Journal of International Scientific Publications: Materials, Methods and Technologies

Volume 8, ISSN 1314-7269 (Online), Published at: http://www.scientific-publications.net

EFFECT OF La DOPANT ON THE PHOTOCATALYTIC EFFICIENCY OF ACTIVATED ZnO NANOPOWDERS

Katya Milenova[1*], Alexander Eliyas[1], Vladimir Blaskov[2], Irina Stambolova[2],

Boris Kunev[1], Slavcho Rakovsky[1]

[1] Institute of Catalysis, Bulgarian Academy of Sciences,

Acad. G.Bonchev St, bl.11, 1113 Sofia, Bulgaria

[2]Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,

Acad. G.Bonchev St, bl.11, 1113 Sofia, Bulgaria

Abstract

Activated ZnO powder was obtained by an original patented procedure and doped with 0.5, 1 and 1.5 wt % La to improve the photocatalytic performance. The crystalline structure, surface morphology and specific surface area were investigated by X-ray diffractometer (XRD), scanning electron microscopy (SEM) and single point Brunauer-Emmett-Teller (BET) method. The XRD analysis of the oxide samples illustrates the formation of wurtzite ZnO. Increasing of La concentration results in higher degree crystallinity of the doped ZnO samples. The doped and non-doped ZnO crystallite sizes are in the range of 54÷57nm. Doping with La leads to increase of specific surface area compared to non-doped ZnO. The course of the photocatalytic reaction was followed spectrophotometrically based on the maximum absorbance wavelength of the model pollutant Reactive Black 5 (RB5). The samples doped with 1.5 wt % La exhibited the highest efficiency for the photocatalytic degradation of RB5 under UV illumination due to the higher degree of crystallinity, formation of solid solution and higher specific surface area.

Key words: *La-doped ZnO nanoparticles, photocatalysis, Reactive Black 5 azodye, waste water discoloration*

1. INTRODUCTION

Despite the efforts in last years to modernize the facilities for wastewater treatment, there are still many enterprises (especially in the textile industry), which do not solve this problem and continue to discharge polluted water into the environment. Around 15% of the production of dyes is lost in the process of dyeing and discarded as waste (Weber 1995). Among the numerous photocatalytic materials (mainly semiconducting oxides) that have been applied recently the attention is shifting from TiO_2 to ZnO (Ullah 2008, Sasikala 2010). Although the band gap energy and photodegradation mechanism are similar for the two oxides, some authors reported that the ZnO photocatalyst had superior performance (Houskova 2007). Moreover, ZnO, in contrast toTiO_2, can be synthesized from common inorganic zinc salts. The precipitation is a common method for large scale production, the unsophisticated equipments are required and the morphology can be modified by addition of appropriate surfactants and dopants (Suwanboon 2011). Recently, a number of studies have focused on improving the ZnO properties by doping with metals. There have been some reports on the effects of La-doped ZnO nanoparticles on the photocatalytic activity La doped ZnO. These were prepared through different methods such as precipitation (Suwanboon 2013), co-precipitation (Anandan 2007), mechanochemical activation (Suwanboon 2013), sol–gel method (Suwanboon 2013) and combustion process (Jose 2012). For example the La-doped ZnO nanoparticles prepared by a co-precipitation method showed that the photocatalytic activity increased with an increase in the La content up to 0.8 wt % and then decreased (Anandan 2007). The aim of this paper is to study the influence of lanthanum doping on the structural and the photocatalytic properties of ZnO nanopowders, activated by an original method.

2. MATERIALS AND METHODS

2.1 Synthesis of the samples

Activated ZnO powders were obtained by procedures, described in Bulgarian patent № 28915/1979. The preparation includes dissolution of commercial ZnO in nitric acid, then simultaneous treatment by adding NH_4OH and bubbling CO_2, leading to precipitation of $Zn(OH)CO_3$. The precipitate was then thermally

decomposed at 400°C. After that, the so activated ZnO powder was impregnated with definite quantities of the aqueous solutions of $La(NO_3)_3$, obtained by dissolving of La_2O_3 in nitric acid.

The final samples having dopant content 0.5, 1 and 1.5 wt. % La (with respect to the Zn amount) were denoted as ZL0.5, ZL1 and ZL1.5, respectively. This interval of dopant contents was selected on the basis of the results by Arun 2012, claiming the existence of a limit for La incorporation.

2.2 X-ray diffraction (XRD) analysis

The XRD patterns have been recorded using TUR M62 diffractometer with CoK_α radiation. The observed patterns were cross-matched with those available in the JCPDS database. The particle size was determined by Scherrer's formula.

