

## Copper doped zinc oxide nanopowders used for degradation of residual azo dyes in wastewaters

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The influence of copper doping (1.5 wt%) on the structural and on the photocatalytic properties of two different types of ZnO nanopowders (commercial one and ZnO activated by an original patented procedure) was studied. The crystallite size and the oxidation state of the dopant were investigated respectively by X-ray diffractometer (XRD), Electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS) methods. The EPR spectra registered isolated Cu<sup>2+</sup> ions in both samples. The photocatalytic efficiency of the prepared nanosized samples was examined in the reaction of oxidative degradation of Reactive Black 5 (RB5) dye under UV light. Examined powders have shown significant degree of degradation of the investigated textile dye pollutant, the maximum value of the rate constant ( $35.9 \times 10^{-3} \text{ min}^{-1}$ ) was obtained for the activated Cu/ZnO. The higher photodegradation activity for Reactive Black 5 of the activated Cu/ZnO sample (99.5%) than that of the commercial copper doped ZnO (98.0%) could be explained by the presence of a second phase of CuO clusters in the former. The present research study established that activated copper-doped ZnO can be used as an effective photocatalyst for the removal of azo dyes in wastewaters.

**Key words:** Cu-doping, ZnO, photocatalytic activity, azo dye pollutant.

### INTRODUCTION

During the last decade, photocatalysts have been developed and applied to the removal of dyes from industrial effluents [1, 2]. One of the most efficient ways of reducing contaminations of water is by photocatalytic treatment [3]. The intrinsic defects of ZnO are beneficial for setting up catalytic systems and also changes of surface properties such as surface defects [4]. The photocatalytic activity of ZnO can be improved by control of the designed shape [5], incorporating another atom into the lattice [6, 7], increase of surface area [8] and so on. Transition metal doped ZnO is attracting the attention of most researchers. The efficiency of the dopant element to the changes of electrical properties depends on its ionic radius and it is also strongly influenced by the synthesis method. Recent inves-

tigations on Cu doped ZnO have reported that Cu exists in 2+ oxidation state in the host lattice [9, 10]. The substitution of Cu into the ZnO lattice improves the photocatalytic activity [11]. Cu-doped ZnO nanopowders have been synthesized by sonochemical method [12, 13], sol-gel method [14], hydrothermal method [15, 16], vapor transport method [17], solution combustion method [18] and co-precipitation method [19, 20]. Photocatalytic activities of copper doped zinc oxides have been investigated by the degradation of Methylene Blue dye [14], resazurin dye [17], Methyl Orange [20, 21].

In the present work copper-doped ZnO samples were prepared by modified deposition method. Two types of ZnO samples were used: ZnO powders activated by an original procedure and commercial – delivered by Chemapol, doped with 1.5 wt.% Cu. The aim was to investigate the influence of copper doping on the structural and on the photocatalytic properties of ZnO nanopowders toward degradation of textile azo dye Reactive Black 5 (RB5) under UV light.

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## EXPERIMENTAL

Two types of Cu/ZnO samples were prepared: commercial – delivered by Chemapol and Cu/ZnO powders activated by an original patented procedure, described in [22]. The preparation includes dissolution of the technical purity grade ZnO in  $\text{NH}_4\text{OH}$ , then simultaneous treatment by adding  $\text{NH}_4\text{OH}$  and bubbling  $\text{CO}_2$ , leading to precipitation of  $(\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2)$ . Then it is filtered, washed and dried at  $90^\circ\text{C}$ . Both the so activated zinc hydroxide carbonate precursor and the commercial ZnO were impregnated with definite quantities of the aqueous solutions of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . The concentration of metal dopant was so calculated as to give 1.5 wt.% Cu (with respect to the Zn amount). These suspensions were stirred continuously at temperature  $70^\circ\text{C}$  under reflux for a short period of time. After that was dried at  $100^\circ\text{C}$  for 6 h. Finally, the resulted powder was calcinated for 3 h at  $350^\circ\text{C}$  in air. The so prepared samples were denoted as Cu/ZnO commercial and Cu/ZnO activated.

