

THE EFFECT OF INTRODUCING COPPER DOPANT ON THE PHOTOCATALYTIC ACTIVITY OF ZnO NANOPARTICLES

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ABSTRACT

Copper-doped ZnO nanoparticles have been prepared by the precipitation method. The dopant contents in the samples were 0.24, 0.35 and 1.07 at.%. A set of techniques including XRD, XPS, TG – DTA, EPR and BET analysis has been applied to characterize Cu-doped ZnO samples. The results showed that the crystallite sizes of ZnO and Cu-doped ZnO nanoparticles were within the range of 45 ÷ 49 nm. The dopant exists in the form of isolated Cu²⁺ ions. According to the XPS analysis the copper ions are located mainly on the surface of the ZnO particles. The photocatalytic activity has been tested in the reaction of Reactive Black 5 discoloration under UV irradiation. Among all the investigated samples pure ZnO samples showed the best photocatalytic properties.

Keywords: ZnO, Cu-doped ZnO, photocatalysis, ultraviolet light, azo dye.

INTRODUCTION

ZnO is an inexpensive, n-type semiconductor with a wide band gap having optical transparency in the visible range. It crystallizes in a hexagonal wurtzite structure (zincite) with the following lattice parameters: $c = 5.205 \text{ \AA}$, $a = 3.249 \text{ \AA}$. The n-type semiconductor behavior is due to the ionization of excess zinc atoms in interstitial positions and the oxygen vacancies [1]. Surface defects play an important role in the photocatalytic activities of metal oxides as they increase the number of the active sites [2, 3]. For this reason it is interesting to study the effect of ZnO doping by transition metals on its photocatalytic properties.

Data are reported in the current literature about the influence of copper dopant in ZnO powders and thin films on the photocatalytic behavior [4-6]. Various

techniques for the preparation of ZnO nanopowders have been applied: sol-gel method [4, 7], “soak-deoxidize-air oxidation” [5], co-precipitation method [6, 8] etc. Among the different methods, the co-precipitation appears to be one of the most promising methods to prepare nanopowders. Some of the most important advantages of the precipitation method are: easiness of the synthesis, low temperature of decomposition and control on the chemical composition. These advantages make the precipitation technique a very attractive preparation method, especially in the case of photocatalytically active ZnO powders [6].

The photocatalytic activities of pure and Cu-doped ZnO powders have been evaluated by measuring the degradation of organic dye Methylene Blue [3] and Methyl Orange [4] in aqueous solutions under the UV-light irradiation. The photocatalytic activities of ZnO/

Cu₂O composite material have been evaluated using Methyl Orange in visible light region [5]. The available data about the influence of copper doping on the photocatalytic activity of ZnO are contradictory. It has been found out that the photocatalytic properties of ZnO/Cu₂O composite, compared with pure ZnO, were improved greatly [5]. The photocatalytic activity of pure ZnO is nearly the same as that of CuO/ZnO powders [6]. Donkova et al. have found a decrease in the photocatalytic performance of ZnO powders after doping with Cu in regard to degradation of Methylene Blue dye [9].

During textile colouring large quantities of toxic azo dyes with intensive colour are disposed of as waste waters and they appear respectively in the water-ways. It has been reported that some of the dyes are toxic and carcinogenic [10]. Reactive Black 5 (RB5) azo dye is commonly used in the textile industry and may cause serious environmental problems. Motivated by this fact, we focused this study of ours on copper doped ZnO powders, obtained by precipitation, and on investigation of their photocatalytic behavior towards degradation of textile dye Reactive Black 5.