2.3 Adsorption – texture analysis

The determination of the specific surface area of the samples was carried out by single point BET method involving nitrogen adsorption from N_2/He mixture at the boiling temperature of liquid nitrogen (77.4 K) using a conventional volume measuring apparatus. Before measuring of the surface area the samples were degassed at 423 K (to liberate the surface from adsorbed contaminants) until the residual pressure became lower than $1.333.10^{-2}$ Pa. The nitrogen (N_2) monolayer formed was used to calculate the specific surface area (A_{BET}) using the BET equation.

2.4 Scanning electron microscopy (SEM)

A scanning electron microscope JEOL, model JEM-200CX, scanning adaptor EM-ASID3D, was used to monitor morphology of the obtained surface species.

2.5 Catalytic activity tests

Reactive Black 5 azo dye is commonly used in the textile industry and it can cause serious environmental problems. For this reason we were used the dye as model pollutant. The photocatalytic degree of discoloring of RB5 (Fig. 1) was determined using 150 ml of dye aqueous solution with 20 ppm initial concentration giving pH 7.

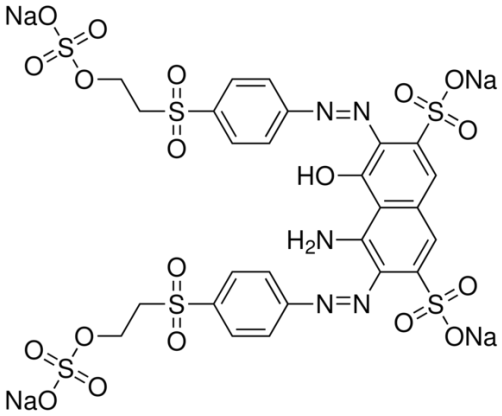


Fig. 1. Structure of textile coloring dye Reactive Black 5 (RB-5)

The photocatalytic activity tests have been carried out using polychromatic UV-lamp (Sylvania BLB, 18 W), with wavelength range 315÷400 nm (λ_{max} = 365 nm). The intensity of illumination upon the sample was 0.66 $mW.cm^{-2}$. The process of discoloring has been monitored by UV-Vis absorbance spectrophotometer BOECO S26 in the wavelength range from 200 to 800 nm. A semi-batch slurry photocatalytic reactor was used feeding continuous air flow. All photocatalytic activity tests have been carried out at a constant stirring rate (400 rpm) under ambient conditions. The samples reach adsorption-desorption equilibrium in the dark within about 30 min before switching on the illumination. To test the photocatalytic activity of ZnO powders, sample aliquots of the suspension have been taken out of the reaction vessel after regular time intervals. The powder was then separated from the aliquot solution by centrifugation before the UV–Vis spectrophotometric measurement of dye concentration. After that, the aliquot solution, together with the photocatalyst powder, were returned back into

the reaction vessel. The degree of discoloration is expressed as –ln (C/Co) (where Co and C are initial concentration before switching on the illumination and residual concentration of the solution after illumination for selected time interval at 599 nm absorbance maximum, corresponding to the peak of the diazo bond (-N=N-).

3. RESULTS AND DISCUSIONS

The X-ray diffraction analysis of the oxide samples (Figure 2) illustrates the formation of wurtzite ZnO phase (JCPDS 36-1451). It can be seen from the figure that the increase in La content results in higher degree of cristallinity of the ZnO samples. Because of the low content (below the threshold of sensitivity) of the used dopants peaks of La are not observed.

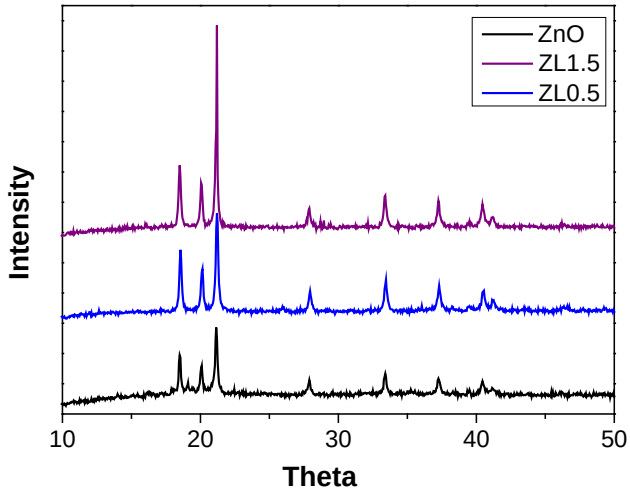


Fig. 2. X-ray diffractograms of non-doped and La doped ZnO samples.