The phase composition of the samples was studied by X-ray diffraction (XRD) with  $\text{CuK}_\alpha$ -radiation (Philips PW 1050). The crystallite size was estimated from the XRD spectra, according to Scherrer's equation.

The EPR spectra were recorded on JEOL JES-FA 100 EPR spectrometer operating in the X-band with standard  $\text{TE}_{011}$  cylindrical resonator at room temperature. The sample was put in special EPR cuvette and was positioned in the center of the EPR cavity.

The X-ray photoelectron spectroscopy (XPS) studies were performed on a VG Escalab II electron spectrometer using  $\text{AlK}\alpha$  radiation with binding energy (BE) of 1486.6 eV under base pressure  $10^{-7}$  Pa and a total instrumental resolution 1 eV. The BE values were determined utilizing the C1s line (from an adventitious carbon) as a reference with energy of 285.0 eV. The accuracy of the measured BE value was 0.2 eV. The C1s, Zn2p, O1s and Cu2p photoelectron lines were recorded and corrected by subtracting a Shirley-type of background and quantified using the peak area and Scofield's photoionization cross-sections.

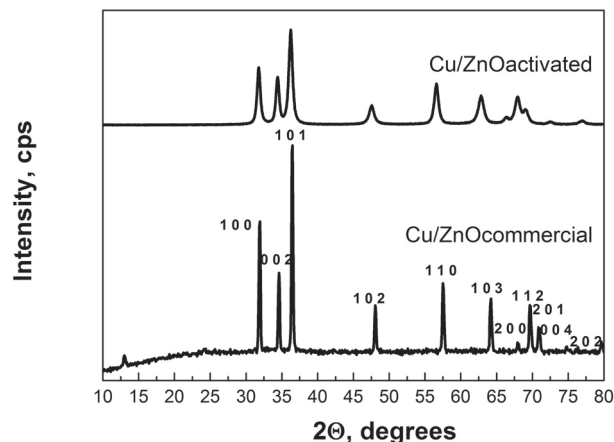
The photocatalytic activities of the prepared nanosized samples were measured in the reaction of photocatalytic oxidative degradation of Reactive Black 5 (RB5) dye in slurry semi-batch reactor under UV light. The photocatalytic studies were performed using UV-Vis absorbance spectrophotometer in the wavelength range from 200 to 800 nm and a polychromatic UV-A lamp illumination (18W) with maximum of the emission at 365 nm and intensity of illumination was  $0.66 \text{ mW}\cdot\text{cm}^{-2}$ . The initial concentration of the used RB5 dye so-

lution was 20 ppm. The investigated systems were equilibrated in the dark period about 30 min before UV irradiation.

## RESULTS AND DISCUSSION

The XRD patterns of both Cu doped ZnO samples – the ZnO activated by an original patented procedure and the commercial one are shown in Figure 1. The X-ray diffraction analysis revealed the formation of hexagonal wurtzite ZnO phase (JCPDS 36-1451). There is no indication of peaks of CuO phase, because of the low content of used dopant. CuO/ZnO commercial sample showed higher degree of crystallinity than the CuO/ZnO activated powder. The crystallites size of the CuO-doped ZnO samples and unit cell parameter (a) and (c) of ZnO phase are represented in Table 1. The CuO/ZnO activated samples show drastic decrease in crystallites size, compared to the commercial CuO/ZnO sample.