EXPERIMENTAL

Synthesis of the samples. Undoped and doped with Cu zinc oxide samples have been prepared by precipitation method. Analytical grade of purity zinc sulfate (heptahydrate) ZnSO₄·7H₂O, sodium carbonate Na₂CO₃ and copper sulfate CuSO₄·H₂O were used as starting materials. In a typical experiment we dissolved 90 g of Na₂CO₃ in 850 ml H₂O under heating and continuous stirring (solution 1). An amount of 20 g ZnSO₄·7H₂O was dissolved in 140 ml H₂O under heating and continuous stirring (solution 2). Different calculated quantities of copper sulfate were added to the solution 2 such to obtain mixture of ZnO doped with 0.24, 0.35 and 1.07 at.% Cu. This mixed solution of ZnSO₄·7H₂O and CuSO₄·H₂O was added drop by drop to the solution 1. After adjusting the pH value to 11, the final mixture solution was stirred under heating for 10 minutes. The precipitate was separated by filtration, washed several times with distilled water to pH value 7 and dried in air. For preparation of the final catalyst samples, the corresponding precursors were heated for 3 h at 500 °C in air.

The final samples doped with 0.24, 0.35 and 1.07 at.% Cu were denoted ZC1, ZC2 and ZC3, respectively.

Sample characterization

AAS analysis. The chemical composition of the samples has been determined using Atomic Absorption Analysis on FAAS - SOLAAR M5 spectrometer. For the preparation of standard solutions "Titrisol" standards produced by Merck (Germany) were used, the concentration of reference metal content was 1000 ppm.

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. X-ray photoelectron spectroscopy (XPS).

The X-ray photoelectron spectroscopy (XPS) studies were performed in a VG Escalab II electron spectrometer using AlK_α radiation with energy of 1486.6eV. The residual gas pressure in the analysis high vacuum chamber was 10⁻⁷ Pa.

Electron paramagnetic resonance (EPR). The electron paramagnetic resonance (EPR) spectra have been registered as a first derivative of the absorption signal within the temperature interval of 100 - 400 K using an ERS 220/Q instrument.

The DTA and TG curves have been recorded on a LABSYSTM EVO apparatus SETARAM (France), at heating rates in air (10°/min) from 25°C to 600°C.

Adsorption – texture analysis. The determination of the specific surface areas of the samples was carried out by nitrogen adsorption at the boiling temperature of liquid nitrogen (77.4 K) using a conventional volumetric apparatus. Before the measurement of the surface areas the samples were degassed at 423 K until the residual pressure became lower than 1.333·10⁻² Pa. The nitrogen (N₂) adsorption-desorption isotherms were used to calculate the specific surface areas (A_{BET}) using the BET equation.

Catalytic tests. The photocatalytic degree of discolouring of RB5 was determined using 150 ml of dye aqueous solution with 20 ppm initial concentration. The photocatalytic activity tests have been carried out using polychromatic UV-lamp (Sylvania BLB, 18 W), with wavelength range 315-400 nm. The light power density on the sample position was 0.66 mW·cm⁻². The process of discolouring has been monitored by UV-Vis absorbance spectrophotometer BOECO S26 in the wavelength range from 200 to 800 nm. All photocatalytic activity tests have been carried out at a constant stirring rate (400

Table 1. Specific surface areas, copper concentrations and crystallite sizes of the prepared samples.

Samples	Cu concentrations at.% (wt. %)	A_{BET} [$\text{m}^2 \cdot \text{g}^{-1}$]	Lattice constants a,c (\AA)		Crystallite sizes [nm]
			$a \pm 0.002$	$c \pm 0.002$	
Ref. JCPDS 36-1451	-	-	3.244	5.205	-
ZnO	-	22	3.24946	5.20689	45
ZC1	0.24 (0.18)	23	3.25042	5.20158	46
ZC2	0.35 (0.28)	23	3.25010	5.20385	48
ZC3	1.07 (0.8)	23	3.25014	5.20363	49

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 degradation of the dye was evaluated using the following equation:

$$\text{Decoloration} = 100 \times \left[\frac{C_0 - C}{C_0} \right] \quad [\%] \quad (1)$$

The degree of decoloration is expressed as C/C_0 (where C_0 and C are initial absorbance before switching on the illumination on and absorbance of the solution after 120 minutes of illumination, respectively at 599 nm corresponding to the peak of the diazo bond ($-\text{N}=\text{N}-$).

