KINETIC STUDY ON THE PHOTOCATALYTIC DEGRADATION OF PARACETAMOL AND CHLORAMPHENICOL IN THE PRESENCE ZNO SOL-GEL FILMS ANNEALED AT DIFFERENT TEMPERATURES

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ABSTRACT:

Nanostructured ZnO films annealed at different temperatures (100, 300 and 500 ^{o}C) are fabricated by sol-gel method using dip coating technique. The effect of annealing temperature on the photocatalytic action of ZnO films is studied. The surface morphology, crystallite size, pH and degradation of drugs are studied by SEM, XRD and UV-visible spectroscopy. The ZnO in as-prepared films is of hexagonal wurtzite structure and has highly preferred growth along the c-axis direction. The ZnO nanocrystallite size is of 30 - 88 nm in dependence on the annealing temperature. The film surface consists of ganglia-like hills, which dimensions increase in size with the rise of annealing temperature.

The photocatalytic efficiency of the samples is tested in UV-light induced degradation of two pharmaceutical products, *Paracetamol* (PCA) and *Chloramphenicol* (CA), in aqueous solutions. The optimal annealing temperature of 500 ^{o}C is experimentally established. Films annealed at 100 ^{o}C photodecompose both drugs most slowly and have lowest photocatalytic activity (PCA - 1.99% and CA - 5.88%) for period of 4 h. The experimental results show, that ZnO films annealed at 500 ^{o}C rapidly degrade the pollutants (PCA - 12.24% and CA - 39.22%) and have better photocatalytic efficiency as compared with annealed at 300 ^{o}C samples (PCA - 2.82% and CA - 30.20%). All films reproducible possess photocatalytic activity.

***Keywords**: zinc oxide, sol-gel, photocatalysis, Paracetamol, Chloramphenicol*

1. Introduction

Nanostructured materials offer promising opportunities for improved and tailored properties for application in environmental catalysis due to their unique physicochemical properties, caused by their nanosized dimensions and large surface/volume ratios [Stock et al., 2000; Burda et al., 2005].

Currently, ZnO semiconductor has stimulated great research interest due to its unique optical and electrical properties (nanolasers [Huang et al., 2001], piezoelectric nanogenerators [Wang et al., 2006], solar cells [Hupkes et al., 2006], gas sensors [Kakati et al., 2010]), good stability [Wang et al., 2008], considerable application in photocatalytic reactions [Pauporte et al., 2007] in the process of elimination of water contaminants (dyes, pharmaceutical drugs) [Chatzitakis et al., 2008; Chakrabarti et al., 2004]. Several works report the synthesis and high photocatalytic efficiencies of ZnO nanoparticles, powders and colloids [Wan et al., 2005; Tong et al., 2009; Dutta et al., 2009]. But for water treatment applications, ZnO thin films are preferred to avoid the separation of the catalyst after the degradation process. Several works have been published in respect to photocatalytic properties of ZnO thin films prepared by different methods - pulsed laser deposition (PLD) [Fan et al., 2005], chemical vapour deposition (CVD) [Waugh et al., 2008], magnetron sputtering [Wang et al., 2003; Kobayashi et al., 2013] and sol–gel [Kaneva et al., 2012; Kaneva et al., 2010; Delgado et al., 2009]. The sol–gel method has been receiving high attention since it enables us to develop low-cost and simple deposition procedure to obtain large area high quality ZnO films for technological applications.

This paper describes kinetic studies on the photocatalytic degradation of pharmaceutical drugs (*Paracetamol* and *Chloramphenicol*) by ZnO thin films annealed at different temperatures. The semiconductor photocatalysts are prepared vie sol-gel method using dip coating technique.

Microstructure, surface morphology and photocatalytic properties of the nanostructure films are explored and discussed.

2. Experimental

ZnO thin films were prepared by the sol-gel method from zinc acetate dehydrate (≥99.5 %), 2-methoxyethanol (≥99.5%), monoethanolamine (≥99.0%); all of them from Fluka. Zinc acetate dehydrate was dissolved in a mixture of 2-methoxyethanol and monoethanolamine [Kaneva et al., 2012]. The mixture solution was stirred at 60 ^{o}C for 1 h to yield a clear and homogeneous solution. After the solution was made 1 day at room temperature (23±2 ^{o}C), it was coated on glass substrates (ca. 76 x 26 mm, from ISO-LAB (Germany)), using dip coating technique (0.9 cm/min). Then precursor thin films were heated at 80 °C for 15 min to remove the solvent and organic residuals. The coating and heating process was repeated for 5 times. Then the as-prepared thin films were inserted to a furnace and annealed in ambient atmosphere at several temperatures from 100, 300 and 500 ^{o}C for 60 min.

