SPRAY PYROLYSIS DEPOSITED ZINC OXIDE FILMS FOR PHOTO-ELECTROCATALYTIC DEGRADATION OF METHYL ORANGE: INFLUENCE OF THE pH

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ABSTRACT

Zinc oxide films were made by spray pyrolysis equipped with an optical system for in-situ thickness measurement; zinc acetate water solution was used as spraying solution. The pH of the spraying solution was modified in order to increase the film porosity. Morphology and structure of the films were analyzed by scanning electron microscopy and x-ray diffraction, respectively. X−ray pattern revealed that films were zincite−like with a preferential growth in the [002]-direction.

The optical absorbance of the methyl orange aqueous solution and the optical transmittance of ZnO-based films were measured in the wavelength range of 350-800 nm. Those measurements allowed both to control the photo-electrocatalytic degradation of methyl orange and to correlate the optical measurements with surface morphology of ZnO-based films.

The zinc oxide based films obtained at different pH conditions of the spraying solution were brought into contact with methyl orange aqueous solution in a reactor in which the photo−electrocatalytically induced degradation under ultraviolet irradiation was investigated; the reactor was provided by an optical system to measure the in-situ optical transmittance of methyl orange solution. Results indicated that there is an increment of the active area of ZnO thin films when the pH of the spraying solution increases.

1. INTRODUCTION

Heterogeneous photocatalysis is a topic of the major and growing interest [1]. It can be used for example to decompose hazardous wastes, which is a very important issue particularly for textile manufactory. Titanium oxide has been extensively studied for these applications [1-3]; zinc oxide can in principle also be useful for this purpose [4-6] since its energy band is appropriate for that [7], however it has not been explored at all. In this paper we report some relevant features of pyrolytic zinc-oxide-based films related to its photo-catalysis properties.

Thin films with high porosity are strongly recommended for photo-electrocatalytic degradation applications, because of the extended interface between the film and the fluid. Porosity is highly depending on deposition technique. Different techniques have been reported for preparing ZnO films; those comprise reactive evaporation [8], sputtering [9], chemical bath [10], spray pyrolysis [11-14], etc. Spray pyrolysis is a simple and rather low cost technique and under appropriate conditions can allow getting different surface morphologies. Pyrolytic ZnO-based films are usually obtained by pyrolytic decomposition of an alcoholic solution of zinc acetate. In general alcoholic solutions are preferred because of their low surface tension and viscosity facilitate the formation of small spraying droplets, which allows to get a continuous and smooth films. In this work we present preliminary results using water as solvent in order to increase film roughness and eventually porosity.

Photocatalysis involves excitation of an electron from the valence band to the conduction band; the remnant hole migrates under the influence of the electric field towards to surface of the semiconductor and reaches a site where it can oxidize an electron donor associated with the pollutant. It has been reported elsewhere that a decrement in the electron hole recombination can be obtained by an applied potential, which increases the migratory effects in the semiconductor-electrolyte interface [15-17].

This paper discusses the photo-electrocatalytic degradation of methyl orange in aqueous solution using ZnO-thin film obtained by spray pyrolysis using water as the spraying solution; morphology and structural characterization in the films were also performed. We have studied the in situ spectral absorbance of the methyl orange in aqueous solution at different degradation

times and determined the enhanced degradation rates of the solution when it is in contact with the ZnO films; those results are correlated with the film morphology variation.

2. EXPERIMENTAL

Zinc oxide films were deposited using reactive spray pyrolysis in a home made system (see Fig 1). An ultrasonic device generated droplets of the spraying solution and compressed air was used as gas carrier. In all experiments the gas carrier pressure was kept at 25 PSI during deposition. The foggy of the spraying solution is carried out to the hot substrate on which the solvent evaporates taking place the pyrolytic reaction and the film starts to grow.