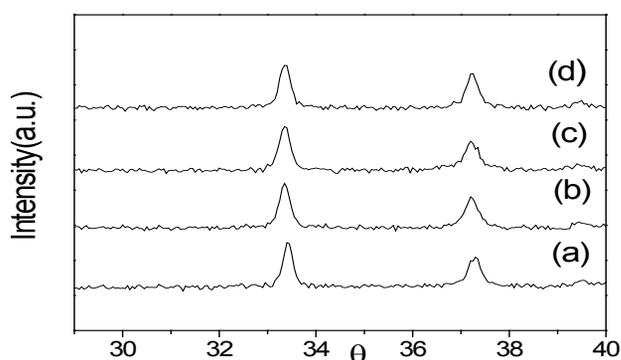


Fig. 1. XRD spectra of: (a) ZnO; (b) ZC1; (c) ZC2; (d) ZC3.

RESULTS AND DISCUSSION

The X-ray diffraction analyses of the samples (Fig. 1) give evidence for the formation of wurtzite phase ZnO (JCPDS 36-1451). The copper dopant concentrations in samples are 0.24, 0.35 and 1.07 at. % (Table 1). According to Fernandes et al. [7] the ideal maximal Cu^{2+} concentration to obtain well-crystallized ZnO phase is less than 1 wt.%, while according to Fu et al. [4] the optimal doping concentration has been found to be 0.5 wt.%.

The lattice parameters of the undoped ZnO crystal are very close to those obtained for zincite structure (JCPDS 36-1451). The introduction of Cu into the ZnO samples leads to shrinking of the unit cell (Table 1). A similar results for Cu doped powders and films has been obtained by Belini and Bahsi [1, 11]. It is well known that in Cu doped ZnO, the Cu^{2+} ions (atomic radii 0,057nm) substitute the Zn^{2+} ions (atomic radii 0,060 nm) (see Table 1). The diffusion process during the sintering may lead to defect formation, in which Cu^{2+} ions substitute

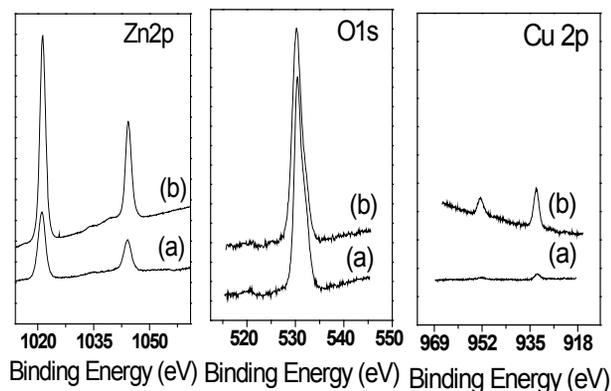
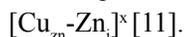


Fig. 2. XPS spectra of Zn 2p, O 1s and Cu 2p core levels for samples: (a) ZC1; (b) ZC2.

Table 2. Surface compositions of the Cu/ZnO samples, determined by XPS analyses.

Samples	O1s, at. %	Zn2p, at. %	Cu2p, at. %
ZC1 (0.24 at.% Cu)	53.59	45.33	1.08
ZC2 (0.35 at.% Cu)	63.64	35.24	1.12

Zn²⁺ cations in the wurtzite unit cell of ZnO and appearance of complex defects:



The compositions and the specific surface areas (A_{BET}) of the pure and the Cu-doped zinc oxide samples are represented in Table 1. It shows that the specific surface areas of all the samples do not differ significantly. The calculated mean size of the crystallites, determined by XRD, was within the range of $45 \div 49$ nm. Compared with the pure ZnO, Cu doping in ZnO samples results in a little increase in the ZnO crystallite size.

