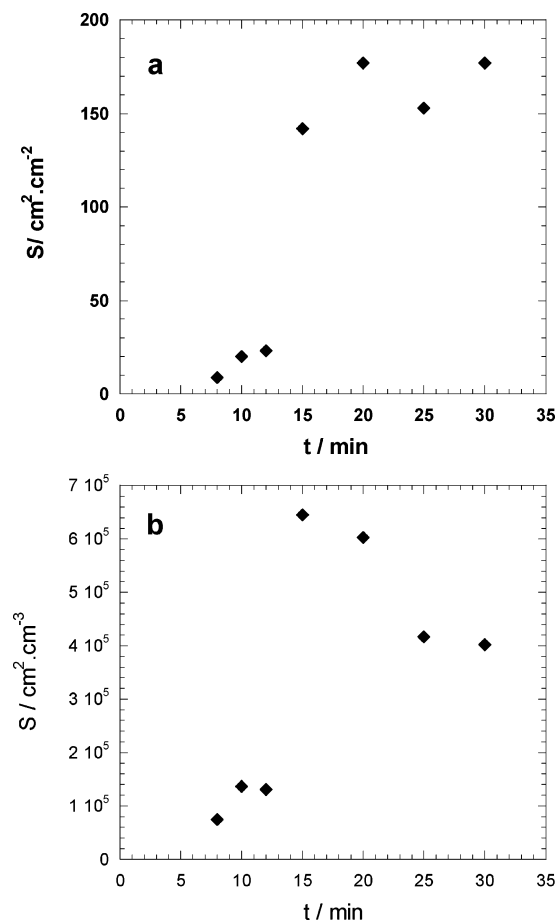


Figure 4. Deposition time dependence of ZnO surface area for films prepared in the presence of 50 μM EY: (a) specific surface area, (b) surface area related to the film volume.

mesopores in the pore size range from 2 to ca. 8 nm, they cannot be observed in larger pores.^{23,24}

Figure 3a shows adsorption isotherms for several samples of ZnO films. All of these isotherms exhibit large hysteresis loops, which correspond to the developed mesoporosity. The lower closure point of the hysteresis loop for the sample prepared with 40 μM EY is mostly shifted to the region of higher relative pressure, and the hysteresis loop is generally flat, which indicates that the pores of this sample are generally larger than ca. 8 nm and the fraction of smaller pores is rather limited. On the other hand, the lower closure point of the hysteresis loop for the sample prepared from a solution with 70 μM eosin is at a relative pressure, P/P_0 , of ca. 0.14, which is an indication for the presence of small pores or even of some pore blocking. Generally, a large limiting adsorption at relative pressures approaching 1, which almost achieves a plateau, shows that the volume of pores smaller than ca. 8 nm is large, i.e., the percentage of the overall porosity consisting of narrow pores is much more significant than that for the sample prepared with 40 μM eosin. At 60 μM EY, the film porosity exhibits intermediate characteristics.

The relationship between the specific surface areas of the films and the EY concentration in the deposition bath is shown in Figure 3b,c. In the latter plot, the specific surface area is related to the film volume. Three regions with respect to the eosin concentration can be distinguished. Below 20 μM , the specific surface area is rather small, probably because of insufficient extraction of the dye. A fraction of the dye remains occluded within the film even after prolonged desorption in a mild alkaline solution. In the intermediate region, between 20

TABLE 1: Deposition Times for the Preparation of 2.0- and 2.9- μm -Thick Porous ZnO Films from Deposition Baths Containing Different Concentrations of Eosin Y

EY concentration (μM)	deposition time (s)	
	2.0- μm -thick	2.9- μm -thick
10	1522	2207
20	1150	1670
30	975	1415
40	900	1280
50	820	1200
60	760	1100
70	720	1044

and 60 μM , the specific surface area increases linearly with dye concentration, with a maximum of the surface area obtained at 60 μM . At higher concentrations, the surface area decreases because of the fragility of the layers. Consequently, it is difficult to maintain the integrity of the layer during all of the treatments and manipulations.