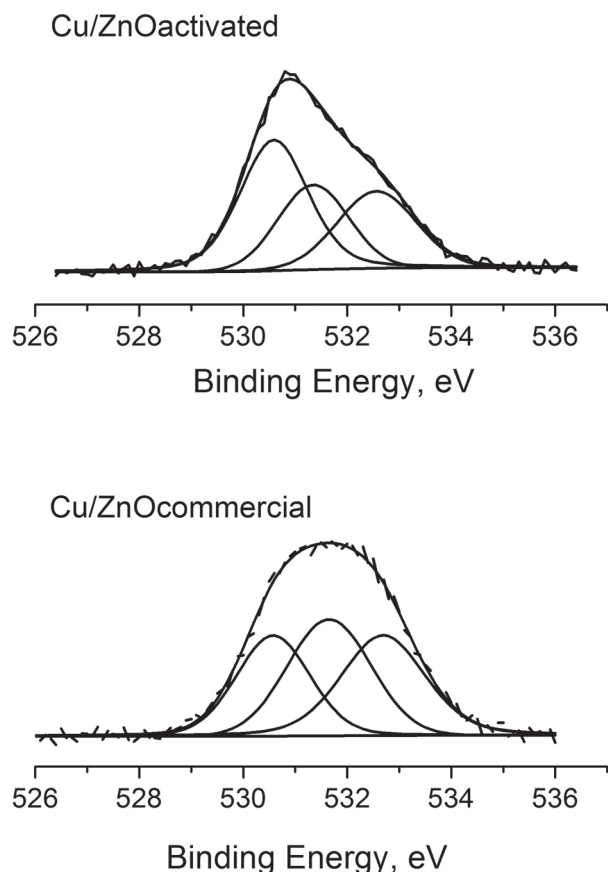
The EPR spectra of the Cu/ZnO commercial sample and the Cu/ZnO activated sample at room temperature are presented in Figure 2. Hyperfine



**Fig. 1.** XRD patterns of: Cu/ZnO activated and Cu/ZnO commercial photocatalyst samples

**Table 1.** Calculated values of mean crystallite size (D), and unit cell parameter (a) and (c) of ZnO phase

Sample	D, nm	a, Å	c, Å
Ref. JCPDS 36-1451	–	3.2440	5.2050
Cu/ZnO activated	16	3.2519	5.2103
Cu/ZnO commercial	40	3.2174	5.1550



**Fig. 2.** EPR spectra of: Cu/ZnO activated and Cu/ZnO commercial photocatalysts

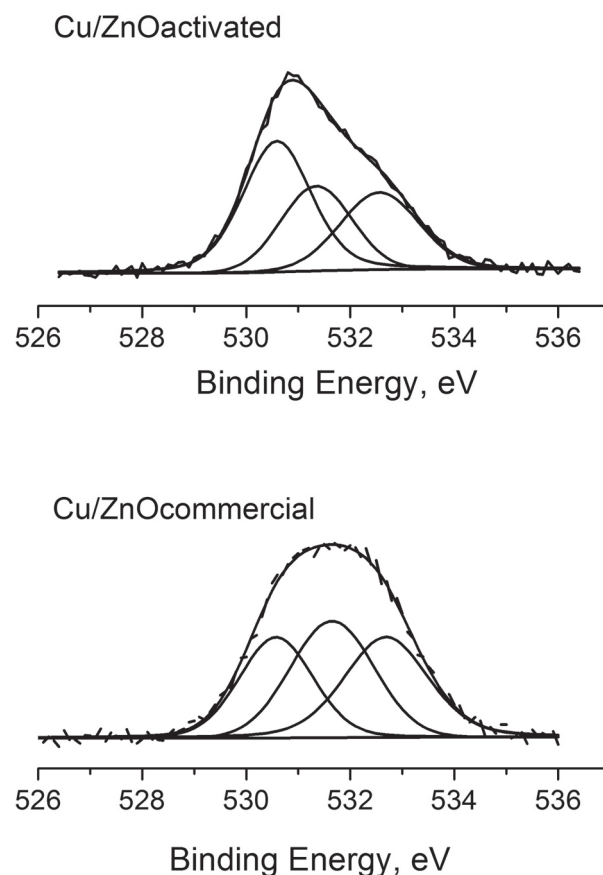
structure due to  $I=3/2$  of  $\text{Cu}^{2+}$  ion in parallel components can be seen in both spectra.

There is an EPR line with  $g_{\parallel} = 2.3845$  и  $g_{\perp} = 2.0959$  observed in the spectrum of commercial Cu/ZnO sample. The resolved hyperfine structure in parallel region suggests the presence of isolated octahedrally coordinated  $\text{Cu}^{2+}$  ions [23, 24].