In order to ensure a homogeneous pyrolytic reaction on the hot substrate, the heater is moved back and fort perpendicularly to the spraying nozzle. An optical system was set up for in-situ thickness measurement during deposition; both a 632.8 nm wavelength laser beam and an array of optical sensors were used for this purpose, which also provided information about the growing film profile (see Fig.1).
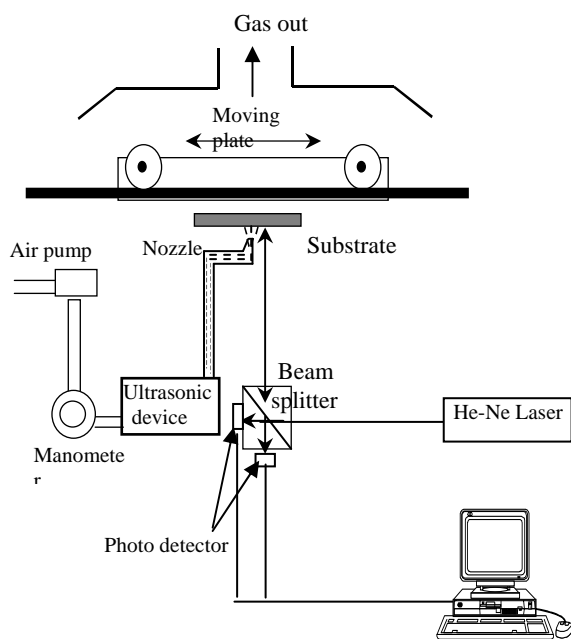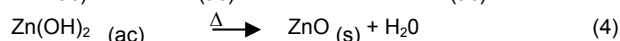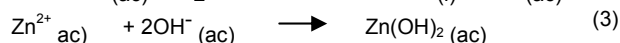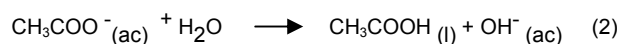
$$Zn(CH_3COO)_2 \ _{(ac)} \longrightarrow Zn^{2+} _{(ac)} + 2CH_3COO^- _{(ac)} \quad (1)$$

$$CH_3COO^- _{(ac)} + H_2O \longrightarrow CH_3COOH _{(l)} + OH^- _{(ac)} \quad (2)$$

$$Zn^{2+} _{ac)} + 2OH^- _{(ac)} \longrightarrow Zn(OH)_2 _{(ac)} \quad (3)$$

$$Zn(OH)_2 \ _{(ac)} \xrightarrow{\Delta} ZnO _{(s)} + H_2O \quad (4)$$

The films were deposited onto a Libbey Owens Ford glass substrate precoated with SnO_2:F, which had a square resistance of 8 Ω. Zinc-oxide films were deposited at different temperatures in the range of 300 °C– 400 °C, and the pH of the spraying solution was also changed in the range of 2 - 5. Spraying was stopped when the thickness of the film reaches ~650 nm, measured in situ during deposition

3. RESULTS AND DISCUSION

3.1 FILM CHARACTERIZATION: STRUCTURE AND MORPHOLOGY

The crystalline structure of the zinc oxide films was studied by X–ray diffraction (XRD) using a Phillips Xpert 1300 diffractometer with Cu anode. Data from ZnO standards were used to identify the diffraction peaks. Figure 2 shows X–ray diffractograms for zinc oxide films deposited at different temperatures and various pHs onto SnO_2:F coated glass substrates.

Figure 1. Spray pyrolysis deposition system including the optical set up for coating profile measurement.
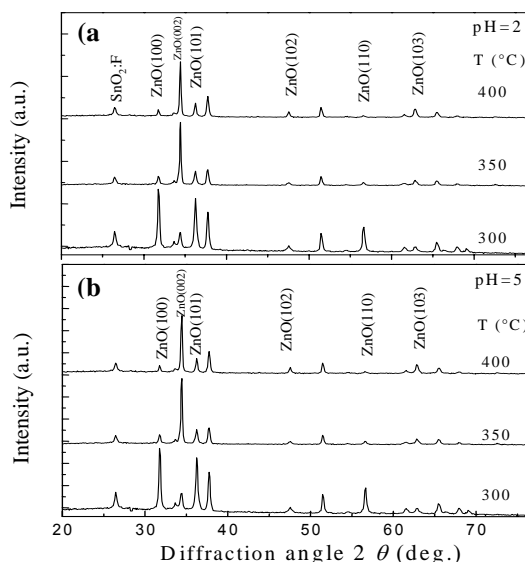

Figure 2. X ray diffractograms for zinc oxide films prepared by spray pyrolysis at pH= 2 (panel a) and pH= 5 (panel b), and at the shown temperatures. The observed peaks correspond to the zincite structures. Additional peaks are due to the transparent conductive layer of SnO_2:F.