Table 1 shows compositions of the samples, crystallites mean size and specific surface area. Doping with La leads to slight decrease of the crystallite sizes in case of sample ZL1.5 and increase the specific surface area compared to pure ZnO. Figure 3 shows typical SEM image of lanthanum-doped ZnO powder (ZL1.5). The microphotograph illustrates that the size of the particles are in the range 0.5÷10 μm. The presence of pores, formed during nitrate decomposition and nitrogen oxide evolution, is also observable.

Table 1. Sample composition, crystallite size and specific surface area

Sample	Content La, wt %	Crystallites size, nm	A_{BET} , m^2/g
ZnOact	0	57	19
ZL0.5	0.5	56	27
ZL1.5	1.5	54	30

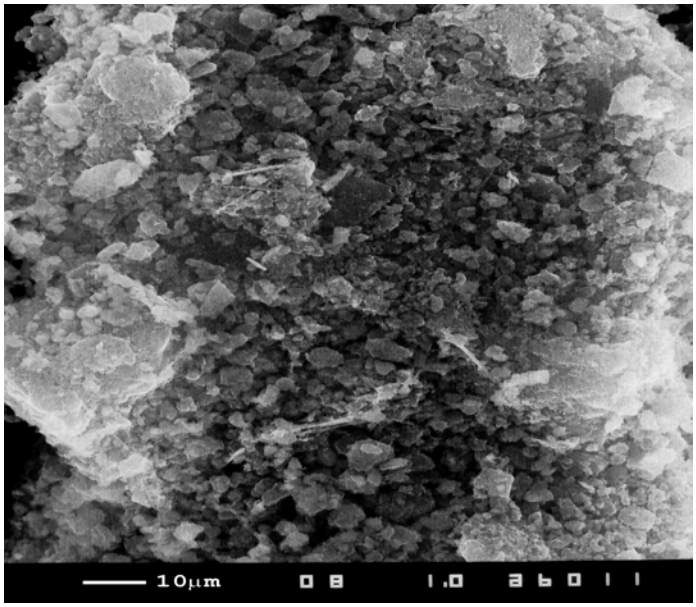


Fig. 3. SEM micrograph of La-doped ZnO

The photocatalytic measurements of the samples showed that pH is an important parameter for the effective discoloration of the Reactive Black 5 (Figure 4). The fastest degradation of the dye was observed in neutral medium (pH =7), while in alkaline medium the process is very slow probably due to dissolution of ZnO in the form of zinc hydroxide and decrease in the suspended quantity of ZnO. On other hand, a noticeable decrease in the rate of degradation under pH 7 is observed. At lower pH factor values below pH 6 there is a tendency of dissolution of ZnO and the effectiveness of the suspension reactor deteriorates again due to decrease in the suspended ZnO amount.

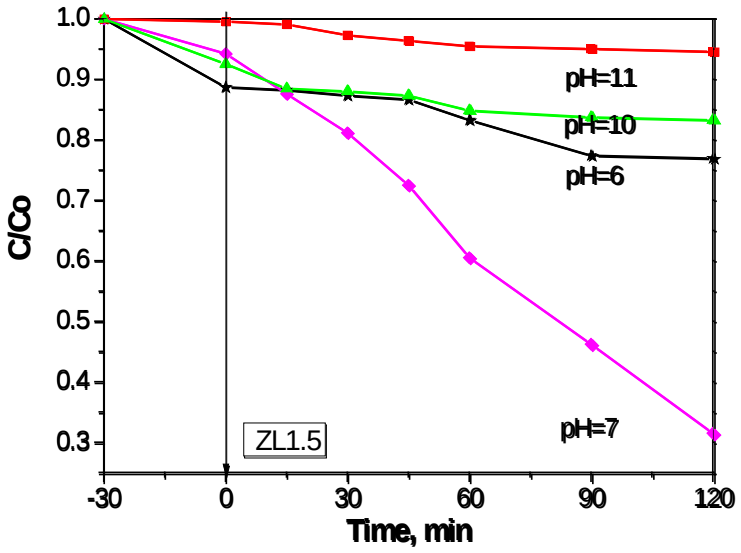


Fig. 4. Concentration changes *vs* pH of the dye solution by La doped ZnO (ZL1.5) nanosized photocatalyst.

Figure 5 shows that the azo dye RB-5 without any catalyst very slowly degraded under UV illumination up to 120 min. In the presence of activated ZnO catalyst the degradation rate increased significantly. The experiment showed that for discoloration of the azo dye RB-5 we need the both UV light and a photocatalyst. The dye

concentration decrease as a result of 30 min adsorption experiment in the dark (before switching on the illumination at moment of time t=0) is also depicted.