In the spectra corresponding to activated Cu/ZnO there are at least two different  $\text{Cu}^{2+}$  species with the values for parallel components  $g_{\parallel} = 2.3845$  и  $g_{\parallel} = 2.3262$ , both having  $A_{\parallel} \approx 12$  mT hyperfine splitting. The value for the normal component of g-tensor is found to be  $g_{\perp} = 2.0959$  and it is not resolved for the two  $\text{Cu}^{2+}$  ions present in the catalyst. The component having resonance parameters  $g_{\parallel} = 2.3845$  и  $g_{\perp} = 2.0959$  can be assigned to  $\text{Cu}^{2+}$  ions substituting the  $\text{Zn}^{2+}$  cations in the ZnO crystal lattice. The interchangeable substitution is possible due to similar ionic radii. These g values of the copper species have been interpreted as existence of  $\text{Cu}^{2+}$  occupying sites vacated by lattice  $\text{Zn}^{2+}$  ions [25]. The other component with parameters  $g_{\parallel} = 2.3262$  и  $g_{\perp} = 2.0959$  have more poorly defined hyperfine splitting and corresponds to the  $\text{Cu}^{2+}$  ions in CuO clusters

[26]. This is probably due to increasing of dipolar interaction between  $\text{Cu}^{2+}$  ions. In conclusion in both cases the values of  $g_{\parallel}$  и  $g_{\perp}$  satisfy the relation  $g_{\parallel} > g_{\perp} > g_e = 2.0023$  ( $g_e$  represents the g factor for a free electron) indicating that the  $\text{Cu}^{2+}$  ions are coordinated by six ligand atoms in an axially distorted octahedron [24].

Figure 3 shows the O1s core level spectra of CuO/ZnO activated as well as CuO/ZnO commercial catalysts. Both spectra are completely different, which is an indication of the different oxygen bonds existing on their surfaces. The spectra were subjected to the fitting procedure, which allows making a detailed analysis of the influence of the activation process over ZnO support and further deposition of the active copper phase. The first oxygen component at 530.0 eV corresponds to oxygen bonded to Zn atom in the ZnO lattice. The second ( $\sim 531.5$  eV) and third ( $\sim 532.5$  eV) components belonged to the oxygen vacancies and to adsorbed oxygen, OH- groups or dissociated oxygen, respectively on the surface of the catalysts. The relative intensity of the second component is proportional to the oxygen vacancies concentrations [27]. The



**Fig. 3.** XPS spectra of: Cu/ZnO activated and Cu/ZnO commercial photocatalysts

relative percentage of the component associated to the oxygen vacancies within ZnO matrix for the studied CuO/ZnO activated and CuO/ZnO commercial catalysts are 27% and 36% of the total oxygen, respectively. Nevertheless the calculated percentage of third type of oxygen present on the surface is the same as that associated with oxygen vacancies for both catalysts. The simultaneous formation of the oxygen vacancies and chemisorbed oxygen is observed and this did not depend of the way of preparation of catalysts. Even so the quantity of the formed defects on the surface of the Cu/ZnO commercial catalyst is more than for the catalyst synthesized by us. The  $\text{Cu}^{2+}$  chemical states of copper were estimated from the Cu2p core level for both investigated catalysts.

Figure 4 presents concentration changes, degradation degree and dependence of  $-\ln(C/C_0)$  with time of UV light illumination of the solution of Reactive Black 5 on two examined catalysts. The sample CuO/ZnO activated exhibits stronger absorption capacity towards RB dye and only after 30 minutes interval in the dark, the concentration of the dye drops down with almost 80%. In the case of CuO/ZnO commercial the adsorption is weaker and after switching on the UV lamp the photocatalytic degradation is initiated. The possible explanation of this could be the fact that the activated sample has higher content of CuO clusters. The photocatalytic efficiencies of both CuO/ZnO activated and Cu/ZnO commercial photocatalysts are almost similar and really high reaching 99.5% on CuO/ZnO activated. Rate constants were calculated using the equation  $-\ln(C/C_0) = kt$  on the basis of the slope of the linear logarithmic function. This photodegradation on

