Comparative study of ZnO photocatalyst samples prepared by different methods

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Three different ways of preparation: activation (ZA), precipitation method using two different ingredients (ZP, ZD) were used to obtain nanosize ZnO powders. The photocatalytic activity was tested in the reaction of oxidative discoloration of diazo dye solution. The ZnO nanoparticle powders were obtained and characterized by XRD, IRS, TG – DTA, XPS and BET methods. The XRD analysis of ZnO photocatalysts showed presence of wurtzite ZnO phase, while IRS proves the formation of Zn–O bonds. The specific surface area of the ZnO sample, obtained by the activation method, was higher, compared to the other samples. The photocatalytic properties of the samples were tested in the reaction of oxidative degradation of Reactive Black 5 azo dye in solution. All the three photocatalysts showed high effectiveness in the dye degradation. The best photocatalyst is the activated ZnO powder, prepared by an original patented method. The highest rate constant of degradation of Reactive Black 5 model contaminant is on the ZA sample (33.8×10^{-3} min^{-1}).

Key words: ZnO; photocatalysis; ultraviolet light; azo dye.

INTRODUCTION

The discharging of waste water from textile industries into waterways is causing a huge environmental problem. The wastewater not only deteriorates the aesthetic view of water, but it is also noxious for aquatic flora and fauna. Among the various dyes, present in wastewaters from textile industries, the azo dyes constitute the largest portion. These dyes are known to be toxic, carcinogenic and they can induce mutations [1]. Different purification technologies such as: biological treatment, adsorption, filtration, ozonation, sedimentation, and UV/visible light/solar photocatalytic processes, etc. have been used for dyes treatment. Among them, the photocatalytic degradation of organic pollutants under UV irradiation has received much attention in view of purifying waste waters [2–8]. When a photocatalyst is irradiated with light having photon energy greater than or equal to the band gap energy, an electron from valence band is excited into the conduction band. The remaining hole oxidizes water molecules giving OH radicals, while the conduction band electron reduces the adsorbed oxygen molecule to give superoxide radical anion, which further results in the formation of additional OH radicals. The OH radical is a strong oxidizing agent via radical-chain mechanism leading to complete mineralization of the dye [9, 10]. The photocatalytic degradation of dyes was studied using commercial ZnO [9, 11] or ZnO prepared by different techniques such as: thermal evaporation [10–12], thermal decomposition of zinc oxalate [11–14] etc. The degradation of various dyes, such as Mordant Black 11 [11], Methyl Orange [12, 14] and Reactive Red 120 [13] was investigated on ZnO.

In the present study we investigate the phase and chemical composition of ZnO samples prepared in three different ways: activation, precipitation method using two different ingredients. The photocatalytic activity was tested in the reaction of oxidative discoloration of Reactive Black 5 azo dye solution.

EXPERIMENTAL

(1) Activated ZnO powder was obtained by original patented method (*Bulgarian Patent* 28915/

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1980), described in ref. [15]. The preparation includes dissolution of commercial ZnO in nitric acid, followed by simultaneous treatment using NH_4OH solution and CO_2 bubbling leading to precipitation of $Zn(OH)CO_3$ (ZH), which was further thermally decomposed at 500°C for 3h. The so prepared powder sample was denoted as **(ZA)**.

(2) Na_2CO_3 was dissolved in H_2O and added dropwise to solution of $ZnSO_4.7H_2O$ under heating and continuous stirring (pH value adjusted to 11). The precipitate was separated by filtration, washed several times with distilled water and dried in air. The corresponding precursor was heated for 3 h at 500 °C in air. The so prepared ZnO sample was denoted as **(ZP)**.

(3) The third sample was synthesized in the same way as the second sample, but using different starting materials – this time $Zn(NO_3)_2·6H_2O$ and NH_4HCO_3. The so prepared powder sample was denoted as **(ZD)**.

For comparison the commercial ZnO sample (denoted as **ZC)** has also been tested.

All the chemicals, used for the synthesis of the ZnO samples: $Zn(NO_3)_2·6H_2O$, $7NH_4HCO_3$, $ZnSO_4.7H_2O$ and Na_2CO_3 have been delivered by the Bulgarian branch of Aquachim Merck (at present Aquachim Beckmann Coulter) and are analytical grade of purity, with the exception of ZnO (Chemapol, Praha), which is technical grade of purity.

