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# Morphological effect of ZnO nanoflakes and nanobars on the photocatalytic dye degradation

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ABSTRACT

ZnO films with nanoflake and nanobar morphologies were obtained by spray pyrolysis by changing the precursor salt and without any structure-directing agents. Nanoflakes were obtained from zinc acetate while nanobars with zinc chloride. Both films presented ZnO hexagonal wurtzite structure, a transmittance above 80% and band gap of 3.2 eV. The photocatalytic activity of the films was evaluated by the degradation of methyl orange and indigo carmine dyes in different concentrations. The film with nanoflake morphology showed the best performance in discoloration (96%) and it achieved a 51% in mineralization. The film with nanobars attained only a 67% in discoloration whereas it failed to mineralize the dye solution. The principal factors involved in the best performance of the nanoflake films were the less defective surface in the ZnO structure that diminished the electron-hole recombination, allowing the generation of hydroxyl radicals in a sufficient amount. The nanoflake film showed also a high stability after 10 degradation cycles, indicating a promising material for photocatalytic water treatment.


## 1. Introduction

The accelerated population increase, industrialization and climate change have accentuated the water problem in a global context and thus, many scientific works have been directed to the water treatment and its disinfection by photocatalysis [1–3]. However, these efforts have been developed majorly on synthesizing novel and functional materials with sophisticated architectures, which require special and costly conditions. This is the case of zinc oxide (ZnO) that has recently become a popular material for the wide variety of nanostructures that can be obtained and its proven outstanding photocatalytic activity [4,5]. However, it is necessary that technologies for water treatment do not generate high costs in order to be truly applied and implemented. Taking into consideration the cost-benefit, spray pyrolysis [6,7] is one of the techniques able to synthesize ZnO films in different surface structures. The main advantage of the use of the photocatalyst in thin film form, instead of powder, is that eliminates the process of its removal from the aqueous medium. Another advantage of the thin films is that they can be supported or growth on different kind of convenient substrates [8]. The exceptional outspread interest in obtaining ZnO nanostructures has led to the production of several morphologies with remarkable photocatalytic activity; but the comparison of the performance of these different morphologies reported by various research groups is not always possible due to the distinct experimental conditions used. There are some comparative works concerning the effect of the morphology on the photocatalytic activity in the powder form [9–11] and on thin films [12–15], most of them focusing on the surface area, but there are still many aspects to address. In our previous work we systematically studied the effect of the precursor solution (type of salt and solvent) in the formation of films with nanoflake and nanorod morphologies by spray pyrolysis [16]. In that work, we found that the nanoflake film was more active in the color removal of methyl orange dye than the nanorod film. Nevertheless, the photocatalytic performance of a material may depend on the chemistry of the model molecule used for the test, because depending on the type of dye (anionic or cationic) its interaction with the semiconductor's surface can affect the degradation rate. Although several works report the photocatalytic degradation of different dyes and toxic compounds by different ZnO morphologies [17–19], none of them have correlated the morphology with the defects in the crystalline structure with the capacity to generate hydroxyl radicals. Hence, this work is addressed to: (i) understand the efficacy of the nanoflake ZnO films (over the nanorod performance) independently of the type of model pollutant by investigating their physical and chemical

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characteristics; (ii) to elucidate the origin of their physicochemical differences and (iii) to determine the degree of mineralization that can be achieved with ZnO films. To accomplish this, two different organic dyes with three different concentrations were evaluated in the photocatalytic tests. Total organic carbon (TOC) measurements were performed to determine the degree of mineralization of the compounds by the two types of ZnO films and it was correlated to the presence of crystal defects in each structure and to their ability for hydroxyl radicals production.

## 2. Materials and methods

### 2.1. ZnO thin films preparation

ZnO films were deposited by pneumatic spray pyrolysis technique on glass substrates. Glass slides were cut into pieces of 1 $cm^2$ for characterisation and of $2.5 \times 1.25\ cm^2$ for photocatalytic experiments. The subtrates were cleaned consecutively with trichloethylene, acetone and methanol for 5 min in an ultrasonic bath, then were dried with compressed nitrogen. Two different precursor salts were used in order to obtain different film morphologies: zinc acetate dihydrate (ZnAc) and zinc chloride ($ZnCl_2$) from Sigma-Aldrich and Alfa Aesar, respectively. The concentration of the zinc solution was 0.1 M in each case and the solvent was deionized water.The deposition temperature was 450 °C with a gas flow rate of 1024 ml/min and a solution flow rate of 5.5 ml/min. No further annealing of the films was necessary.

### 2.2. ZnO thin films characterization

The films were characterized by X-ray diffraction (XRD) by using a Rigaku Ultima IV diffractometer (Cu Kα radiation λ = 0.15418 nm). The morphological analysis was carried out using a Jeol 7600F scanning electron microscope (SEM). The optical properties of the films were studied using a Shimadzu 1800 UV–vis spectrophotometer. The fluorescence measurements were performed using a spectrofluorimeter Fluorolog3, Horiba with Xe lamp (λ = 350 nm). Photoluminescence properties of the films was measured by using a He-Cd laser (λ = 325 nm, 20 mW) recorded from 350 to 700 nm. Additional thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was made for both precursor salts by using a STA 1000 simultaneous thermal analyzer at a heating rate of 10 °C/min from 25 to 700 °C with air flow of 10 ml/s.