By the same method, the effect of deposition time on porosity was investigated with the EY concentration fixed at 50 μM . In Figure 4a,b are presented the specific surface areas of the films and the surface area related to the film volume, respectively. All of the films were almost fully bleached after dye desorption treatment. The specific surface areas of dye-desorbed films deposited for 10–12 min were found to be rather small, achieving a value of only 20 $\text{cm}^2 \cdot \text{cm}^{-2}$ (Figure 4a). The isotherms show no hysteresis loop, and no capillary condensation occurs, which means that no mesopores narrower than ca. 8 nm are present and the films contain exclusively larger mesopores or macropores. For a deposition time of 15 min, narrow mesopores were observed, with a reproducible specific area value of 140 $\text{cm}^2 \cdot \text{cm}^{-2}$. Although the maximum surface area was attained after 20 min, there was no significant increase in the specific surface area per geometric area even for longer deposition times, despite the increase in film thickness. This is most likely due to the poor mechanical strength of the thick layers.

The porosity and specific surface area data presented in this study provide evidence for the fact that a dye concentration of 50 μM EY and a deposition time of 20 min as reported in previous studies on solar cell² and luminescence³ applications represent a good compromise between a large surface area and good mechanical stability of the films, even though the surface area was not measured in these studies.

3.2. Dye Photodegradation by Porous Thin Films of ZnO.

3.2.1. Methylene Blue (MB) Photodegradation. In the previous section, we showed that the film surface area per cubic centimeter increases with the deposition time and thus also with the film thickness (Figure 4a). As a consequence, a higher photodegradation efficiency is to be expected for thicker films. We independently studied two sets of films with thicknesses of 2.0 and 2.9 μm that were prepared from baths with varying EY concentrations. The variations of the deposition time and eosin concentration to obtain the two sets of films are reported in Table 1.

Methylene blue (MB) is a brightly colored, blue cationic thiazine dye with maxima of absorbance at 660 (the most prominent), 614, and 292 nm.¹² It has often been used as a model compound to test the photocatalytic degradation of organic materials. To achieve total mineralization, MB requires 102 oxidizing equivalents.¹² To avoid the formation of its colorless leuco form upon illumination, a slightly basic pH and aerobic conditions were chosen.¹² The first steps of MB photodegradation were monitored by measuring the variation in the solution

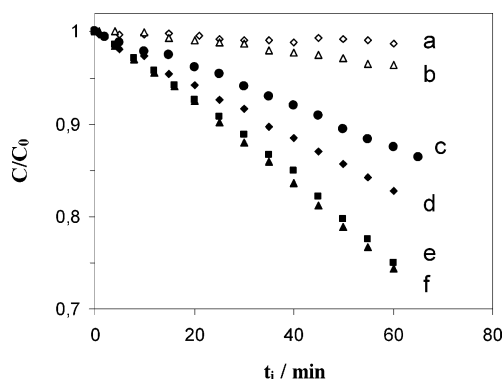


Figure 5. Variation with time of the relative concentration of methylene blue: (a) 2- μm -thick film prepared with 70 μM EY and kept in the dark and (b–f) films irradiated with a xenon lamp, including (b) dense ZnO sample deposited on glass by sputtering and 2- μm -thick films prepared with (c) 10, (d) 20, (e) 30, and (f) 70 μM EY.