Surface morphology of the thin films deposited on glass substrate was measured by Scanning Electron Microscopy (SEM, JSM-5510 (JEOL)). The crystallization behavior of the ZnO thin films deposited was analyzed by X-ray diffractometer (XRD, Siemens D500 with CuKα radiation within 2θ range 30-70 deg at a step of 0.05 deg 2θ and counting time 2 s/step). The average crystallite sizes were estimated according to the Scherrer's equation.

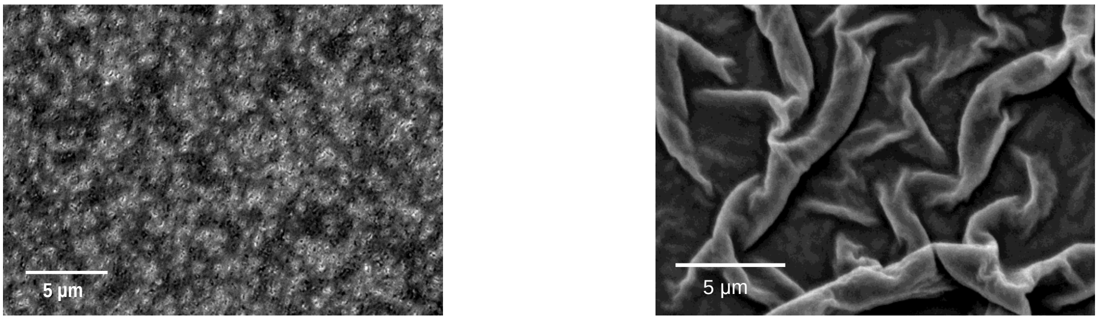
The pharmaceutical drugs – *Paracetamol* ($C_8H_9NO_2$, Actavis) and *Chloramphenicol* ($C_{11}H_{12}Cl_2N_2O_5$, Actavis), widely used products, were employed as a representative analgesic and antibiotic to evaluate the photocatalytic activity of ZnO thin films. The experiment was performed in a 150 ml glass reactor, equipped with magnetic stirrer (rotating speed ~ 500 rpm controlled by stroboscope) and UV-lamp (Sylvania BLB, 315-400 nm of emission range, 18 W). The light power density at the sample position was 0,66 mW/cm^2 as measured with Research Radiometer of Ealing Electro-optics, Inc.). The distance between the sample and the high pressure mercury lamp was 15 cm. The mineralization of the PCA and CA solutions were measured at intervals of 1h and the total irradiation time is 4 h by UV-VIS absorbance spectroscopy (spectrophotometer Evolution 300 Thermo Scientific, wavelength range from 200 to 400 nm). The extent of photocatalytic degradation could be evaluated by measuring the absorbance of the solutions at 243 and 278 nm. The degradation efficiency (*D*) of PCA and CA were calculated using the equation:

$D\% = (C_0 - C)/C_0 * 100$ (1),

where C_0 represents the initial concentration, C_t represents the concentration after t min reaction of the *Paracetamol* and *Chloramphenicol*.

3. Results and discussion

Figure 1a shows the surface morphology of ZnO thin films annealed at 100 ^{o}C, with very smooth surface, covered by round grains. Therefore, these films have the lowest activity. The sol-gel films, annealed at 500 ^{o}C, are more uniform and show much better adhesion of the layers and the highest density of the film. There is ganglia typical surface structure of the film. The surface morphology of the samples (Fig. 1b) is represented by different ganglia-like hills with typical width of about 1 μm and a height of 5-10 μm.



(a) (b)

Fig. 1. SEM images of ZnO thin films annealed at 100^{o}C (a) and 500^{o}C (b).

XRD patterns of the ZnO thin films are presented in Fig. 2. The lack of three characteristic peaks of ZnO (Fig. 2a) shows that at 100 ^{o}C temperature the material is still in its hydroxide form of rather amorphous state. The crystallite sizes estimated by the Sherrer's formula are about 30.0 nm. Increasing the annealing temperature causes a transition from orthogonal in to hexagonal structure, respectively from $Zn(OH)_2$ toward ZnO. The diffraction peaks of the sol-gel films (annealed at 500 ^{o}C, Fig. 2b) can be indexed to (100), (002), (101), (102), (110), (103), (200), (112) and (201) diffraction planes at 2θ = 31.77^{o}, 34.42^{o}, 36.25^{o}, 47.54^{o}, 56.60^{o}, 62.86^{o}, 66.37^{o}, 67.96^{o} and 69.09^{o}, respectively. The films produced are polycrystalline, showing the wurtzite ZnO hexagonal structure, while there is no evidence for the presence of other phases.