Film deposition takes place according to the following global reactions:

The diffractograms display that, regardless of the pH values, the crystalline structure in zincite like films appears in the range temperature between 300 $^{\circ}$C and 400 $^{\circ}$C. For films prepared at 300 $^{\circ}$C, parallel planes in the (100), (101) and (110) directions can be observed. As the deposition temperature increases, the (002) direction is preferred vis-a-vis other directions, which start then to decrease. The mean grain size D for the films was estimated from the XRD data by applying Scherrer´s formula as follows

$$D = \frac{0.9\lambda_x}{\beta\cos\theta}$$

(5)

where λ_x is the X–ray wavelength in the K_{α} band for Cu equal to 1.54 Å, and β is the full width at half the maximum diffraction peak. Applying this formula, the grain size was found to be ~23 nm measured in the (002) peak.

Surface morphology was studied with SEM using a Philips 300 instrument operated at 20 kV. Figures 3 and 4 display the surface of zinc oxide films deposited at different temperatures and pHs onto a conductive transparent layer of SnO_2: F, respectively. In Fig. 3 is observed that increasing deposition temperature, increase the particles size until transform it in round nodules reducing in that sense the surface area. In the case of Fig. 4 is observed that pH variation on the deposition conditions of zinc oxide films produce a change of shape in the particles, from planar, obtained in films deposited at pH= 2, to round, obtained in films deposited at pH=5. An increase of film´s surface area is observed at the last case.
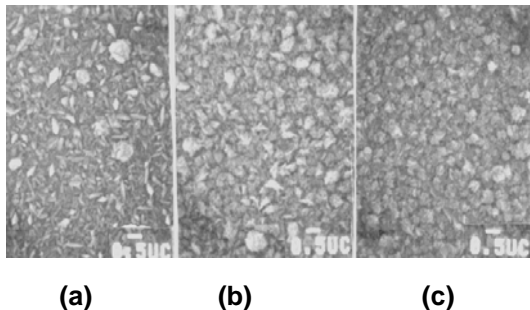

(a)   **(b)**   **(c)**

Figure 3. SEM micrographs of the surface of zinc oxide films deposited by spray pyrolysis at 400 $^{\circ}$C onto a tin-oxide-precoated glass substrate. Films were deposited using pH = 5 for spraying solution and substrate temperatures: (a) T=300, (b) T=350 and (c) T=400.
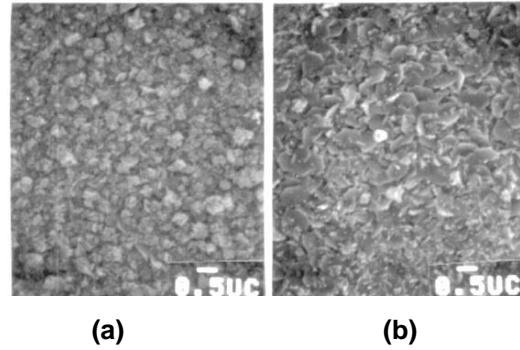

(a)   **(b)**

Figure 4. SEM micrographs of the surface of zinc oxide films deposited by spray pyrolysis at 400 $^{\circ}$C onto a tin-oxide-precoated glass substrate. Films were deposited using pH=5 (inset a) and pH=2 (inset b) in the spraying solution.

3.2 FILM CHARACTERIZATION: OPTICAL PROPERTIES

For zinc oxide films deposited onto glass at 400 $^{\circ}$C and different pH values, total normal transmittance T was recorded in the 300 < λ < 800 nm wavelength range with an Optometrics RS-350 single beam spectrophotometer. Films were ~650 nm thick, as observed with the in situ thickness measurement system mounted in the deposition system.

As a general trend, it is observed that decrements of transmittance appear as the pH in the solution increases. They are correlated with the increment of the films´diffusive characteristics, which can be due to the fact that spherical particles obtained at pH=5 are more light dispersive that planar particles obtained at pH=2, as shown in Fig. 4.
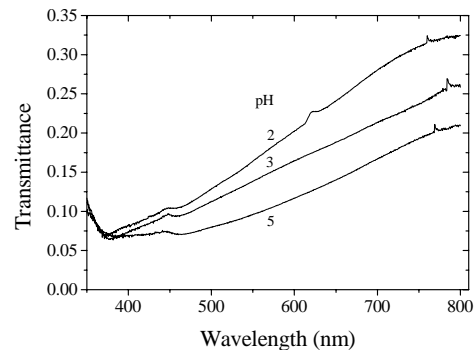

Figure 5. Spectral transmittance for zinc oxide films deposited on glass by spray pyrolysis at 400 $^{\circ}$C and at the shown pHs.