The phase composition of the samples was studied by X-ray diffraction (XRD) with CuK_α-radiation (Philips PW 1050). The crystallite size, was estimated from the XRD spectra, according to Sherrer's equation.

The DTA and TG curves have been recorded on a LABSYSTEM EVO apparatus SETARAM (France), at a heating rate of 10°/min starting from 25 °C until reaching 600 °C in alumina crucible in air. The determination of the specific surface area of the samples was carried out by the 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 entire surface from 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 (A_{BET}) using the BET equation.

The IR spectra were recorded in the range of 4000 to 400 cm^{-1} on a IFS 25 spectrometer (Bruker) with resolution of less than 2 cm^{-1}. The samples were prepared in the form of KBr tablets, containing the investigated samples.

The X-ray photoelectron spectroscopy (XPS) studies were performed in a VG Escalab II electron spectrometer using $AlK\alpha$ radiation with energy of 1486.6 eV under base pressure 10^{-7} Pa and a total instrumental resolution 1eV. The binding energies (BE) were determined utilizing the C1s line (from an adventitious carbon) as a reference with energy of 285.0 eV. The accuracy of measuring the BE values was 0.2 eV. The C1s, Zn2p and O1s 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.

Reactive Black 5 (RB5), a toxic azo dye was used as a model pollutant for the evaluation of photocatalytic activity. The absorption of RB 5 on suspended ZnO oxides was measured as follows: 0.15 g of sample powder was suspended in 150 ml of dye aqueous solution (Reactive Black initial concentration, 20 ppm giving pH=7), which was then stirred with a magnetic stirrer at a constant magnetic stirring rate (400 rpm) under oxidative conditions (bubbling air through two frits to achieve water saturation in oxygen) at room temperature. The photodegradation of Reactive Black 5 (RB5) was studied under standard reference conditions of 1mg/ml suspension. The photocatalytic degree of oxidative degradation of RB5 has been carried out using polychromatic UV-A lamp (Sylvania BLB, 18 W), with wavelength range 315-400 nm (with a maximum of the irradiation at 365 nm). The light power density on the sample position was 0.66 $mW.cm^{-2}$. The changing concentration of dye in the course of the reaction was monitored using UV-Vis absorbance single beam spectrophotometer CamSpec M501 (UK) at operating in the wavelength range from 190 to 800 nm. After reaching adsorption equilibrium for 30 min in the dark, the lamp was switched on to initiate the photocatalytic reactions.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of precursors and zinc oxide powders are represented in Figure 1. The X-ray diffraction analysis of the ZA precursor revealed the formation of phase $Zn_5(OH)_6.(CO_3)_2$ according to PDF 72-1100. The sizes of crystallites of t_{200} are 21 nm, calculated by Debye-Scherer's equation. The sample ZD precursor show existence of the same phase, but it is amorphous to some extent and a lot of peaks are superimposed. The sizes of crystallites of t_{200} are 6 nm. The third sample- ZP precursor shows existence of mixture of ZnO (PDF 36-1451) and $3Zn(OH)_2.2ZnCO_3$. The X-ray diffraction patterns of investigated zinc oxides synthesized from the above mentioned precursors are also shown in Figure 1. The three of them- ZA, ZD and ZP displayed wurzite ZnO phase (JCPDS 36-
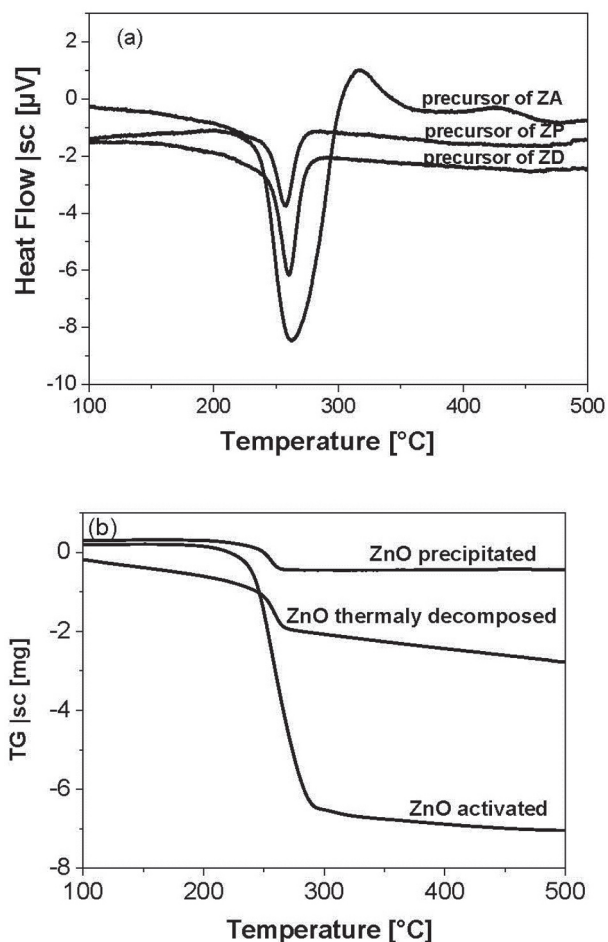
Fig. 1. X-ray diffractograms of ZnO precursors (a) ZA, ZD, ZP and (b) zinc oxides- ZD, ZA and ZP

