GRAIN SIZE EFFECT ON PHOTOCATALYTIC PROPERTIES OF NANOCRYSTALLINE ZnO

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The aim of this study represents the synthesis, characterization and photocatalytic activity determination of ZnO nanopowders synthesized using modified Pechini method. The obtained powders were characterized in what concerns their composition using X-ray diffraction, morphology using scanning electron microscopy and transmission electron microscopy and in what concerns the photocatalytic activity. The powders were heat treated in the 500 – 800^oC temperature range when the obtained powders are having an average grain size of 24 nm for the 500^oC heat treatment temperature and 302 nm for the 800^oC one. The photocatalytic activity decreased with the increase of particle size.

Keywords: Hexagonal ZnO, TEM, photocatalytic activity

1. Introduction

Zinc oxide is known as a n-type semiconductor with a wide band-gap (3.3eV) with a large exciton binding energy (60 meV). It is also a promising candidate for nanoelectronics and photonics and an intense interest has been paid to its optical and electronic properties. Pure zinc oxide has transparent properties in the visible range of the spectrum and good absorption of the UV radiation. Therefore, it is used in the production of many optoelectronic devices but also in the fields of chemical sensors [1], photocatalysts [2, 3], phosphors [4], thin films [5] and dye-sensitized solar cells [6].

Its optical properties also made ZnO to be toughly investigated as a coating material, from paints [7], to sunscreens [8] and fabric coating [9]. The photocatalytic activity of ZnO is well known and has been investigated versus a

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wide variety of pollutants. There are some application where a high photocatalytic activity is desirable [10], but there are also some application where ZnO capacity to degrade various organic substrate is an impediment, like fabric or paper coating.

A variety of structural defects may exist in the ZnO nanoparticles, which will influence the electronic and optoelectronic properties. Kohan et al [11] have reported a detailed description of the intrinsic defects usually found in ZnO. These defects are zinc interstitials (Zni), zinc vacancies (VZn), oxygen interstitials (Oi), oxygen vacancies (V_O), oxygen antisites (OZn), and zinc antisites (ZnO).

All these defects induce changes in the photoluminescence spectra of specific ZnO sample. The UV emission corresponds to the near band edge (NBE) emission (is due to the radiative annihilation of excitons) and the visible emission is commonly referred to as a deep-level or trap-state emission [12]. The relative strength of NBE to deep level defect emissions exhibits a dramatic threshold dependence on surface roughness. Surface optical emission efficiency increases over tenfold as roughness decreases to unit cell dimensions, highlighting the coupled role of surface morphology and near-surface defects for high efficiency ZnO emitters [13].

In view of fundamental studies as well as industrial applications of nanoparticles, chemically pure or compositionally well-defined ZnO is required. Therefore developing a method of obtaining cheap, pure ZnO with small, controlled size is highly desirable. Common synthesis methods include precipitation from zinc salts solution with an alkali such as sodium hydroxide, force hydrolysis, sol-gel or pyrosol [14-17].

2. Experimental procedure

2.1 Sol-gel synthesis

The modified Pechini method has been used for ZnO synthesis due to its advantages, such as good homogeneity, smaller particles sizes due to interaction in liquid phase at atomic scale and relatively cheap synthesis route. The method principle is based on formation of a sol, jellification, followed by elimination of the solvent and appropriate thermal treatment as presented [BV]. Briefly, the precursors such as zinc nitrate (Sigma Aldrich), citric acid (Sigma Aldrich), ethylene glycol (Sigma Aldrich) and the necessary distilled water were mixed and maintained under stirring and temperature of 60°C for 2 hours. After a short time, the precipitation has been observed. The formation of ZnO nanoparticles has been obtained after the white colour of the precipitate. The obtained gel was left to maturate for 3 hours and the next step was the elimination of the solvent for 24 hours into an oven at 110°C. The synthesized powder was then heat treated at 500°C, 600°C, 700°C, 800°C in order to remove the organic part and to obtain a crystalline powder.

2.2 Powders Characterization

The obtained powders were characterized using X-ray diffraction (XRD), high resolution/transmission electron microscopy with selected area electron diffraction (TEM/HRTEM/SAED) and UV-Vis spectrophotometry.

X-ray diffraction analysis was carried out on Panalytical X'Pert Pro MPD equipment, with a CuKα radiation, over a scan range of $2\theta = 100$ to angle $2\theta = 900$.