3.3. DATA ON PHOTO – ELECTROCATALYTIC DEGRADATION OF METHYL ORANGE

We used zinc oxide films to study the photo–electrocatalytic degradation of a methyl orange water solution by using a specially designed reactor. The reactor consists of a cylindrical Teflon container. The open end – which can be irradiated by ultraviolet (UV) light – has provisions for mounting a sample with the zinc oxide film facing the interior of the cylinder. Light passing through the conductive transparent substrate will make then possible to illuminate the zinc oxide films. Two parallel quartz windows are arranged at right angles to the cylinder axis so as to allow spectrophotometric transmittance measurements for probing the cylinder´s contents. A three–electrode arrangement was used in the experiments. It includes a Pt foil as counter electrode, and a Ag/AgCl electrode as a reference electrode. This setup is referred to as a "single compartment cell" in earlier work by us [17].
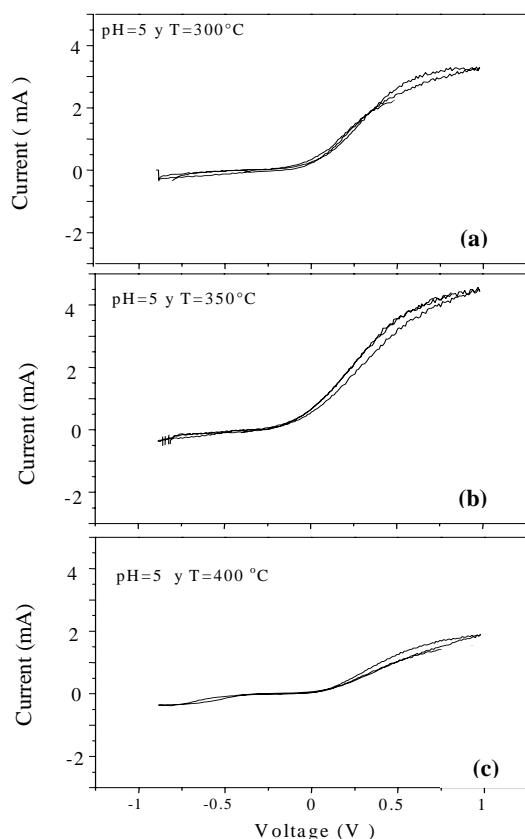
The experimental data, to be reported below, were obtained with 8 ml KCl 0.1 M in the container, in the case of photocurrent measurements (Figures 6 and 7), and of 35×10^{-5} M methyl orange in the container, in the case of photocatalytic degradation of methyl orange. In the latter case, a distilled water solution with pH = 5.5 was used. Irradiation was accomplished with a Phillips Hg 250 W lamp mounted 15 cm in front of the sample. In order to avoid thermal effects, a water filter was mounted between the lamp and the photoreactor. The intensity in the UV–A spectrum (315 to 400 nm)-measured with an UDT 300 radiometer- was 3 mW. The photoreactor was positioned in the sample compartment of a RS 325 Optometrics Single beam spectrophotometer operating at 340 < λ < 800 nm. A mechanical chopper system was employed to avoid UV irradiation during the spectrophotometer recordings.

Electrochemical measurements were taken with a Wenking POS 73 potentiostat interfaced to a computer. Experiments were performed at 10 mV/s. In the dark non electrochemical reactions were observed in the –1 V- 1V scanned range.
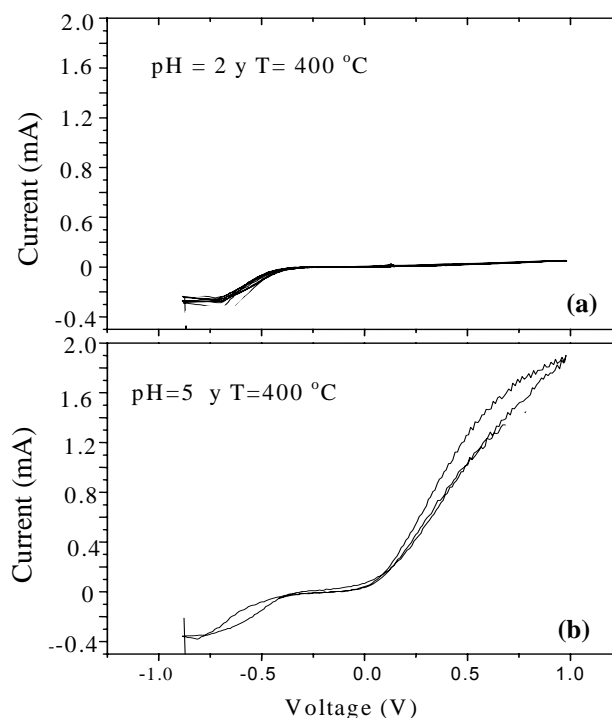