The surface composition and chemical state of the Cu doped ZnO powders have been investigated by XPS. Figure 2 shows the Zn 2p, O1s and Cu2p photoelectron spectra. The Zn 2p_{3/2} signals of ZnO for both samples are similar and have a maximum at 1021.7 eV, typical of ZnO. The O1s peaks are located at 530.3 eV – they are attributed to O²⁻ ions in ZnO crystal lattice. Table 2 shows the surface chemical composition of the ZC1 and ZC2 samples. It can be seen in the table that zinc-copper ratios are much higher than that in the initial composition. This is an indication of segregation of the doping element on the surface of the ZnO particles. This result is in accordance with the studies of Bellini et al. [11]. Figure 3 represents the EPR spectrum of the Cu/ZnO (ZC1) catalyst sample. The analysis confirms the presence of isolated Cu²⁺ ions [12, 13].

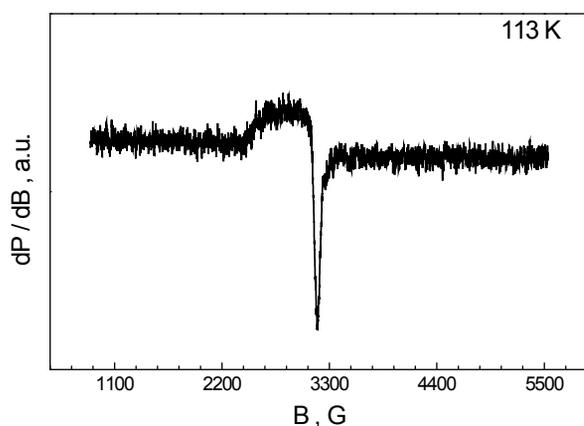


Fig. 3. EPR spectrum of sample ZC1.

A strong endothermic peak due to the zinc hydroxide precursor decomposition has been registered on the DTA curve (Fig. 4). The precursor decomposition begins at 230°C and it is completed at 270°C.

The degrees of discolouring of the dye solution in the cases of undoped and Cu doped ZnO catalysts after 120 minutes of irradiation are shown in Fig. 5. As it can be seen for catalyst charge amount of 0.08 g, the decrease of the Cu content leads to enhancement of the photocatalytic activity. Similar behavior has been registered with 0.3 g catalyst amount. The ZnO samples (0.3 g) exhibit higher activities than those of the samples containing 0.08 g catalyst. Among all the investigated samples the pure ZnO samples showed the best photocatalytic properties (Figs. 5 and 6). Liu et al. [6] reported that the

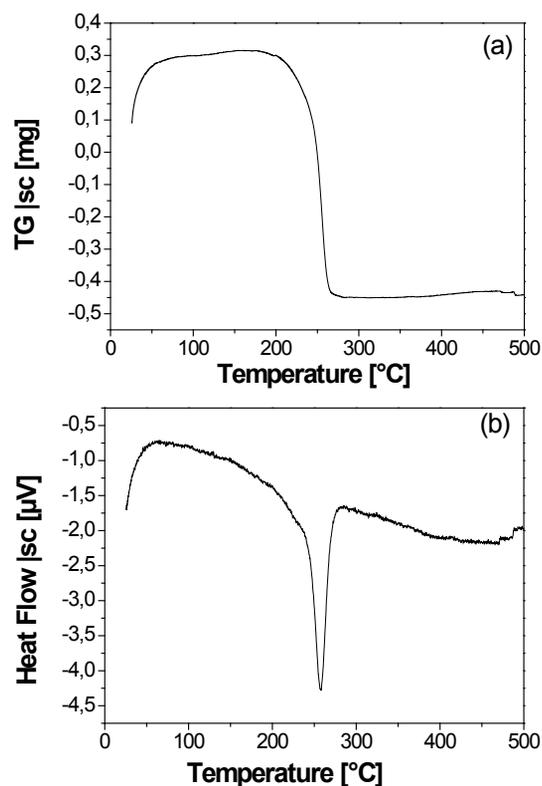


Fig. 4. DTA of zinc carbonate dried at 120°C (a) and TG curve (b).