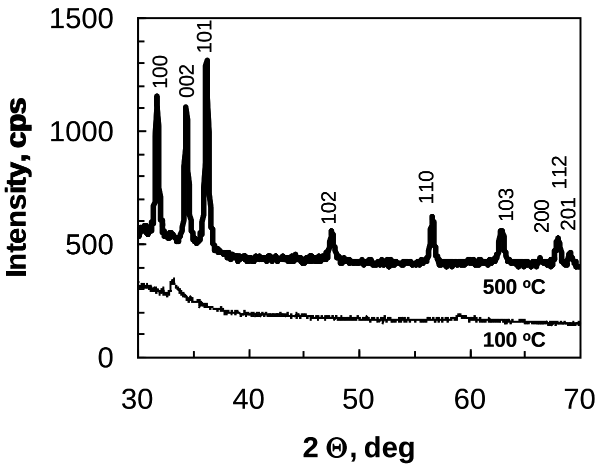
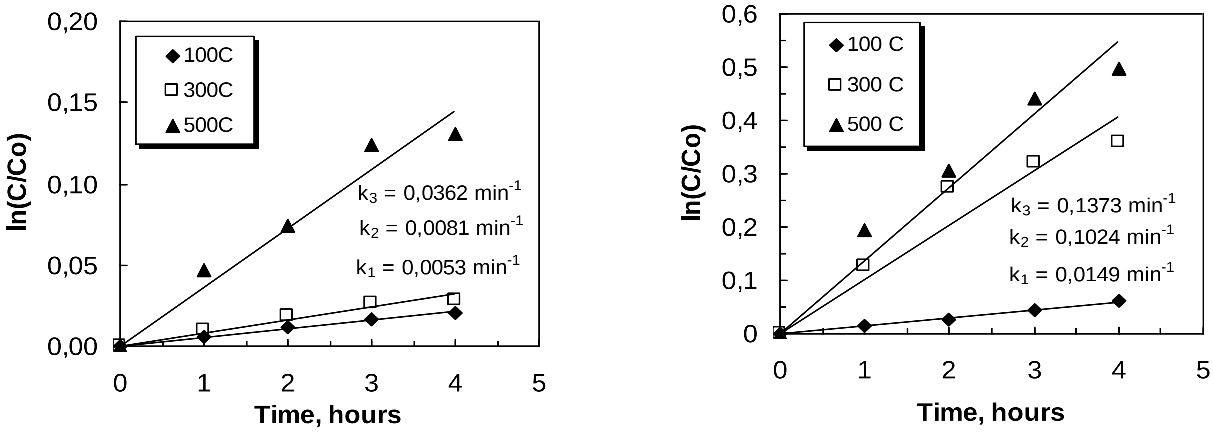


Fig. 2. XRD spectra of ZnO sol-gel films annealed at 100 and 500^{o}C.

Photocatalytic tests are carried out for all the thin films. *Paracetamol* and *Chloramphenicol* are used as a test contaminant. The initial concentrations of the drugs are 15 and 8 ppm. The pH values are observed during the photocatalytic reactions (PCA – 5.58 ÷ 6.69 and CA – 5.31 ÷ 6.49).

Figure 3 demonstrate the bleaching kinetics of the PCA and CA in aqueous solutions by ZnO films (annealed at 100, 300 and 500^{o}C) under UV-light illumination. It can be seen that the degradation efficiency of the thin films increases with increasing annealing temperature. The experiments show that the decolorization of PCA and CA under UV illumination follows pseudo first-order kinetics expressed by $\ln(C/Co) = -kt$. The slope of logarithmic scale represents linear fits of the experimental data points by the equation. The corresponding rate constant of photocatalysis *k* are also given in the Figure 3.



(a) (b)

Fig. 3. Photodegradation curves of *Paracetamol* (a) and *Chloramphenicol* (b) using ZnO thin films as photocatalysts.

The films annealed at 300 ^oC have higher photocatalytic activity (PCA - k= 0.0081 min^{-1} and CA - k= 0.1024 min^{-1}) than those, prepared at 100 ^oC (PCA - k= 0.0053 min^{-1} and CA - k= 0.0149 min^{-1}). As seen from the figure, the films obtained at 500 ^oC have the highest photocatalytic activity (PCA - k= 0.0362 min^{-1} and CA - k= 0.1373 min^{-1}). The values k of the rate constants are confirmed by rate of degradation of the pharmaceutical products. The degradation is calculated using Eq.1.

Nanostructured ZnO films annealed at 500 ^oC have a highest photocatalytic efficiency (PCA - 12.24% and CA – 39.22% for four hours), while samples obtained at 100 ^oC have a lowest activity (PCA -1.99% and CA – 5.88%).

4. Conclusion

In summary, ZnO thin films are deposited by sol–gel method using dip coating technique. The thin films consist of homogeneous and ganglia-like structures belonging to hexagonal wurtzite structures. The crystallites sizes are increased with rise of the annealing temperatures. The enhanced photocatalytic activity of ZnO thin films might be ascribed to the increase of surface to volume ratio, roughness and mean grain size. The good performance of ZnO thin films indicates that it can be used as a promising photocatalyst for the practical application in photocatalytic decolorization of pharmaceutical products.

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