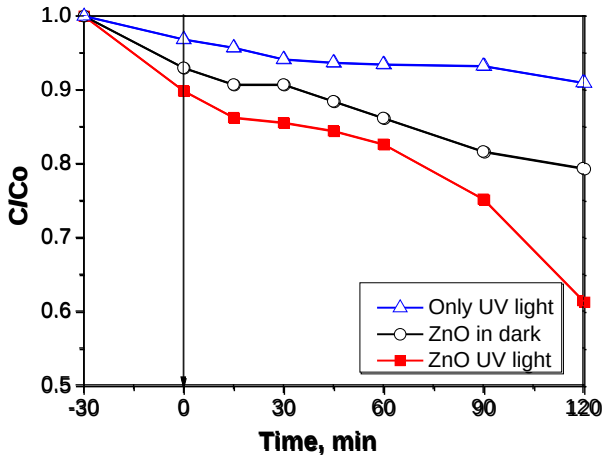


Fig. 5. Course of the RB5 degradation reaction as a function of time of illumination with UV light

Figure 6 compares the performance of the best doped sample 1.5 wt % La (ZL1.5) with that of the non-doped sample in decoloration of RB5 under UV-light illumination. The samples containing 0.5 and 1 wt % La have similar photocatalytic activity comparing with that of non-doped ZnO photocatalyst.

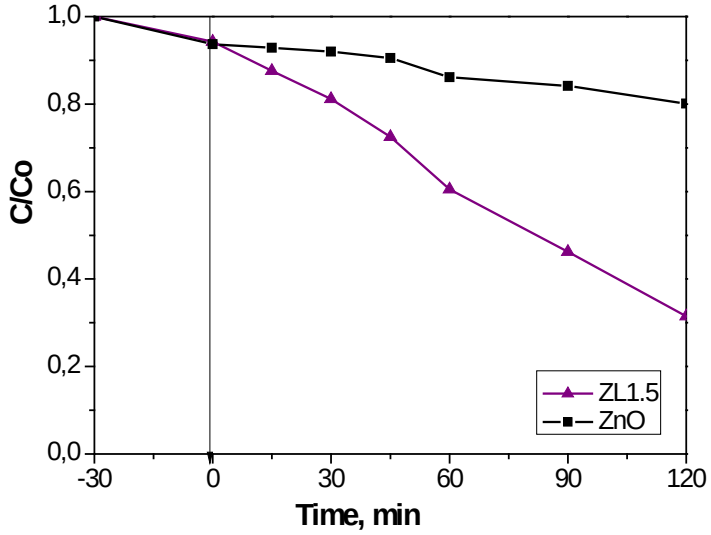


Fig. 6. Concentration changes *vs* time of illumination by non-doped ZnO and ZL1.5 samples.

The degree of conversion has been calculated and it is represented in Figure 7. We can see that after La doping with 1.5wt% of ZnO the activity increase twice for 120 min from 32% to 67% conversion degree.

