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Effect of milling speed on the precursor Zinc acetylacetonate destined to obtain ZnO thin films

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Abstract— **In this work, zinc oxide (ZnO) thin films were deposited on glass substrates by the ultrasonic spray pyrolysis technique, USP, the starting precursor (zinc acetylacetonate) was milled by planetary ball milling. The milling conditions were, 60 minutes and milling speed ranging from 300 to 600 rpm. The ball to power ratio was 7:1 in a tungsten carbide vessel. For depositing the ZnO thin films, a 0.2 M starting solution was prepared by dissolving the milled precursor in a mix of methanol, water, and acetic acid. Films were deposited at 400 and 450 °C with a time deposition of 6 minutes. These films were tested for measure the photocatalytic degradation of methylene blue (MB) dye under UV light irradiation. The effect of milling speed of the zinc precursor on the photocatalytic degradation has been studied in this work. Both Zn precursor powders and ZnO thin films were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). Thin films deposited at 400°C from a precursor milled at 300 rpm presented the maximum catalytic degradation, around 99%, after being exposed to UV radiation during 5 hr.**

Keywords: Zinc oxide; mechanical milling; photocatalysis.

I. Introduction

Photocatalysis is a promising technique for environmental detoxification. ZnO, with a band gap energy (3.2 eV), has attracted much attention for different photocatalytic applications, such as the degradation of various pollutants. The high photosensitivity of the ZnO makes possible its application in this field. Many different metods have been used to synthesize ZnO such as sputtering [1], sol-gel [2], electrodeposition [3], spray pyrolysis [4], etc. In order to obtain different structures, as nanobelts, nanosperes, nanorings, [7], nanosheets, nanoparticles, thin films [5-7]etc.

Regarding to mechanical milling, this is an efficient and simple method used for the preparation of nano-crystalline particles and amorphous material [8]. Physical and chemical transformations can take place, depending on milling conditions and nature of raw materials; the mechanochemical reactions can be classified into two categories; the first are presented during the mechanical activation process, and the second during the subsequent thermal treatment [9]. Some important variables in milling process are milling time, milling speed, temperature, milling atmosphere (wet or dry) [10, 11], filled level of the ball milling vessels, etc.

In general, it has been shown that the mechanical activation modifies the crystal structure, increases the density of defects, improves the diffusivity of the reactants, increases the nucleation sites, and consequently favors the formation of compounds at low temperatures [12].

Additionally, it has been reported that the vessel and balls material influences on the manufacture of compounds, leading to a reduction of the synthesis temperature [13]. It has been reported that using balls and vessels made from tungsten carbide, the manufacture of $MoSi_2$ can be decreased in 200 °C as compared with the use of steel and zirconia balls and vessels; this result is associated to the lower impact energy of steel and zirconia balls and vessels. Additionally, steel and zirconia produced a higher contamination of processed materials.

In this work, we are stating the following hypothesis: a way of improving the photocatalytic properties of the ZnO films deposited by USP is by mechanical activation of the precursors, carried out by a high energy ball milling process. In this respect, the effect of the milling conditions of the ZnO precursor (zinc acetylacetonate) on the ZnO thin films properties and the photocatalytic degradation of methylene blue, was studied.

II. Experimental procedure

2.1. Milling of Zn precursor

The milling process of the ZnO precursor (zinc acetylacetonate) was performed in a Fritsch Pulverisette 7 planetary ball mill, using a rotation speed ranging from 300 to 600 rpm. The material of balls and vessel was tungsten carbide, with a constant 7:1 ball-to-powder weight ratio, and a milling time of 60 min.

2.2. Film Preparation

The ZnO thin films were deposited from a 0.2 M starting solution prepared from unmilled and milled precursors dissolved in a mix of methanol, water, and acetic acid. The films deposition was carried out in a home-made system, based on a commercial humidifier that works at a constant frequency of 30 KHz, adapted for atomizing the starting solutions. A molten tin bath was used for substrate heating; the temperature of the bath is electronically controlled and monitored by a K-type thermocouple. The deposition time was of 6 minutes, and the substrate temperatures were, 400 and 450 °C. Gas nitrogen was used as carrier gas.

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2.3. Characterization

The morphology of unmilled and milled Zn precursors, and ZnO thin films were examined by using a scanning electron microscope (HRSEM- AURIGA) operating at a voltage of 20 kV. The structural identification was carried out using an X-ray diffractometer (XRD, X´Pert Pro PANalytical system,) with CuKα radiation with a wavelength (λ) of 0.15406 nm. Thickness films were around 200 nm, which were measured from profilometry with a KLA-P15 talystep. Finally, the photocatalytic activity of the ZnO thin films was tested by the degradation of methylene blue (MB) in an aqueous solution. This characterization consisted of immersing the ZnO thin films into a quartz cell containing 3 ml of $2.5x10^{-5}$ M of MB, and then irradiated with an UV lamp (G15T8 germicidal 15 W with major emission at 254 nm) located at 4 cm from the cell. The irradiation was kept during 5 hours; nevertheless the sample were taken away every hour in order to measure optical absorbance of the MB solution, measured at 664 nm using an UV-VIS Spectrophotometer, for estimating the residual concentration of MB. Table 1 reports the used milling conditions of the Zn precursor. Table 2 reports the deposition conditions of ZnO thin films by the USP technique.