Figure 2 represents the DTA (a) and TG (b) patterns of precursors of all samples. A strong endothermal peak has been registered on the DTA curve for the three precursors under 300 °C, which is the result of zinc hydroxide decomposition. The maximum of the endothermal peak for ZA, ZP and ZD is 258 °C, 263 °C and 260 °C, respectively. The thermally decomposed ZnO (ZD) showed a max-
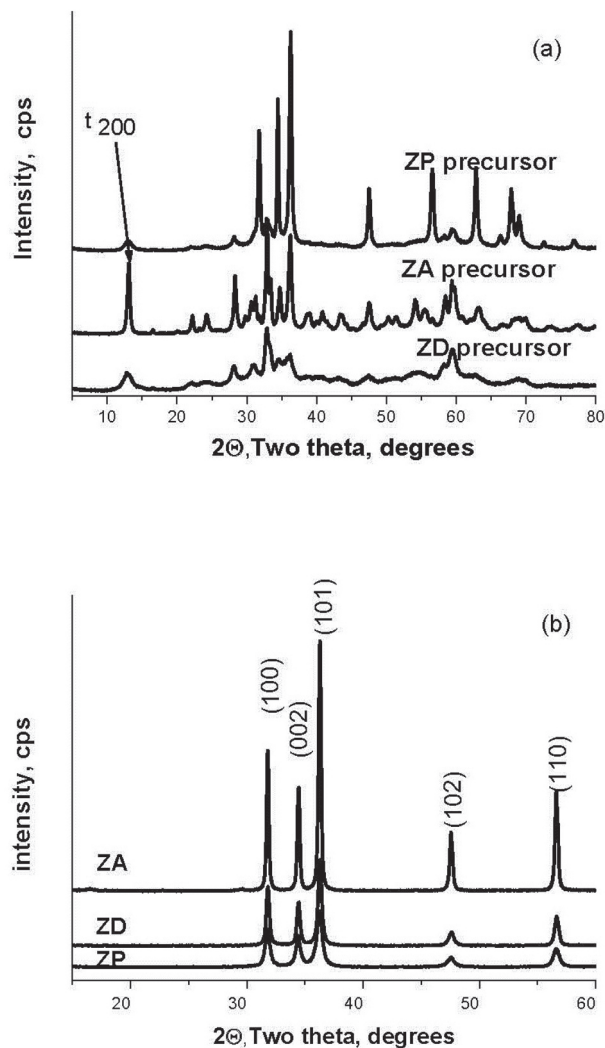
Fig. 2. (a) DTA and (b) TG curve of zinc precursors

1451). Crystallites size (D), specific surface area (A_{BET}), lattice constants of ZnO, calculated mass change (Δm) and rate constants (k) are presented in Table 1. The specific surface area of the ZA sample is 40 m²/g, i.e. much higher than those of ZP and ZD samples. The crystallites size of ZA, ZP and ZD samples are 67 nm, 28 nm and 31nm, respectively. This contradiction could be explained by possible agglomeration between the particles of ZP and ZP samples.