absorbance. Figure 5 shows the performance of a series of films with a thickness of 2.0 μm that were prepared by using EY solutions of different concentrations. The results are compared with those for a dense ZnO film prepared by sputtering and with a ZnO film prepared from a 70 μM EY solution that was not illuminated. In the dark and without a film, there is almost no change in the concentration of methylene blue (not shown). With a dense film of ZnO, the degradation rate is rather low and of the same order of magnitude as that for the direct photolysis of MB under visible-light irradiation. The photobleaching rate increases rapidly for films prepared using 10–30 μM EY solutions. For films prepared from 30–70 μM EY solutions (only the two limiting concentrations are shown in Figure 5), there is almost no effect of the change in the EY concentration on the photocatalytic activity. The observed performance can be correlated with the porosity of the films. In the region of fast increase in the degradation rate, i.e., for eosin concentrations in the deposition solution between 10 and 30 μM , the porosity and accessible surface area substantially increased. At higher eosin concentrations, the porosity reaches a limiting value close to 60%, whereas the specific surface area continues to increase, and the degradation rate remains almost constant. Therefore, the photocatalytic performance of the films seems to be more correlated with the porosity parameter than with the active surface area. This shows that smaller pores that are present in films prepared from the most concentrated solutions do not contribute significantly to the MB bleaching reaction. Because the concentration of MB decreases linearly with the irradiation time in all experiments, the concentration–time dependence does not follow first-order kinetics. Consequently, it must be limited either by a surface reaction or by the diffusion of oxygen.

The results obtained with 2.9- μm -thick porous films are presented in Figure 6 and are compared with the photocatalytic activity of a nonporous ZnO film prepared in the absence of eosin. In the latter case, the degradation rate is rather low (curve a). The decomposition rate increases dramatically for the porous films prepared with EY, but does not depend much on the concentration of eosin used. A slight increase for concentrations between 10 and 40 μM was observed, but for higher concentrations, the reaction rate was not influenced. The small effect of the porosity variation for the thicker films indicates that the surface areas of all the films are large enough to be sufficient even for the least porous ones (Table 2). From the highest degradation rate (0.3 h^{-1}) and the UV illumination power, it was calculated that the maximum photocatalytic efficiency is

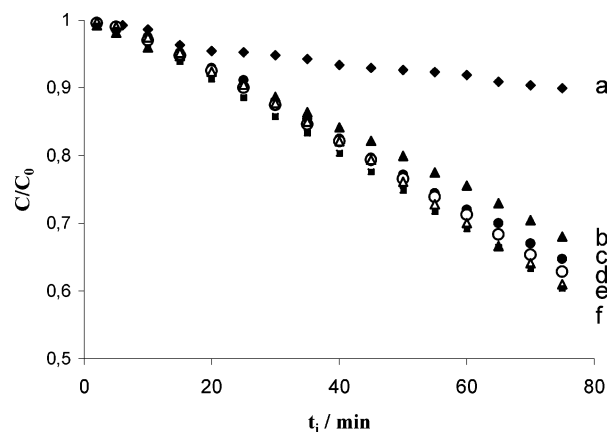


Figure 6. Variation with time of the relative concentration of methylene blue for films irradiated with a xenon lamp: (a) dense ZnO film prepared without EY with a deposition time of 20 min and 2.9- μm -thick porous films prepared with (b) 10, (c) 20, (d) 30, (e) 40, and (f) 70 μM EY.

TABLE 2: Effect of the Film Thickness on the Degradation Rate of MB

eosin concentration (μM)	degradation rate [$\Delta(C/C_0)/\Delta t$ (h^{-1})]	
	2.0- μm -thick	2.9- μm -thick
10	0.12	0.24
70	0.26	0.30

2.7% if one considers that MB molecules are fully mineralized by the photodegradation process.

ZnO stability is an important concern from an application viewpoint given that ZnO is dissolved in both acidic and highly alkaline solutions.²⁵ The measured Zn^{2+} concentration in the reaction solution after photodegradation for 75 min on a 50 μM EY ZnO film equaled 3.02 mg/L, which corresponds to the dissolution of only 5.1% of the film. This value is in agreement with the equilibrium concentration of Zn^{2+} calculated from the pKs value of ZnO (16.49)²⁵ at the chosen experimental pH of about 8.