SAMPLE	MILLING SPEED
M0	Unmilled
M1	300
M2	400
M3	500
M4	600

Table 1. Milling conditions of the zinc precursor, zinc acetylacetonate.

SAMPLE	MILLING SPEED	DEPOSITION TEMPERATURE (°C)
a	0	400
b	0	450
c	300	400
d	300	450

Table 2. Deposition conditions of ZnO thin films by the USP technique.

III. RESULTS

IIIa. Structural Characterization

X-rays diffraction patterns of unmilled and milled precursors are showed in fig 1. It can be observed that similar spectra are presented in all films, indicating that milling process does not produce new phases. Any peak presented in the spectra was identified due to the lack of respective cards.

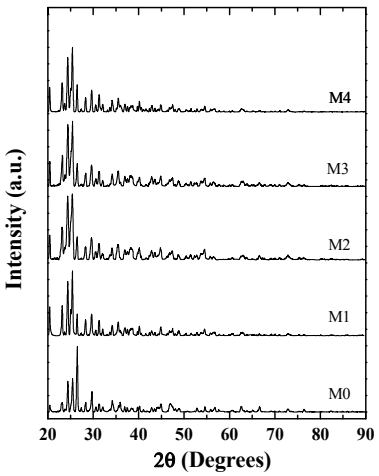


Fig. 1 X-ray diffraction patterns of milled powders at different milling speeds, 0, 300, 400, 500, and 600 rpm; for MO, M1, M2, M3, and M4 samples, respectively.

Fig. 2 shows XRD patterns of ZnO thin films deposited at 400 and 450°C from unmilled and milled precursors at 300 rmp during 60 minutes. All ZnO thin films show a crystalline hexagonal wurtzite phase with a preferred growth along the (002) plane. Four main diffraction peaks were observed, namely, (002), (011), (012) and (113). Sample c and d presents peaks with higher intensity; this result can be associated to the quality film.

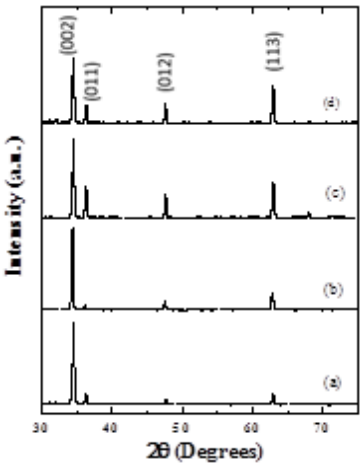


Figure 2. X-ray diffraction spectra of ZnO thin films deposited at two different substrate temperatures by ultrasonic spray, from unmilled and milled precursors. (a) unmilled precursor, 400 °C; (b) unmilled precursor, 450 °C; (c) milled precursor, 400°C; (d) milled precursor, 450 °C.

IIIb. Morphological Characterization of precursor powders

Figure 3, shows the morphology of precursor (zinc acetylacetonate) powders milled at different speeds. The powders exhibit a structure of fine fibers at low milling speed,

whereas for the highest speed, 600 rpm, the structure of samples changes to a like-sponge past.

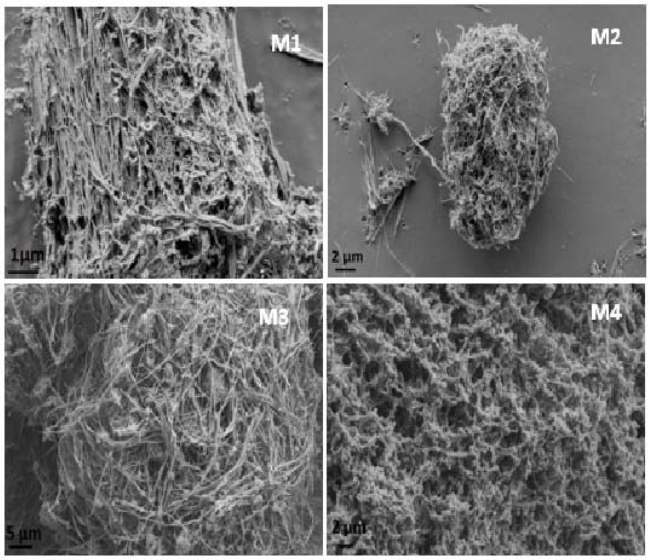


Figure *3*: SEM micrographs of *milled* powders at different milling speeds, 300 (M1), 400 (M2), 500 (M3), and 600 (M4) rpm.