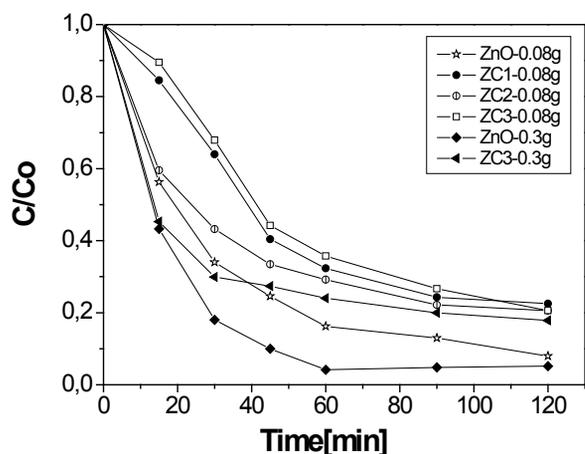


Fig. 5. Degree of decoloration of the RB5 dye (concentration 20 ppm), based on changes in the intensity of the peak, corresponding to azo bond ($-N=N-$) with the course of time.

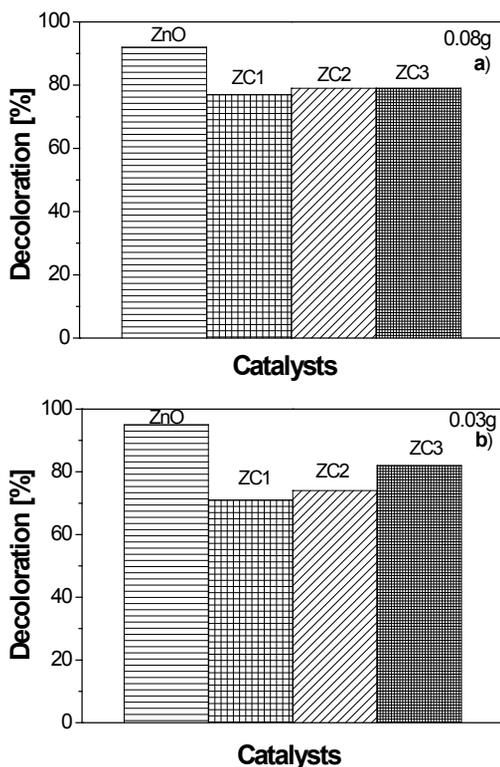


Fig. 6. Degree of decoloration of the dye after 120 minutes of illumination using ZnO, ZC1; ZC2; ZC3; and UV light photocatalyst content (a) 0.08 g and (b) 0.3 g.

photocatalytic degree of degradation of Methyl Orange on pure ZnO has nearly the same value as that of CuO/ZnO, calcined at 450° C. Donkova et al. [9] have also found a decrease in the photocatalytic conversion degree on ZnO powder samples after doping them with Cu in

the reaction of Methylene Blue dye degradation because of increased charge carriers recombination rate.

It is also possible that the absorption capacity of the Cu-doped samples decreases upon increasing the Cu contents, which is in accordance with the results, obtained by Muthukumaran et al. [8].

CONCLUSIONS

Copper doped (0.24÷1.07 at.%) ZnO wurtzite nanoparticles, prepared by the precipitation method, have been tested in the reaction of Reactive Black 5 decoloration under UV irradiation. The average sizes of the crystallites of doped and undoped ZnO are below 49 nm. The XRD results proved that the increase in copper concentration causes a slight decrease in the degree of crystallinity. TG-DTA data for zinc hydroxide precursor registered strong endothermic peak at 250°C. The EPR spectra registered isolated Cu^{2+} ions. The XPS analysis showed that zinc-copper ratios are much higher than those in the experimentally evaluated compositions of the samples. This result is an indication that segregation of doping element is occurring on the surface of the ZnO particles. The decrease in the Cu content in ZnO samples leads to enhancement of their photocatalytic activities. The pure ZnO samples exhibit the best photocatalytic properties.

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