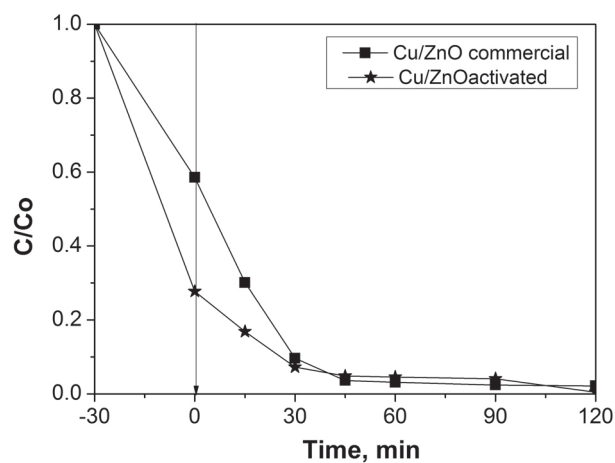


Fig. 4. Dye solution concentration decrease in the course of time of illumination by Cu/ZnO activated and Cu/ZnO commercial photocatalysts

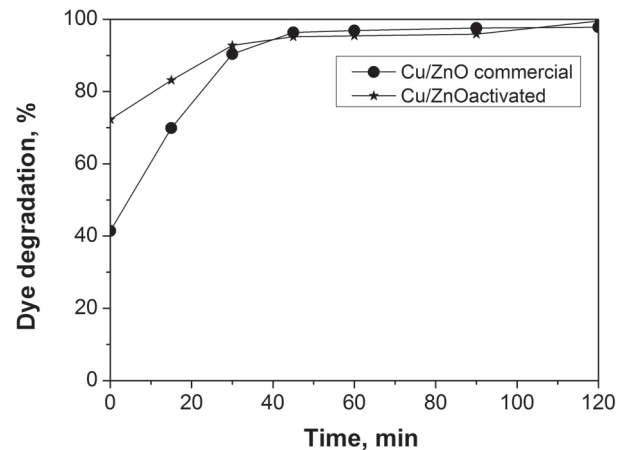


Fig. 5. Oxidative conversion degrees over Cu/ZnO activated and Cu/ZnO commercial photocatalysts

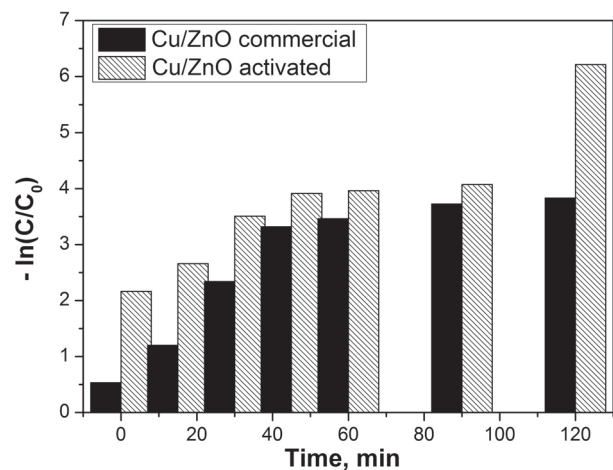


Fig. 6. Dependence of  $-\ln(C/C_0)$  on the time of illumination over Cu/ZnO activated and Cu/ZnO commercial photocatalysts

CuO/ZnO powders followed the pseudo-first-order reaction kinetics. Rate constants for two compared catalysts CuO/ZnO commercial and CuO/ZnO activated are:  $35.0 \times 10^{-3} \text{ min}^{-1}$  and  $35.9 \times 10^{-3} \text{ min}^{-1}$  respectively.