ZnO thin films

IVa. Morphological Characterization of ZnO thin Films

The SEM micrographs of the ZnO thin films (figure 4) indicate that surface particles of film deposited from unmilled precursor are uniform and flat, presenting a regular size hexagonal-shaped grains; whereas films processed from milled precursor present surface particles with helicoidal growth of hexagonal-shaped particles or grains. We expect this morphology will increase the surface area, which in turn could improve the photocatalytic response. Our morphological results are similar to reported by Smith et al. [14].

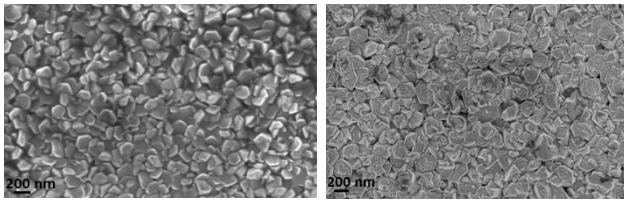
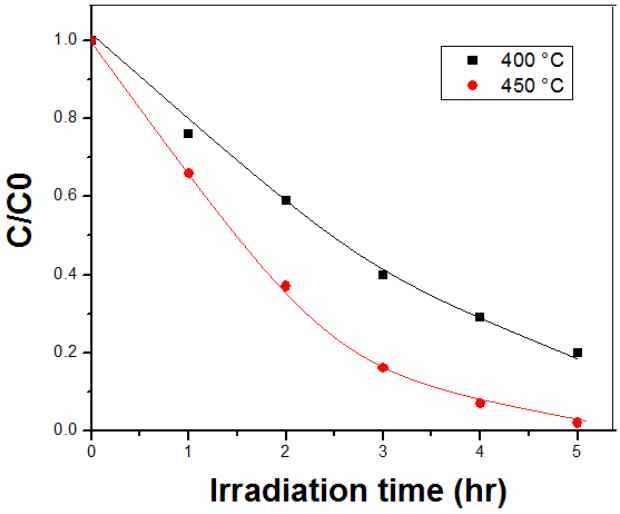


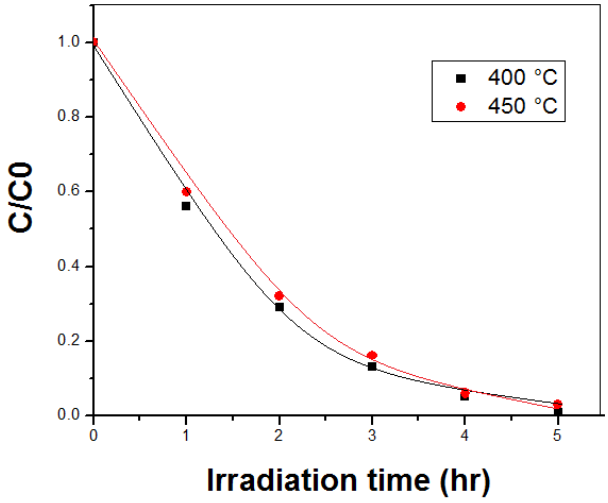
Figure 4: SEM micrographs of ZnO thin films deposited at 400°C from unmilled (a), and milled precursor (b).

IVb. Photocatalysis

Figure 5, shows the photocatalytic response of ZnO thin films deposited from unmilled and milled precursors. It can be seen that ZnO thin films deposited from the unmilled precursor has a better photocatalytic response at a deposition temperature of 450C°, reaching 100% of degradation in five hours, whereas ZnO film deposited at 400°C presented only 80% in the same exposure time. Films deposited from milled precursor presented a total degradation after five hours, irrespective of deposition temperature. That means, milling process favors the photocatalytic response, under a methylene blue environment, of ultrasonically sprayed ZnO thin films.



(a)



(b)

Figure 5:. Evolution of C/Co as a function of irradiation time of ZnO thin films deposited at 400°C; (a) from unmilled precursor, and (b) milled precursor at 300 rpm..

V. Conclusions

ZnO thin films have been deposited on glass substrates by the ultrasonic spray technique for testing their photocatalytic properties in a 2.5×10^{-5} M methylene blue solution. The influence of the milling precursor and films deposition temperature on the structural, morphological, and photocatalytic response, was investigated. It was obtained that, milling process,

performed to the precursor, presented an evident effect on the photocatalytic properties of ultrasonically sprayed ZnO thin films, reaching a total degradation of the testing solution after five hours, irrespective of the deposition temperature. However, in ZnO films deposited from unmilled powders the effect of the deposition temperature is important, since films deposited at 450°C presented a higher degradation, in the order of 20%, as compared with those deposited at 400°C. This work demonstrates that methylene blue dye could be successfully decolorized by using ZnO thin films.

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