The bright field and high resolution images coupled with SAED were obtained using a Tecnai G^2 F30 S-TWIN transmission electron microscope (FEI, the Nederland's), equipped with a STEM/HAADF detector, EDAX spectrometer (for energy dispersive X-ray analysis) and Gatan EELS spectrometer (for electron energy loss spectroscopy). The microscope operates at an acceleration voltage of 300 KV (Shottky field emitter) with a resolution of 1 Å. The sample preparation for TEM measurements was done as follows: a small amount of powder was diluted into pure ethanol and left into an ultrasonic bath for approximately 15 minutes. After that, a small drop of the diluted solution was put onto a 400 mesh holey carbon coated copper grid and left to dry for approximately 30 minutes, prior to be analyzed.

The photocatalytic activities of ZnO nanopowder catalysts were tested by using methylene blue (MB) degradation. ZnO nanopowder samples, 25 mg of as-obtained samples were dispersed in 20 mL MB aqueous solution with the concentration of 10mg/L. The suspension was magnetically stirred first for 30 min in dark at ambient temperature. After that, the dispersion was irradiated by a 200 W visible-light halogen lamp with a maximum emission at 640 nm. The surface of the dispersion was maintained a distance of 25 cm from the light source to avoid heat effect.

The concentration of residual MB in the solution after irradiation was determined by monitoring the absorbance intensity of solution samples at their maximum absorbance wavelength 664 nm by using an Able Jasco V560 UV-Vis specrophotometer with a 1 cm path length spectrometric quartz cuvette at room temperature.

3. Results and discussions

3.1 X-ray diffraction characterization

The powders were analysed for the qualitative phase composition by using X-ray diffraction, the XRD patterns being presented in Fig. 1.

By analysing the XRD spectra obtained on heat treated at 500^{o}C, 600^{o}C, 700^{o}C, 800^{o}C ZnO powders, we can state that the only phase formed is the wurtzite structure of hexagonal zinc oxide.

In Table 1 is presented the grain size variation against the temperature of thermal treatment. These values were obtained using Schrerer's formula. We can

see that, for all thermal treatment temperatures, nanocrystalites with sizes varying from about 16 – 19 nm were obtained.

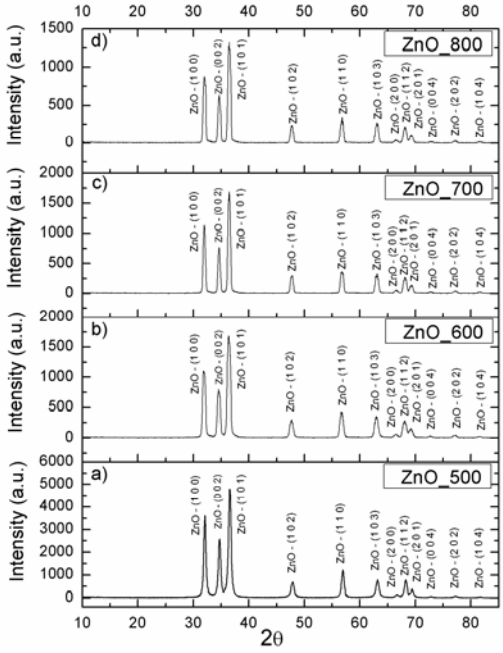


Fig. 1 X-ray diffraction pattern for ZnO powders obtained through sol-gel method and calcinated at a) 500°C, b) 600°C, c) 700°C, d) 800°C and concentration of precursor solution of 0.1 M

Table 1

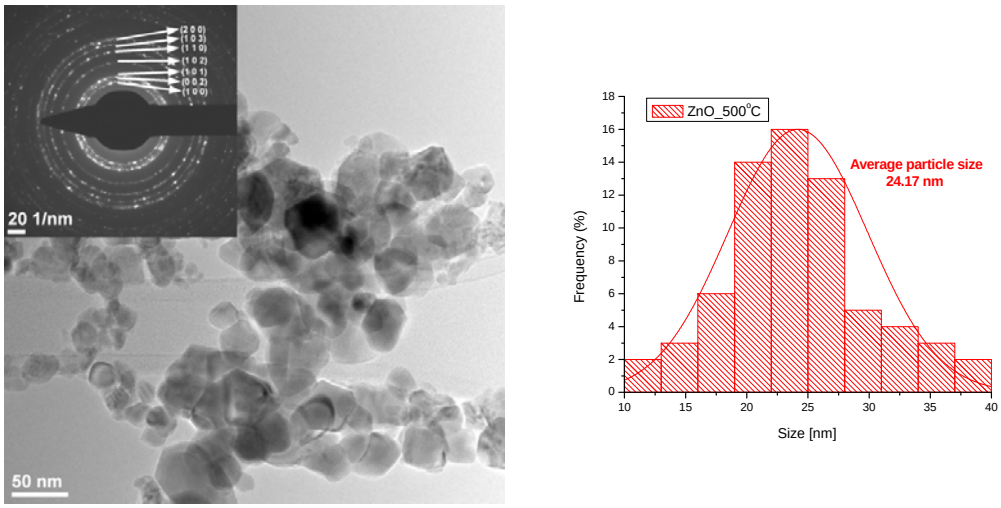
Crystallites size variation against sintering temperature and concentration of precursor solution from X-ray diffraction analysis