Table 1. Specific surface area (A_{BET}), crystallites size (t), lattice constants of ZnO, calculated mass change (Δm) and rate constants (k)

Sample	A_{BET} (m²/g)	t (nm)	a (Å)	c (Å)	Δm (%)	k ($\times 10^{-3}$ min⁻¹)
ZA	40	67	3.2484	5.2019	20.251	33.8
ZP	25	28	3.2497	5.2083	7.189	23.6
ZD	22	31	3.2499	5.2076	48.335	12.8

imum at 260 °C, it decomposition begins at 247 °C and it is completed at 273 °C. From DTA-TG analysis we can calculate the mass change (Δm) as $\Delta m = (m_0 - m_t / m_0) \times 100$ (%), where m_0 is initial mass and m_t is mass at the temperature, where the process is finished for investigated samples. The exact values of mass change are given in Table 1.

The ZnO catalysts synthesized in different ways have been subjected to X-ray photoelectron spectroscopy investigation in order to elucidate the influence of preparation procedure on the photocatalytic activity, manifested in a degradation of Reactive Black 5 (RB5) used as a model pollutant. The results of the recorded O1s core level are presented in Figure 3. Due to their complex structure the obtained spectra have been fitted with 3 components. The first sharp peak having binding energy at about 530.0eV shows the existence of Zn-O bonds that belonged to the ZnO lattice. The well pronounced shoulder from the higher binding energy side consisted of two peaks according to the applied fitting procedure. The first one is associated with existing of oxygen vacancies and binding energy is about 531.5 eV, while the second one having binding energy at 532.5 eV belongs to the chemisorbed oxygen or OH- groups on top of the studied catalysts surfaces. The catalytic activities of the studied cata-

lysts depend on the quantity of the formed defects on the surface as it has already been reported by other authors [16]. The calculated percentage of the oxygen vacancies is the following: 24% (ZA), 30% (ZP) and 24% (ZD). Equal quantities of oxygen vacancies are present on the surface of the ZA and ZD catalyst and nevertheless ZA catalyst demonstrates higher activity in a degradation of RB5. Reasonable explanation could be the fact that there is some difference in the relative percentage on the surface of the catalysts due to the OH- groups chemisorbed or dissociated oxygen. Most probably a synergistic effect exists between them playing an important role for the catalytic activity.

The degree of purity and molecular structure of the products were analyzed by the IR spectroscopy (Figure 4). The ZA sample showed strong narrow peak at 437 cm⁻¹, while for the ZD and ZP samples a broad band was observed around 382–602 cm⁻¹, which is typical of ZnO. According to other investigations this peak can be ascribed to Zn–O stretching vibration [13, 17]. The ZnO prepared, by a different method, showed a broad band with two maxima, due to the change in morphology of ZnO [18].

The reaction course as a function of the time interval of illumination (C/C_0) and dye degradation conversion degrees [$(Co-C)/Co$] of the Reactive
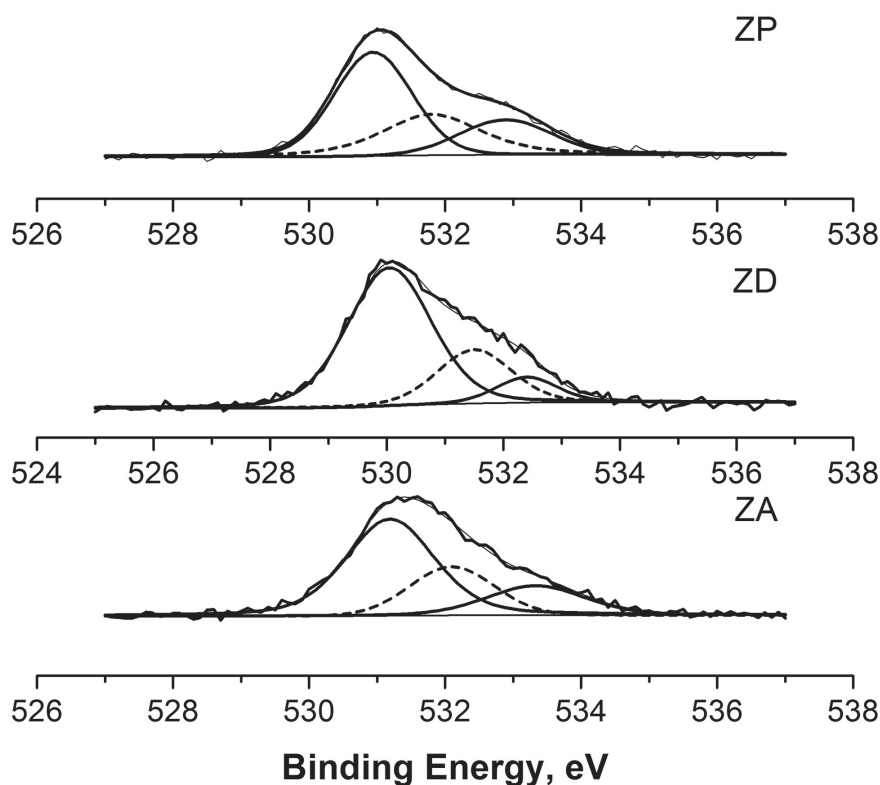

