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DOPING SILVER TO ACTIVATED ZnO TO PROMOTE THE PHOTOCATALYTIC EFFICIENCY FOR AZO DYE DEGRADATION

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Abstract

Various silver doped ZnO activated powders were prepared through an original method of activation. The samples were characterized using XRD analysis, single point BET method, scanning electron microscopy (SEM). The photocatalytic properties of the samples were tested in the reaction of Reactive Black 5 azo dye (model waste water contaminant) oxidative discoloration in a semi-batch reactor. The silver doped samples have higher degree of cristallinity in comparison to the undoped sample and superior photocatalytic performance under UV-A light illumination. Another factor promoting the photocatalytic properties is the increase of the dopant content decreasing the ZnO particle mean size and increasing the specific surface area of the doped samples. The role of silver nanoparticles is to serve as traps for the photoexcited electrons thus preventing recombination and increasing the lifetime of the positively charged holes, acting as oxidation active sites.

Key words: *zinc oxide, silver doping, photocatalytic activity, azo dye pollutant*

1. INTRODUCTION

Nowadays, the uncontrolled release of colored waste water contaminated with dyes from textile, paper, rubber and plastic industries have led to serious environmental contamination (Pekakis 2006). The azo dyes constitute the largest and the most important class of commercial dyes and are toxic or carcinogenic (Constapel 2009). Currently available water treatment technologies are: adsorption, coagulation, sedimentation, filtration, chemical and membrane technologies (Chong 2010). Recent studies have shown that heterogeneous semiconductor photocatalysis can be an alternative to conventional methods for the removal of dye pollutants from water (Kyung 2005). There are a number of semiconductors that could be used as photocatalysts, such as TiO_2, ZnO, WO_3, Fe_2O_3 etc. Among them, ZnO attracts the attention of the researchers because it is nontoxic, biocompatible and low cost photocatalyst. In some cases, zinc oxide shows higher photocatalytic efficiency than TiO_2 (Baruah 2010).

The modification of ZnO with noble metals (Ag, Au, Pt, Pd etc.) is found to be effective way for preparation of highly active photocatalysts (Hermann 1997, Kamat 2002). Incorporating silver in ZnO is now an exciting area in research for developing electronic applications. Ag- doped zinc oxide and Ag-N co-doped zinc oxide photocatalysts showed higher photocatalytic activity for degradation of methyl red (MR) dye compared to pure zinc oxide both under UV irradiations by facilitating electron-hole pair separation. It is also found that Ag-N co-doping in zinc oxide had synergistic effect in enhancing its photocatalytic activity (Welderfael 2013). The photocatalytic activity of Ag-ZnO photocatalyst was studied by analysing the degradation of an organic dye and it was found that 3 mol % silver modified shows approximately four times higher rate of degradation than that of undoped ZnO (Georgekutty 2008). Subash et.al (2012) prepared Ag-ZnO and Zr/Ag co-doped ZnO by precipitation method for degradation of azo dye.

The aim of this paper is to study the influence of silver dopant on the structural and the photocatalytic properties of ZnO powders, activated by an original method.

2. MATERIALS AND METHOD

2.1 Synthesis of the samples

Activated ZnO powder was 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 CO_2 bubbling (barbotage) leading to precipitation as $Zn(OH)CO_3$, which was thermally

decomposed at 400° C. After that, the so activated ZnO powder was impregnated with definite quantities of the aqueous solutions of $AgNO_3$. The final samples doped with 1, 1.5 and 3 wt. % Ag were denoted as ZA1, ZA1.5 and ZA3, respectively.

2.2 *X-ray diffraction (XRD) analysis*.

The XRD patterns have been recorded using TUR M62 diffractometer with CoKα 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 Brunauer-Emmet-Teller (BET) method involving nitrogen adsorption from mixture 30% N_2 + 70% He at the boiling temperature of liquid nitrogen (77.4 K) using a conventional volumetric apparatus. Before measuring the specific surface area the samples were degassed at 423 K for 30 min to liberate the surface adsorbed impurities until the residual pressure became lower than $1.333.10^{-2}$ Pa. The nitrogen (N_2) monolayer formed was used to evaluate the specific surface area (ABET) using the BET equation.