Temperature (°C)	Dimension (nm)
500	16.82
600	16.73
700	16.22
800	19.35

3.2 TEM analysis

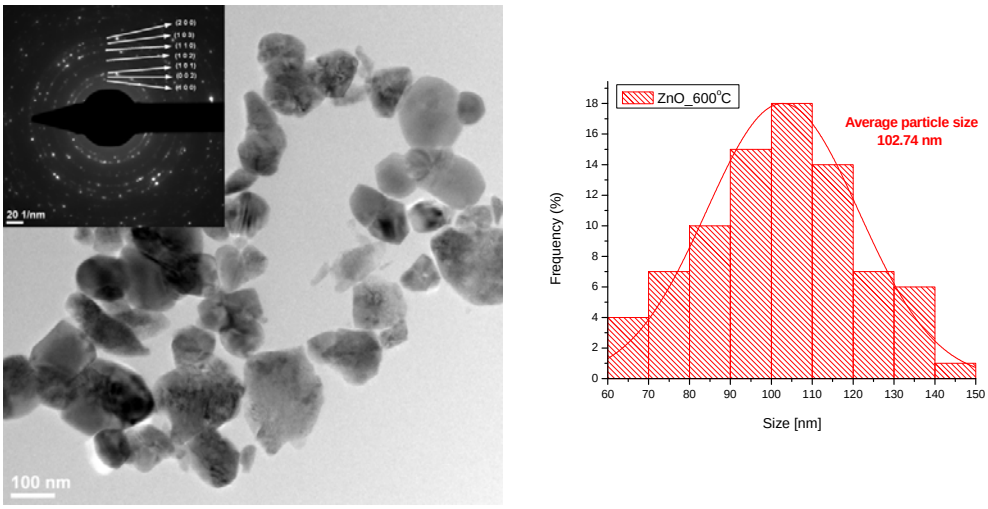
The TEM images obtained on ZnO samples synthesised through Pechini method are presented in Figs. 2 – 5.

The TEM bright field images obtained on heat treated powders at temperatures ranging from 500 to 800°C reveal the fact that with the increase of thermal treatment temperature the average particle size increases from about 24 nm to 301 nm, with monomodal distribution.



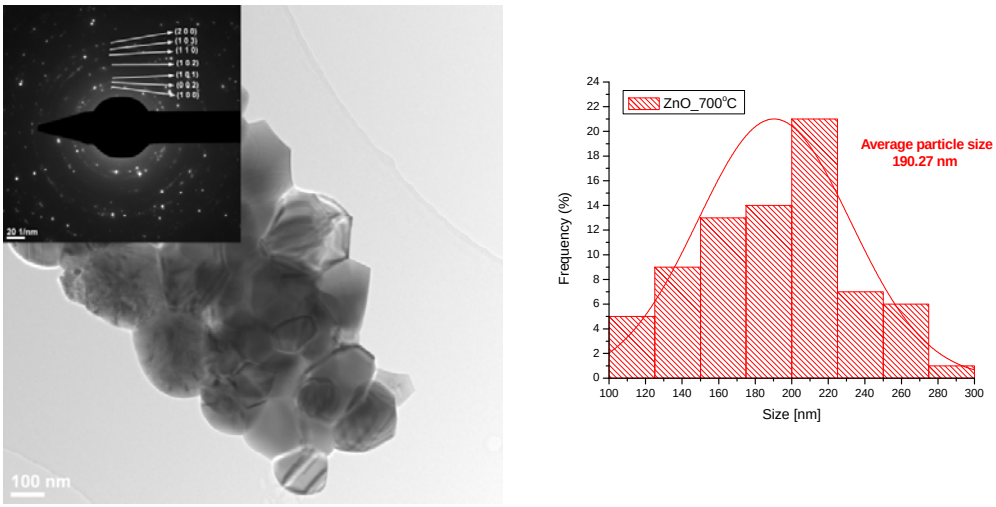
a) b)