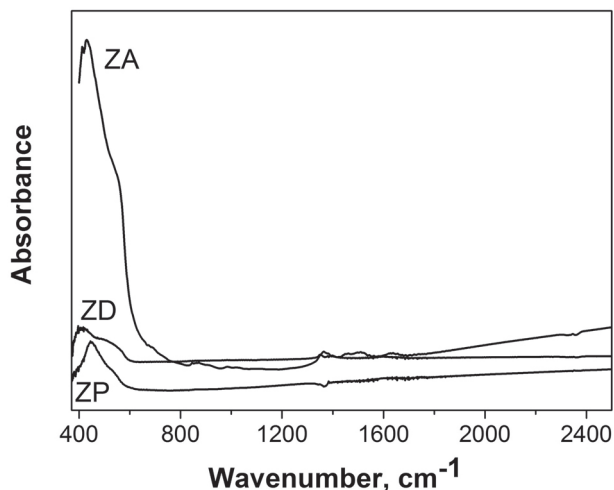**Fig. 3.** X-ray photoelectron spectroscopy of ZD, ZA and ZP
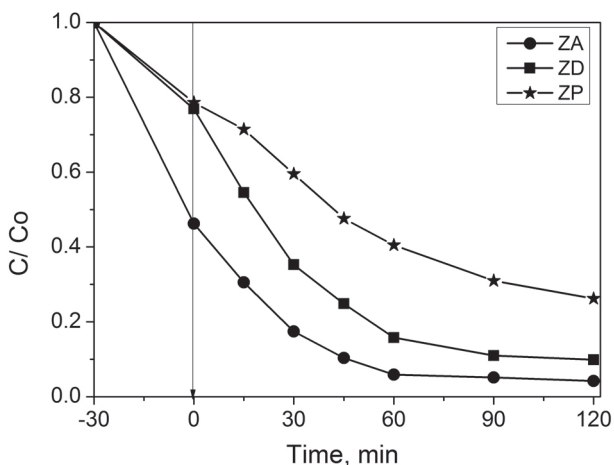
Fig. 4. IR spectroscopy of ZD, ZA and ZP

Fig. 6. Dye degradation of ZD, ZA and ZP

Fig. 5. Reaction course as a function of the time interval of illumination (C/C$_0$) of ZD, ZA and ZP

is one and the same with all ZnO samples – the active sites (positively charged holes in the valence band) produce the active particles (hydroxyl radicals) by oxidation of adsorbed water molecules. The only difference is the number of the active sites on the surface as a result of the different synthesis procedures. The number of active sites is proportional to the value of the specific surface area. Here we should point out that the role of the sodium ions (ZP sample) is unfavourable, leading to smaller value of the specific surface area in comparison to the case when ammonium carbonate is used (ZA and ZD samples). The difference between the two latter samples can be explained in view of the DTA pattern – there is exothermal peak at about 320 °C, which is evidence for the formation of intermediate phase, decomposing further into more active ZnO phase. The best photocatalytic sample ZA is superior in its performance to the commercially available ZnO sample.