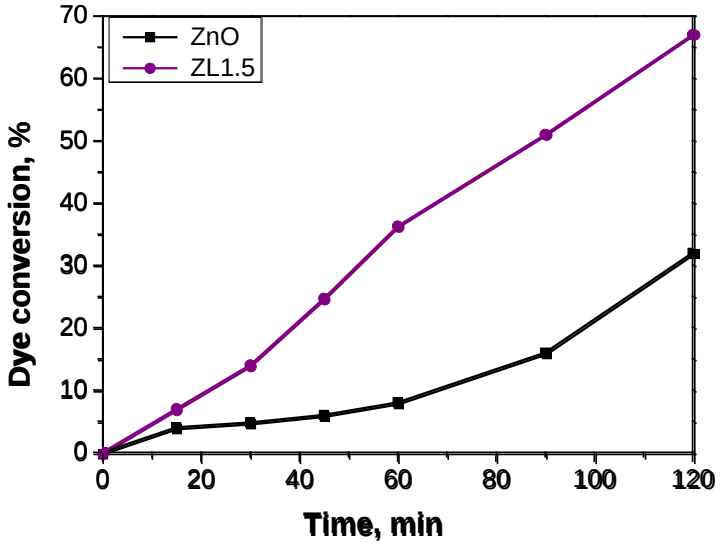


Fig. 7. Degree of conversion as a function of the time of illumination

The increased efficiency of 1.5 wt% La doped (ZL1.5) ZnO can be explained by the following considerations. The degree of crystallinity of the doped samples is increased. It was well known that the photocatalytic activity of the catalysts depends strongly on the degree of crystallinity. The doped samples possess larger specific surface area than the non-doped samples leading to larger number of active sites. The ionic radius of the La^{3+} ion (116 pm) is larger than the ionic radius of the Zn^{2+} ion resulting in the existence of a limiting content of incorporation, observed by the authors of the present article and also by Arun 2012. This is in good agreement with the Hume-Rothery rules as the highly concentrated solid solutions cannot be formed due to the big difference in atomic radii of the La^{3+} and the Zn^{2+} (more than 15%). For this reason, part of the La^{3+} ions at higher content prefer to occupy interstitial positions in the ZnO lattice where they form a complex with the surface oxygen of the ZnO nanoparticles as reported elsewhere (Suwanboon 2013).

4. CONCLUSION

Various content La doped and non-doped ZnO photocatalysts were prepared by an original patented method. The structural properties of the resultant materials were characterized by XRD, SEM, BET methods. Doping with La leads to increase in the degree of crystallinity at somewhat smaller crystallite sizes and increase in the specific surface area compared to non-doped ZnO. The fastest degradation of the model pollutant Reactive Black 5 azodye was observed in neutral medium (pH =7), while in alkaline and acidic media it is very slow. The La doping promotes the photocatalytic behavior due to the higher degree of crystallinity, formation of solid solution and higher specific surface area. Dependence of dye discoloration on the time interval of UV-light illumination for the non-doped ZnO and 1,5% La doped showed that La doped ZnO the activity reaches 67% conversion degree, compared to 32% conversion with the non-doped sample after 120 min of illumination.

ACKNOWLEDGEMENT

Financial support by the European Social Fund within the framework of Operating Program “Development of Human Resources” (BG051PO001-3.3.06-0050) for covering the expenses for participation in Materials, Methods & Technologies, 16th International Conference, Elenite Holiday Village, Bulgaria-2014 is gratefully acknowledged.

This work was supported by BSF Project (No DVU 02 36/10).

REFERENCES

Anandan, S, Vinu, A, Sheeja Lovely, K, Gokulakrishnan, N, Srinivasu, P, Mori, T, Murugesan, V, Sivamurugan, V, Ariga, K 2007, "Photocatalytic activity of La-doped ZnO for the degradation of monocrotophos in aqueous suspension", *J Mol Catal A Chem*, vol. 266 pp. 149–157.

Houskova, V, Stengl, V, Bakardjieva, S, Murafa, N, Kalendova, A, Oplustil F 2007, "Zinc oxide prepared by homogeneous hydrolysis with thioacetamide, its destruction of warfare agent and photocatalytic activity", *J Phys Chem*, vol. 111(20) pp. 4215-4221.

Jose, L, Linet, J, Sivasubramanian,V, Arora, A, Raj, C. , Maiyalagan T, Das S 2012, "Optical studies of nano-structured La-doped ZnO prepared by combustion method", *Mater Sci Semicond Process*, vol.15, pp.308-313.

Sasikala, R, Shirole, A R, Sudarsan, V, Kamble, V S, Sudakar, C, Naik, R, Rao, R, Bharadwaj, S R 2010, "Role of support on the photocatalytic activity of titanium oxide", Appl Catal A Gen, vol. 390, pp. 245–252.

Suwanboon, S, Amornpitoksuk, P, Sukolrat, A 2011, "Dependence of optical properties on doping metal,crystallite size and defect concentration of M-doped ZnO nanopowders (M=Al, Mg,Ti)", *Ceram Int*, vol. 37 pp. 1359–1365.

Suwanboon, S, Amornpitoksuk, P, Sukolrat, A, Muensit, N 2013, "Optical and photocatalytic properties of La-doped ZnO nanoparticles prepared via precipitation and mechanical milling method", *Ceram Int*, vol. 39, pp. 2811-2819.

Suwanboon, S, Amornpitoksuk, P, Bangrak P, Muensit N 2013, "Optical, photocatalytic and bactericidal properties of Zn_{1-x} La_xO and Zn_{1-x} Mg_xO nanostructures prepared by a sol–gel method", *Ceram Int*, vol. 39, pp. 5597–5608.

Ullah R, Dutta J 2008, "Photocatalytic degradation of organic dyes with manganese-doped ZnO nanoparticles", *J Hazard Mater*, vol.156, pp. 194–200.

Weber, E, Adams, R 1995, "Chemical and Sediment Mediated Reduction of the Azo Dye Disperse Blue", *Environ. Sci. Technol*, vol. 29, pp 1163–1170.