2.4 Scanning electron microscope (SEM)

A scanning electron microscope (SEM) JEOL, model JEM-200CX, scanning adaptor EM-ASID3D, was used for morphology observations of the samples.

2.5 Catalytic activity tests

Reactive Black 5 (RB5) azo dye is commonly used in the textile industry and it can cause serious environmental problems. For this reason we used the dye as model pollutant. The photocatalytic degree of oxidative discoloration of RB5 was determined using 150 ml of dye aqueous solution with 20 ppm initial concentration. The calibration straight line of the absorbance maxima of RB5 dye at wavelength 599 nm versus the dye concentration is shown in Figure 1.

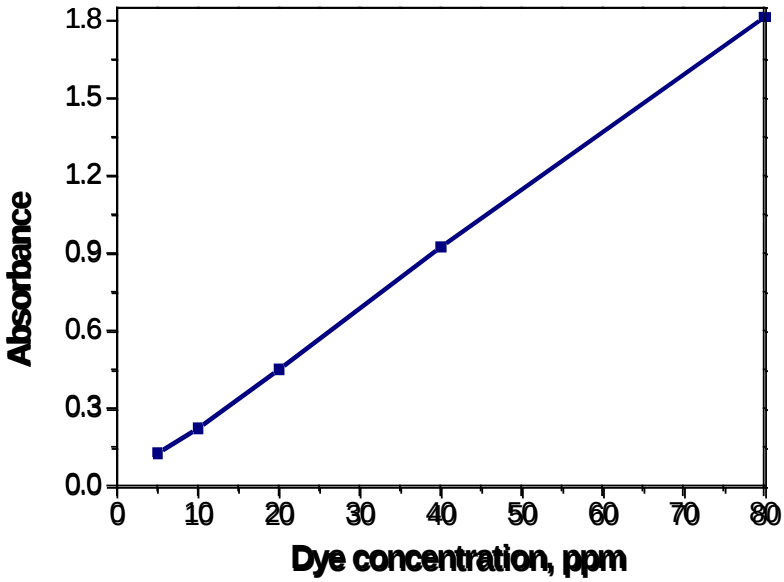


Fig.1. Calibration linear dependence of the absorbance maxima of RB5 dye at wavelength 599 nm versus the dye concentration

The photocatalytic activity tests have been carried out using polychromatic UV-A lamp (Sylvania BLB, 18 W), with wavelength range 315÷400 nm (with a maximum at 365 nm). The light power density on the sample position was 0.66 $mW.cm^{-2}$. The process of discoloration 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 rpm) under oxidative conditions (continuous air flow) at room temperature (semi-batch reactor). 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 at 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 to preserve constant reaction volume. The degree of discoloration is expressed as functional dependence versus time –ln (C/Co) = f(t) (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 (maximal absorbance specific for RB5) corresponding to the peak of the diazo bond (-N=N-). The dye concentrations Co and C were evaluated from the calibration line of the absorbance maxima (Figure 1).

3. RESULTS AND DISCUSIONS

The X-ray diffraction analyses of the samples (Figure 2) give evidence for the formation of wurtzite phase ZnO (JCPDS 36-1451) and the characteristic peak of metallic silver. Silver doped samples showed higher degree of crystallinity than the undoped ZnO powder. The specific surface area (A_{BET}) and crystallites size of the undoped and silver-doped ZnO samples are represented in Table 1. It shows that the metal doping of activated ZnO leads to decrease in the crystallites mean size. Comparing to the undoped ZnO, the doping of ZnO gives as a result an increase in the specific surface area. This is probably as a result of increased porosity of the samples due to the gases evolution during the decomposition of the metal nitrates.