It is known from literature that, various behaviors of ZnO are due to the presence of native defects, such as oxygen vacancies and zinc vacancies. With EPR measurements are confirmed defect structures due to presence of  $\text{Cu}^{2+}$  ion in the ZnO crystal lattice [18, 28]. The increased photocatalytic activity of Cu-doped ZnO is attributed to intrinsic oxygen vacancies due to high surface to volume ratio in nanoparticles and extrinsic defect due to Cu doping [17].



## CONCLUSIONS

The influence of copper doping on the structural and on the photocatalytic properties of ZnO nanopowders was studied. Copper-doped ZnO samples with dopant content of 1.5 wt% were prepared by modified deposition method. Two types of ZnO samples were used – commercial one and ZnO activated by an original patented procedure. The EPR spectra registered two types of Cu<sup>2+</sup> ions: isolated Cu<sup>2+</sup> (both in commercial Cu/ZnO and ZnO activated) and Cu<sup>2+</sup> ions in CuO clusters (ZnO activated). The photocatalytic efficiencies of the prepared nanosized samples were tested in the photocatalytic oxidation of Reactive Black 5 (RB5) dye under UV light illumination. Examined powders have shown significant degree of degradation of the investigated textile dye pollutant, the maximum value of the rate constant ( $35.9 \times 10^{-3} \text{ min}^{-1}$ ) was obtained for the activated CuO/ZnO. The photodegradation conversion for Reactive Black 5 of activated CuO/ZnO is 99.5% and 98.0% for commercial copper doped ZnO. The possible explanation of this difference could be the fact that the activated sample has an additional phase of CuO clusters and smaller ZnO crystallite size. The present research study established that activated copper-doped ZnO can be used as an effective photocatalyst for the removal of azo dyes in wastewaters.

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## REFERENCES

1. J. Yun, D. Jin, Y.S. Lee, H.I. Kim, *Mater. Lett.*, **64**, 2431 (2010).
2. S. Gelover, P. Mondragón, A. Jiménez, *J. Photochem. Photobiol. Chem.*, **165**, 241 (2004).
3. M. Hoffmann, S. Martin, W. Choi, D. Bahnemann, *Chem. Rev.*, **95**, 69 (1995).
4. R. Mohan, K. Krishnamoorthy, S-J. Kim., *Solid State Comm.*, **152**, 375 (2012).
5. L. Yang, S. Dong, J. Sun, J. Feng, Q. Wu, S. Sun, *J. Hazard. Mater.*, **179**, 438 (2010).
6. J. Sun, S. Dong, J. Feng, X. Yin, X. Zhao, *J. Mol. Catal. Chem.*, **335**, 145 (2011).
7. J. Kong, A. Li, X. Li, H. Zhai, W. Zhang, Y. Gong, H. Li, D. Wu, *J. Solid State Chem.*, **183**, 1359 (2010).
8. W. Chiu, P. Khiew, M. Cloke, D. Isa, T. Tan, S. Radiman, R. Abd-Shukor, M. Hamid, N. Huang, H. Lim, C. Chia, *Chem. Eng. J.*, **158**, 345 (2010).
9. T. Heng, S. Lau, S. Yu, J. Chen, K. Teng, *J. Magn. Magn. Mater.*, **315**, 107 (2007).
10. C. Chien, S. Chiou, G. Gao, Y. Yao, *J. Magn. Magn. Mater.*, **282**, 275 (2004).
11. Y. Sonawane, K. Kanade, B. Kale, R. Aiyer, *Mater. Res. Bull.*, **43**, 2719 (2008).
12. B. Babu, T. Aswani, G. T. Rao, R. J. Stella, B. Jayaraja, R. V. Ravikumar, *J. Magn. Magn. Mater.*, **355**, 76 (2014).
13. D. Sahu, N. Panda, B. Acharya, A. Panda, *Ceram. Int.*, **140**, 11041 (2014).
14. P. Jongnavakit, P. Amornpitoksuk, S. Suwanboon, N. Ndiege, *Appl. Surf. Sci.*, **258**, 8192 (2012).
15. J. Huang, Y. Dai, C. Gu, Y. Sun, J. Liu, *J. Alloy. Comp.*, **575**, 115 (2013).
16. S. Lam, J. Sin, A. Abdullah, A. Mohamed, *Separ. Purif. Tech.*, **132**, 378 (2014).
17. R. Mohan, K. Krishnamoorthy, S-J. Kim, *Solid State Comm.*, **152**, 375 (2012).
18. A. Reddy, M. Kokila, H. Nagabhushana, R. Chakradhar, C. Shivakumara, J. Rao, B. Nagabhushana, *J. Alloy. Comp.*, **509**, 5349 (2011).
19. M. Ashokkumar, S. Muthukumar, *Opt. Mater.*, **37**, 671 (2014).
20. Z. Liu, J. Deng, J. Deng, F. Li, *Mater. Sci. Eng. B*, **150**, 99 (2008).
21. M. Ahmad, E. Ahmed, Z. Hong, X. Jiao, T. Abbas, N. R. Khalid, *Appl. Surf. Sci.*, **285P**, 702 (2013).
22. D. Shishkov, C. Velinova, N. Kassabova, C. Canov, D. Ivanov, D Klissurski, V Iordanova, I. Uzunov, Bulgarian Patent 28915/1980, C I: C 01 G 9/02, 1980.
23. P. Ratnasamy, D. Srinivas, C. V. V. Satyanarayana, P. Manikandan, R. Senthil Kumaran, M. Sachin, *J. Catal.*, **221**, 455 (2004).
24. G. Li, N. M. Dimitrijevic, L. Chen, T. Rajh, K. A. Gray, *J. Phys. Chem. C*, **112**, 19040 (2008).
25. N. C. Giles, N. Y. Garces, L. Wang, L. E. Halliburton, in: Quantum Sensing and Nanophotonic Devices (Proc. of SPIE, Bellingham, WA, 2004), Manijeh Razeghi, Gail J. Brown (eds.), Bellingham, 267, 2004, p. 5359.
26. I. Ardelean, M. Peteanu, R. Ciceo-Lucacel, I. Bratu, *J. Mater. Sci. Mater. Electron.*, **11**, 11 (2000).
27. S.-M. Park, T. Ikegami, K. Ebihara, *Thin Solid Films*, **513**, 90 (2006).
28. Y. Mei, W.-C. Zheng, L. Zhang, *Opt. Mater.*, **36**, 535 (2013).