Fig. 2. TEM a) and histogram b) obtained on 500°C heat treated ZnO powder



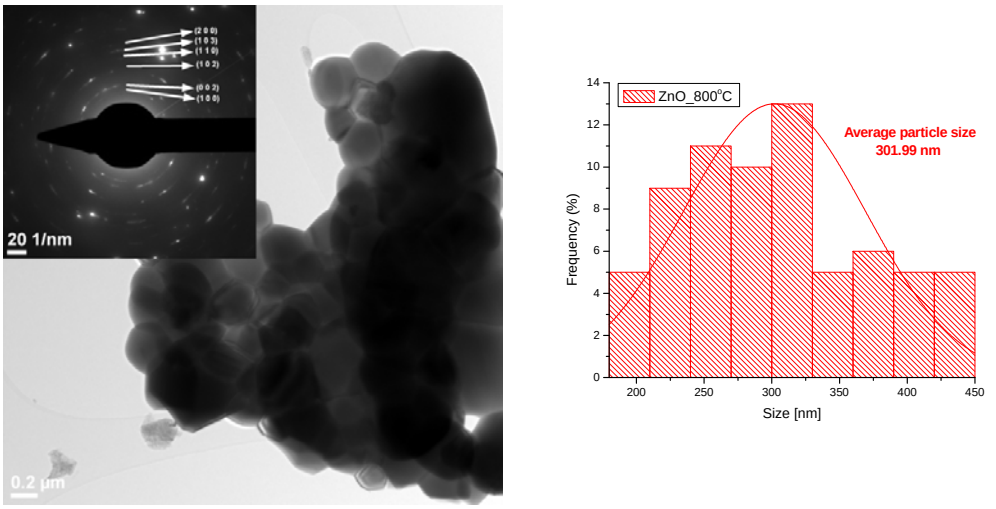
a) b)

Fig. 3. TEM a) and histogram b) obtained on 600°C heat treated ZnO powder



a) b)

Fig. 4. TEM a) and histogram b) obtained on 700°C heat treated ZnO powder



a) b)

Fig. 5. TEM a) and histogram b) obtained on 800°C heat treated ZnO powder

The values are presented in Table 2. Also, the particles present a more pronounced tendency to form hard agglomerates with the increase of heat treatment temperature. From the obtained SAED images (insets) we can state the only phase formed from the synthesis is the hexagonal wurtzite form of ZnO.

Table 2

Grain size variation against the thermal treatment temperature as measured from TEM

Temperature (°C)	Grain size (nm)
500	24.17
600	102.74
700	190.27
800	301.99

3.4 Photocatalytic activity

The obtained samples were characterised in what concerns their photocatalytic activities. The data are presented in Fig. 6 and Table 3.

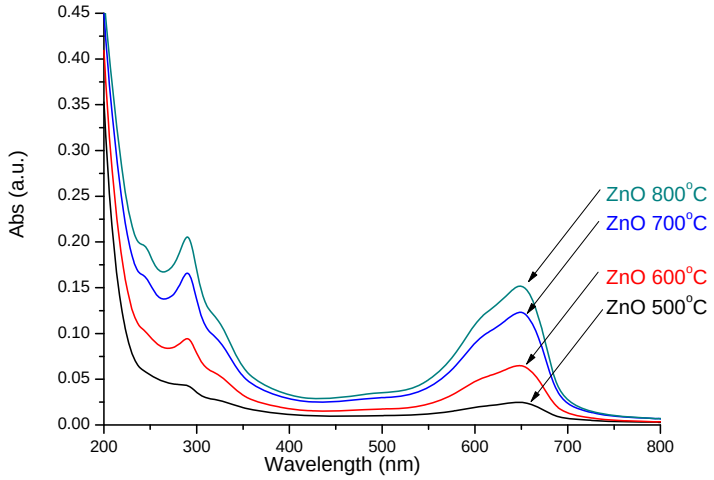


Fig. 6. The absorption spectrum for MB after 3 hours of irradiation in presence of ZnO nanopowders

The photocatalytic activity of ZnO nanopowders were examined by the photo degradation of methylene blue under visible light irradiation. MB was used as an indicator for the photocatalytic activities [18, 19] owing to its absorption peaks in the visible range.