3.2.2. Congo Red Photodegradation. Azo dyes are an abundant class of synthetic, colored compounds that are characterized by the presence of one or more azo bonds ($-\text{N}=\text{N}-$).²⁶ As they are generally very stable and resistant to aerobic degradation, their biodegradation is not effective, and they present a danger to the environment because of their toxicity. Congo red (CR) is an example of an anionic secondary diazo dye, which is even more difficult to degrade photocatalytically because of its large and complicated structure, which contains one central biphenyl group and two symmetric naphthalenic groups.^{8,27} Its UV/vis absorption spectrum shows a characteristic intense peak at around 498 nm in aqueous solution.

Figure 7 shows the effect of the EY concentration in the deposition solution on the photodegradation of congo red on 2.9- μm -thick films. The nonporous film prepared without the addition of eosin is completely inactive (curve a). For porous ZnO films, the dye concentration decreases linearly with irradiation time, as already observed with MB. The decoloration is very slow with the film prepared at low EY concentrations (10 μM). For films prepared with 20 and 40 μM EY, the degradation rate increases rapidly. Above 40 μM , the improvement is only weak (curves e–g). In summary, the photocatalytic performance of mesoporous ZnO films in the degradation of congo red is similar to that observed for MB, as can be seen by comparing Figures 5 and 7. This is in agreement with the nearly zero charge on the film surface at the pH chosen, which prevents

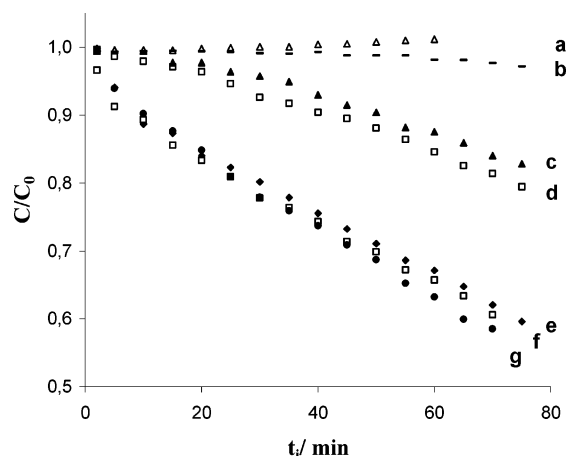


Figure 7. Variation with time of the relative concentration of congo red for films irradiated with a xenon lamp: (a) dense ZnO film, electrodeposited without any additive for 20 min, and 2.9- μm -thick porous films prepared with (b) 10, (c) 20, (d) 30, (e) 40, (f) 50 and (g) 70 μM EY in the electroplating bath.

any strong interaction between the charged dye molecules and the ZnO surface. Therefore, we propose that photooxidation occurs by a similar indirect pathway involving OH^\bullet as the oxidizing intermediate. In both cases, mesopores narrower than 8 nm were found to be much less efficient than larger pores.

Conclusions

Mesoporous thin films of ZnO were prepared by a simple low-cost electrochemical method using eosin Y dye as a structure-directing agent. After EY removal from the structure, practically transparent colorless ZnO films were obtained. Their porosities and specific surface areas were measured by krypton BET. Deposition parameters such as the deposition time and EY concentration in the electroplating bath were optimized for the preparation of films with the largest possible surface area and good mechanical properties. The best films were produced from solutions containing 50–60 μM of EY with film thicknesses of 2–3 μm . These films were shown to be much more efficient than dense ZnO films in the photodegradation of model pollutants, namely, methylene blue and congo red. For both dyes, the photodegradation rate reached its maximum for mesoporous films prepared with EY concentrations above 40 μM . Photodegradation was found to occur preferentially in the larger pores of the films, whereas mesopores with pore diameters less than 8 nm did not contribute to a large extent to

photodegradation. The obtained data convincingly show that mesoporous films of ZnO have significant potential not only in dye-sensitized solar cells but also in photocatalysis as being relatively efficient in the decomposition of organic pollutants.

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