### 2.3. Photocatalytic experiments

The photocatalytic activity of the films was evaluated by the degradation of a methyl orange solution (MO, $C_{14}H_{14}N_3NaOH_3S$) and indigo carmine (IC, $C_{16}H_8N_2Na_2O_8S_2$) with different initial concentrations (2.5, 5, 10 and 15 ppm). The irradiation source was a UV lamp ($26\ W\ m^{-2}$) with its emission maximum centered at 380 nm. The films were immersed in 10 ml of the dye solution and left 30 min in the dark with constant stirring to attain the equilibrium. Then, they were exposed to UV light and the absorbance of an aliquot of the solution was measured in different time intervals by UV–vis spectrophotometry in order to follow their discoloration-degradation kinetics. A pseudo first order kinetic model was used to fit the experimental data and to calculate the rate reaction constants. The relative concentration of the dye solution was measured with a Shimadzu 1800 UV–vis spectrophotometer and the total organic carbon in the solution was determined by using a TOC-L Shimadzu Total Organic Carbon analyzer by using NPOC method in high sensibility mode. Water containing 1 PPB of carbon (Zero water, from Shimadzu) was used for the samples preparation.

The •OH radical generated by the ZnO film was evaluated by using the following procedure: terephthalic acid (TA) ($5 \times 10^{-4}$ M) was dissolved in a water/NaOH solution ($2 \times 10^{-3}$ M). The films were immersed in 10 ml of the TA solution and left 30 min in the dark and irradiated with the UV lamp, at the same photocatalytic conditions. Fluorescence spectra of formed 2-hydroxyterephthalic acid (HTA) was performed using a spectrofluorimeter Fluorolog3, Horiba with Xe lamp (λ = 350 nm).

## 3. Results

### 3.1. Structure and morphology of the ZnO thin films

The crystalline structure of the films showed that with both precursors, ZnAc (sample named SA) and $ZnCl_2$ (sample named SC), the hexagonal wurtzite phase of ZnO was obtained (ICDD data base PDF 00-036-1451) with the characteristic reflections (100), (002), (101), (102), (110), (103) and (112) as can be seen in Fig. S1 (in the Supplementary information). No secondary phases, carbon or chlorine compounds were detected, respectively. The essential difference between both patterns is the relative intensities of the main peaks. The highest intensity peak on sample SA is (101) reflection while for the SC is the (002), indicating different growth orientations. The crystallite sizes were estimated using the Scherrer's formula [20]. The FWHM values used were those for the reflections: (002), (101), (102) and (103) as they were the four most intense in the samples. The values are $29 \pm 5$ and $35 \pm 3$ for the film SA and SC, respectively.

For the ZnAc precursor, the morphology shows randomly oriented nanoflakes with irregular spike-like shapes (Fig. 1a). These nanoflakes exhibit a randomly growth and some of them are interpenetrated. On the other hand, for the $ZnCl_2$ precursor hexagonal columnar growth is obtained (Fig. 1b). Some hexagonal bars are fused but it is possible to observe their vertical growth. The contact area (CA) of the nanostructures was estimated using the SEM images. The ratio of the CA between SA and SC films was $CA_{SA}/CA_{SC} = 1.42$, indicating a 42% more exposed area in the nanoflakes films than in the nanorods morphology.

The TG analysis and DSC of the precursor salts showed difference in its thermal decomposition (Fig. 1c,d). For the zinc acetate, the TG curve exhibited two weight loss processes; the first one occurs between 60 and 126 °C, associated with an endothermic event at 86 °C, attributed to the dehydration process of two water molecules [21]; the large second weight loss begins at about 160 °C and ends at 293 °C. It has been assigned to the decomposition of anhydrous $Zn(AC)_2$ into ZnO, however, the extra weight losses (22 wt.%) and the endothermic event at about 244 °C suggests that part of precursor salt was sublimed [22]. For the $ZnCl_2$, the TG curve exhibits a slight weight loss between 25 and 317 °C; however, three endothermic events were observed, suggesting the dehydration process of water molecules in agreement with the hygroscopic nature of $ZnCl_2$. Subsequently, a huge weight loss of 83 wt.% is observed from 350 to 550 °C, associated to a pronounced endothermic event at about 537 °C, which is due to sublimation and transformation of $ZnCl_2$ into ZnO [23]. Considering that the ZnO film was prepared at 450 °C, at this temperature the acetate precursor is completely transformed into ZnO. According to other authors [24,25], the use of organic salts leads to an effective decomposition in which the subproducts are volatile and easily withdrawn giving nanoflakes form. The result is a smooth and good quality film. Conversely, the sublimation and decomposition of the inorganic salt ($ZnCl_2$) occurs at high temperature (500–550 °C), hence the formation of ZnO cannot happen; however, in aqueous solution, this precursor salt forms a zinc hydroxide chloride hydrate that can be sublimed and decomposed to ZnO at 450 °C [23]. In our case, zinc hydroxide chloride hydrate is responsible of the nanobars formation.

The optical transmittance in the visible region was 86% for the films prepared with ZnAc and 85% for those synthesized with $ZnCl_2$;

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