Figure 6. Cyclic voltammograms obtained under UV irradiation for zinc oxide films prepared at pH = 5 and at the shown temperatures: (a) T = 300, (b) T = 350 and (c) T = 400. Experiments were performed at 10 mV/s. Plots show the fifth cycle in each experiment.

Figure 7. Cyclic voltammograms obtained for zinc oxide films under UV irradiation. Films were prepared at 400 °C, using spraying solutions with: (a) pH = 2, (b) pH = 5. Profiles were obtained at 10 mV/s scan rate and plots were registered after five cycles.

In Figures 6 and 7, cyclic voltammograms show the effect of the deposition parameters:

temperature and pH on the photoactivity of zinc oxide films.

Experiments were performed under UV illumination. In the dark, the obtained current across the scanned range was zero before and after illumination. In Fig. 6 shows films deposited at 400 ^{o}C present slightly lower photocurrent that films deposited at lower temperatures. In Fig. 7, a dramatic increment in the photocurrent is observed when the pH of the deposition conditions is increased.

An applied bias potential of 0.7 V vs. the Ag/AgCl reference electrode was used to avoid electron–hole recombination in the irradiated samples; this effect may otherwise be significant, mainly as a consequence of traps and surface states. In order to diminish the influence of free oxygen, a well-known electron scavenger, nitrogen bubbles were introduced continuously into the sample compartment so that the solution was kept uniformly mixed. Figure 8 shows the resulting photocurrent in a typical experiment of methyl orange 35×10^{-5} M obtained using two zinc oxide films as photocatalyst. It may be seen that for the films deposited pH=5, the photocurrent is higher than for those deposited at pH =2. However, a consistent decrement as a function of time is observed in the films deposited at pH=5, probably due to limitations in the diffusion of dye from the bulk of the solution into the semiconductor.
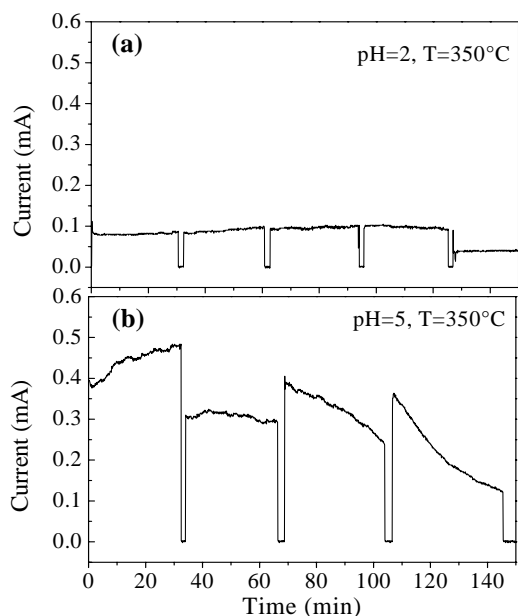
Reaction products such as hydrazine are expected to appear as a result of the photocatalytic degradation of methyl orange [18]. These products, as well as the methyl orange itself, display characteristic optical absorption at 460 nm and ~245 nm, respectively. The latter substance is an intermediate of the photo–electrocatalytic degradation of methyl orange to harmless products so they can be identified by spectrophotometry. Figures 9 a,b show typical absorbance spectra of the methyl orange solution during photo–electrocatalysis with zinc oxide films prepared at different pHs under UV irradiation. 0.7 V of anodic potential was applied. Photocurrent measured values were presented in Fig 8.