Black 5 on ZD, ZA and ZP are shown in Figure 5 and 6 respectively. The ZA sample exhibits highest degradation of the dye (96%) than those of ZP (90%) and ZD (74%). The activated ZnO powder showed the highest adsorption capacity. The rate constants k (min^{-1}) are calculated using logarithmic linear dependence of the concentrations ratio on the time: $-\ln(C/C_0) = k.t$. Their values give the following order of activities: ZA (33.8×10^{-3} min^{-1}) > ZP (23.6×10^{-3} min^{-1}) > ZC (16.1×10^{-3} min^{-1}) > ZD (12.8×10^{-3} min^{-1}). The activated ZnO possesses the best photocatalytic efficiency due to influence of the following factors: high degree of crystallinity (proved by both XRD and IR spectra) and higher specific surface area. The degradation mechanism
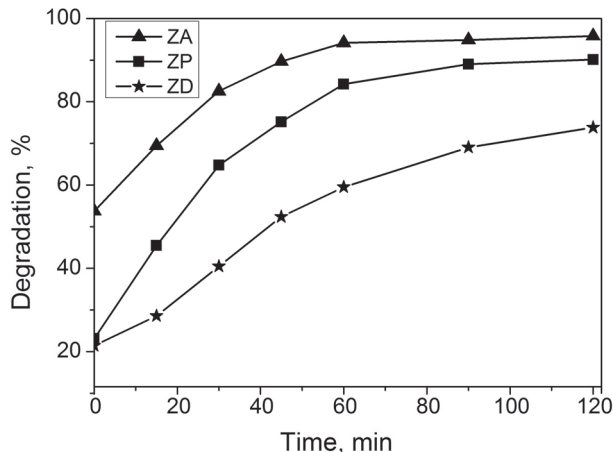
CONCLUSIONS

ZnO powder was activated using an original patented method and its performance was compared with that of the other two ZnO samples prepared by the precipitation method. According to XRD and IRS data only ZnO is being registered. The photocatalytic properties of the samples were tested in the reaction of oxidative degradation of Reactive Black 5 azo dye used as model waste water pollutant in a semi-batch photo-reactor. All the three investigated photocatalysts, show high effectiveness in the dye decomposition, but the best performance with the highest conversion degree (96%) was observed with the activated ZnO (ZA). The sample ZA per-

formance exceeds that of the other ZnO due to its: (i) higher degree of crystallinity, (ii) higher surface area, (iii) higher adsorption capacity. The order of activities (based on rate constants k) in degradation of Reactive Black 5 model contaminant for the three samples is as follows: ZA > ZP > ZC>ZD, which coincide with the decreasing values of specific surface areas.

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СРАВНИТЕЛНО ИЗСЛЕДВАНЕ НА ZnO ФОТОКАТАЛИЗАТОРНИ ПРОБИ, ПОЛУЧЕНИ ПО РАЗЛИЧЕН НАЧИН

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(Резюме)

За получаването на образци от наноразмерен прахообразен ZnO са използувани три различни подхода: активиране (образец ZA), утаяване чрез използуването на два различни реагента (образци ZP и ZD). Измерена е тяхната фотокаталитична активност в реакции на окислително обезцветяване водни разтвори на диазо багрила. Получените наноразмерни прахообразни образци от ZnO са охарактеризирани чрез рентгенофазен анализ (РФА), инфрачервена спектроскопия (ИЧС), термогравиметрия в съчетание с диференциален термичен анализ (ТГ–ДТА), рентгенова фотоелектронна спектроскопия (РФС) и измерване на специфичната площ на повърхността по БЕТ метода. РФА анализа на получените фотокатализатори от ZnO показа наличие на вюрцитна фаза ZnO, докато ИЧС указва формиране на Zn–O връзки. Специфичната площ на повърхността на ZnO, получен по метода на активация е по-висока, в сравнение с другите проби. Фотокаталитичните свойства на образците бяха изпитани в реакцията на окислително разлагане на Реактивно Черно 5 азо-багрило. И трите образеца имат висока ефективност за разграждане на багрилото. Най-добрият фотокатализаторен образец е активираният прахообразен ZnO, получен по оригинален патентован метод. Скоростните константи на превръщане на моделния замърсител Реактивно Черно 5 над отделните образци дават следния ред активност: ZA $(33.8 \times 10^{-3}$ min-1) > ZP $(23.6 \times 10^{-3}$ min^{-1}) > ZD $(12.8 \times 10^{-3}$ min^{-1}).