Table 2. Specific surface areas, silver concentrations and crystallite sizes of the prepared samples

Sample	Content Ag, wt %	Crystallites size, nm	A_{BET} , m^2/g
ZnO	-	57	19
ZA1.5	1.5	50	32
ZA3	3	52	30

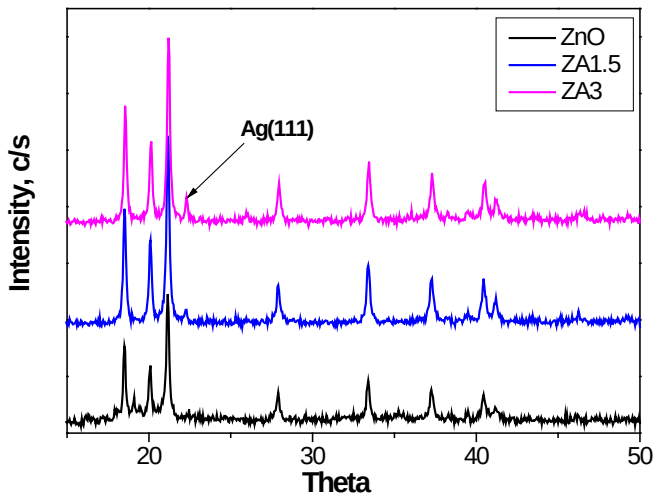


Fig.2. XRD spectra of ZnO and silver doped samples.

Figure 3 shows typical SEM image of silver-doped ZnO powder (ZA1.5). The microphotograph illustrates that the size of the particles are in the range 0.6÷5 μm – some pores are also observable.

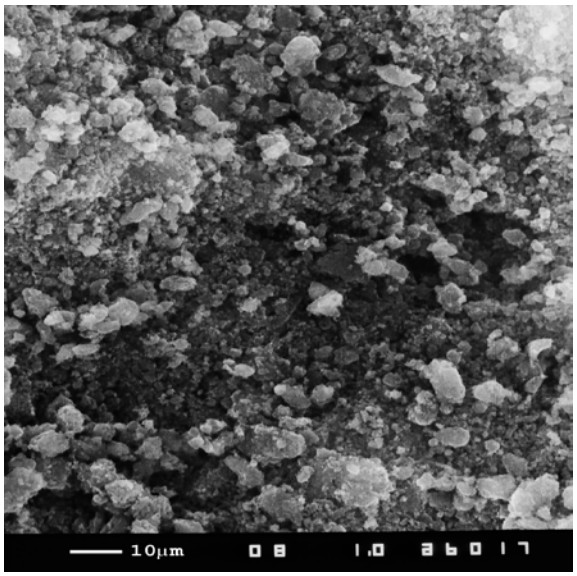


Fig.3. SEM picture of silver-doped ZnO

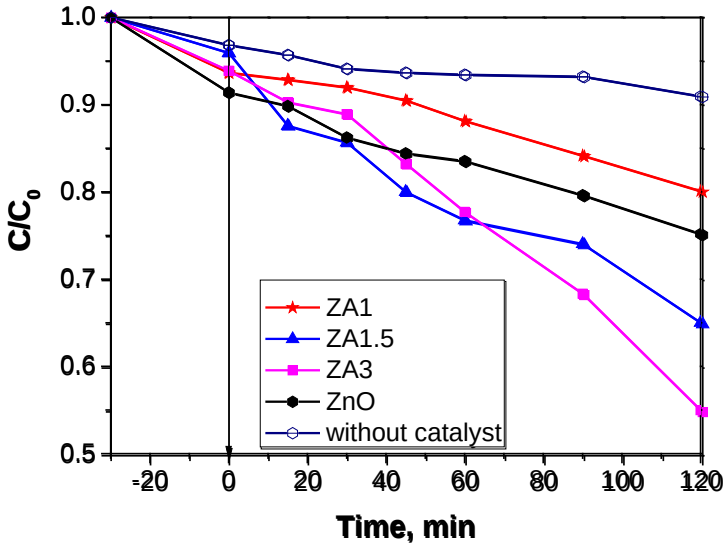


Fig.4. Discoloration degree of the RB5 dye (concentration 20 ppm), based on changes in the intensity of the absorbance peak, corresponding to azo bond (-N=N-) with the course of time.