ЦИНКОВО ОКСИДНИ ПРАХОВЕ, ДОТИРАНИ С Cu,  
ИЗПОЛЗВАНИ ЗА РАЗЛАГАНЕ НА ОСТАТЪЧНИ  
АЗОБАГРИЛА В ОТПАДНИ ВОДИ

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(Резюме)

Изучено е влиянието на дотирането с мед (1.5 wt%) върху структурните и фотокаталитични свойства на два различни вида ZnO нанопрахове (търговски и ZnO, активиран чрез оригинална патентована процедура). Размерът на кристалитите и степента на окисление на допанта бяха изследвани съответно с рентгенофазов анализ (XRD), електронен парамагнитен резонанс (EPR) и рентгенова фотоелектронна спектроскопия (XPS). От EPR спектрите са регистрирани изолирани Cu<sup>2+</sup> йони и в двете проби. Фотокаталитичната ефективност на получените наноразмерни проби е изследвана за окислително разграждане на багрилото – Реактивно Черно 5 (RB5), под действието на ултравиолетова светлина. Изследваните прахове показаха значителна степен на разграждане на изследвания замърсител (текстилно багрило), като максимална стойност на скоростната константа ( $35.9 \times 10^{-3} \text{ min}^{-1}$ ) е получена за активирания Cu/ZnO. По-високата активност за фоторазграждане на Реактивно Черно 5 за проба – активиран Cu/ZnO (99.5%), от тази на мед, дотиран търговски ZnO (98.0%), може да бъде обяснена с наличието на CuO клъстери в първия. Настоящото научно изследване установи, че активираният Cu/ZnO може да се използва като ефективен фотокатализатор за отстраняване на азобагрила в отпадни води.