The spectral data display pronounced absorption at ~460 nm due to methyl orange. Fig. 9a shows, for the case of films prepared at pH=2, that this absorption drops slightly under UV irradiation. However, for pH=5 presented in Fig. 9b, the absorption drops monotonically, concomitantly with an increase of the absorption at 350 nm, probably due to an hydrazine derivative. However, more research is needed in this case. Intermediates of the photo–electrocatalytic degradation, have been observed to increase in concentration at the beginning of the photocatalytic reaction. They, as in the case of hydrazine can disappear after hours in air solutions [18] or can be photodegraded during the photoelectrocatalysis in a parallel process.
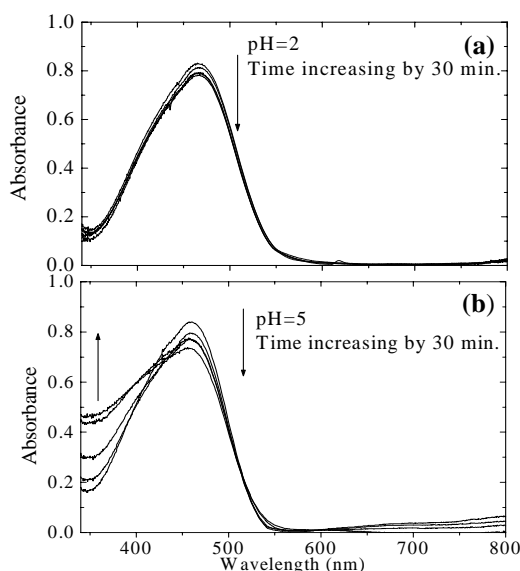

Figure 8. Photocurrent as a function of time for 650 nm - thick zinc oxide films in a 35×10^{-5} M of methyl orange water solution under UV irradiation. The data pertain to films obtained by spraying solution with: (a) pH = 2, (b) pH = 5.

Figure 9. Spectral absorbance of an aqueous solution of 35×10^{-5} M methyl orange after UV irradiation and using a photocatalytic zinc oxide films obtained from spraying solutions with: (a) pH = 2, (b) pH = 5.

Figure 10 shows the relative concentration of the methyl orange during its photo–electrocatalytic degradation using zinc oxide irradiates with UV. The data are based on the intensity of the absorption at $\lambda = 460$ nm of experiments shown in Figs 8 and 9.
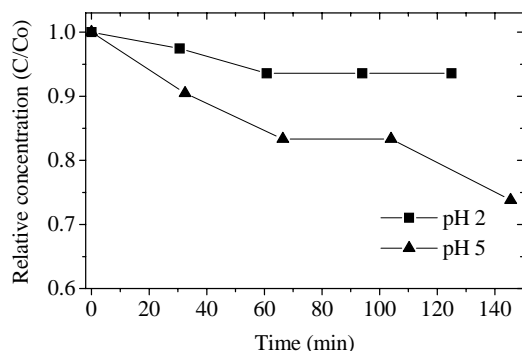

Figure 10. Spectral absorbance of an aqueous solution of 35×10^{-5} M methyl orange after UV irradiation and using a photocatalytic zinc oxide films obtained from spraying solutions with: (a) — ■ — pH = 2, (b) — ▲ — pH = 5.

It is evident that thin film manufacturing plays an important role in photodegradation. After ~3 h, the concentration of methyl orange in the solution has decreased only a quarter of the initial concentration in the best of the cases. We note that the photo–electrocatalytic degradation rate correlates with the optical absorption at short wavelengths, as evident from Fig. 5. We should point out that for the used lamp, the maximum of the irradiation spectra is around 350 nm, matching a minimum of the methyl orange absorption. This can explain why UV light without zinc oxide cannot degrade the methyl orange. In addition, illuminating the films through the substrate will cut off the irradiation below 300 nm, due mainly to the glass absorption, shadowing most of the absorption of the zinc oxide films.

4. CONCLUSIONS

We prepared zinc oxide films by spray pyrolysis under conditions giving high porosity films. Films deposited at low pH values have shown to be more compact and do not present much photoactivity. compared with films deposited at higher values. In the range of the used deposition temperatures, from 300 $^{\circ}$C to 400 $^{\circ}$C, a preferred structural (002) direction is observed. A slight decrement in photoactivity can be seen in films deposited at 400 $^{\circ}$C compared to those deposited at 350 $^{\circ}$C, due to crystal growth and a smaller surface area.

The photo-electrocatalytic ability of the films to degrade methyl orange was investigated in detail in a reactor allowing optical measurements to document the presence of methyl orange as well as the intermediated reaction product hydrazine. Degradation rates have shown to be more efficient with films deposited at high pH values, thus favoring the increment of the film´s surface area .

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