The degrees of discoloring of the dye solutions in the cases of undoped and Ag doped ZnO catalysts after 120 minutes of irradiation are shown in Figure 4. As it can be seen for all of the catalyst samples, the increase in the silver content leads to enhancement of the photocatalytic activity. The ZnO sample exhibits lower activity than those of the catalyst containing 1.5 and 3 wt % silver – the latter one (ZA3) showing the best performance in oxidative discoloration of the model pollutant. Figure 5 illustrates comparatively the results concerning degree of

discoloration of the dye over the studied materials. The degree of discoloration of dye RB5 after 120 minutes of illumination for undoped ZnO is 18 %, while that for sampleZA1.5 and ZA3 is 32% and 41 %, respectively.

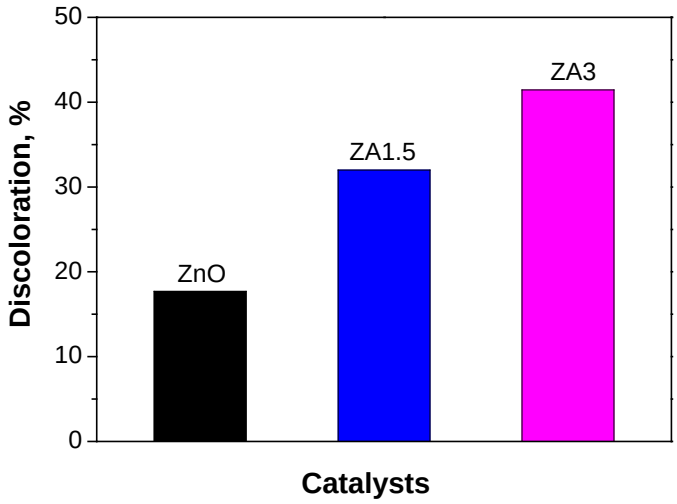


Fig.5. Degree of discoloration of the dye after 120 minutes of UV-A illumination over ZnO, ZA1.5; ZA3 under UV light illumination.

The increased efficiency of silver doped ZnO can be interpreted as follows. The degree of cristallinity and specific surface area of the doped samples are increased. As it is well known the photocatalytic activity of the catalysts depends strongly on the degree of crystallinity. The electron trapping effect of Ag is essential - its particles act as acceptor species, hindering the recombination of charge carriers on ZnO (Liqiang 2006).

Our data about higher degree of cristallinity are in contradiction with the results, obtained by Wang (2006). They claim formation of lattice defects and distortion of crystal lattice in the Ag doped ZnO are proved by XRD analysis, because the ionic radii of Ag^+ (r = 1.26 Å) is larger than that of Zn. This contradiction can be explained by the difference in the synthesis method and conditions. In our case we have activated ZnO, unlike the case of Wang (2006). On the other hand our results are in good agreement with the Hume-Rothery rules, as substitutional solid solution cannot be formed, if the atomic radii of the silver differ from the Zn by more than 15% (Hume-Rothery 1969). For this reason, the Ag ions prefer either to occupy interstitial positions in the ZnO lattice where they form a complex with the surface oxygen of the ZnO nanoparticles or to form separate Ag particles.

4. CONCLUSIONS

Activated nanosized ZnO (Bulgarian Patent) is superior in its photocatalytic properties to the non-activated ZnO. Doping of ZnO by Ag increases the degree of cristallinity of wurtzite. The decrease in ZnO particle mean size upon increasing dopant content promotes the specific surface area of the photocatalyst samples (19÷30 m^2/g). The role of silver nanoparticles is to serve as electron traps for photoexcited electrons preventing recombination and leaving the oxidative active sites – the positively charged holes to decompose the model pollutant Reactive Black 5 in aqueous solution. The best photocatalytic performance is manifested by the sample containing 3 wt.% Ag resulting in 41% degree of conversion (discoloration) within 120 min time interval of UV-A light illumination.

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