A variety of structural defects may exist in the ZnO nanoparticles, which will influence the electronic and optoelectronic properties. The intrinsic defects commonly found in ZnO are zinc interstitials (Zn_i), zinc vacancies (V_{Zn}), oxygen interstitials (O_i), oxygen vacancies (V_O), oxygen antisites (O_{Zn}), and zinc antisites (Zn_O). Kohan et al [11] have reported a detailed description about these defects. Photocatalytic activity of undoped ZnO is attributed both to the donor states caused by the large number of defect sites such as oxygen vacancies (Vo) and

interstitial zinc atom (Zn_i) and to the acceptor states that arise from zinc vacancies (VZn) and interstitial oxygen atoms (Oi). The calculated energy levels of the intrinsic defects in ZnO are reported, and the calculated energy levels of V_{Zn}, Zn_i, V_O, O_i, and O_{Zn} are 3.06, 2.9, 1.62, 2.28, and 2.38 eV, respectively [20].

Here we assume that interfacial electron transfer takes place predominantly between these donor states and acceptor states. Being a cationic dye MB acquires electron from excited donor states and decomposes.

It is clear that the decomposing ratio increased with the degradation time for all samples. It is observed that the degradation of MB is highest in the case of ZnO nanopowder calcinated at 500°C. As the sample's temperature of calcination increase the rate of MB degradation decrease.

As air or oxygen annealing of ZnO usually diminishes the Vo defect density, but also increase the number of O_i type defects, we can correlate the diminish intensity of the photocatalytic activity with the decrease of V_O type defects number as calcination temperature increase. Another factor that is contributing to the decrease of the photocatalytic activity is the increase of particle size with the annealing temperature.

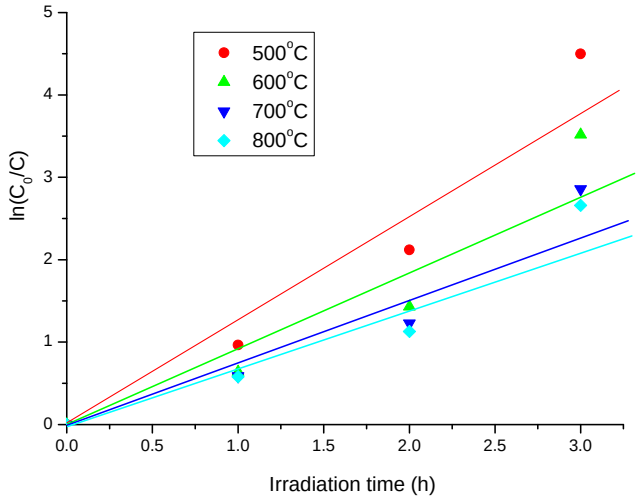


Fig. 7. Degradation rate constant determination

Table 3.

Degradation rate constant

No.	Sample	Degradation rate constant (min^{-1})
1	ZnO 500°C	$2.23 \cdot 10^{-2}$
2	ZnO 600°C	$1.67 \cdot 10^{-2}$
3	ZnO 700°C	$1.38 \cdot 10^{-2}$
4	ZnO 800°C	$1.29 \cdot 10^{-2}$

A global first order kinetic model was used to study the degradation reaction kinetics, where C and C_0 are respectively the residual dye concentrations at each measurement time and at t = 0. The rate constant, k (listed in Table 3) is the apparent first order constant relative to degradation kinetics. A graph was drawn between irradiation time vs $\ln(C_0/C)$ and the degradation rate constants were calculated from the Fig. 7 and equation $\ln(C_0/C) = kt$. The results show that the photodegradation reaction kinetics is approximately the first-order. It is observed from Fig. 7 that ZnO sample heat treated at 500^{o}C is having the highest value of degradation rate constant.

4. Conclusions

ZnO was synthetized by the modified Pechini method, in the range of temperatures 500 - 800^{o}C. The obtained ZnO nanoparticles have an average grain size varying from about 24 nm to 300 nm as the temperature increases, while the crystallites size is increasing from about 16 nm to 19 nm. The method produces a nanopowder that contains only crystalline ZnO, with no detectable secondary phases. TEM and XRD data sustain the formation of a single phase, monodisperse crystalline ZnO nanopowder.

With increasing of the heat treatment temperature, we notice a decrease in the photocatalytic activity of ZnO nanopowder. This decrease in the photocatalytic activity can be attributed to the increase of the ZnO grain size, but also to the decrease of V_O type defects number in the nanoparticles, as the temperature for thermal treatment increases.

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