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Preparation of ZnO photocatalysts by copolymer Pluronic-assisted hydrothermal process

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Mesoporous ZnO powders were prepared by hydrothermal treatment (HT) of a three-block copolymer (P123) containing precipitate. Well-crystallized wurtzite ZnO phase powders were obtained. The particles consisted of oval nest-like units, which contained both non-uniformly distributed nanosheets and nanorods. Increasing the Pluronic (P123) content up to a certain value led to a larger share of the mesopores at the expense of micropore part. The ZnO samples, obtained from polymer-modified HT precipitate, exhibited a higher photocatalytic activity in oxidative discoloration of Reactive Black (RB5) dye than that of the reference sample. A larger surface area and a larger pore volume provided a larger number of surface active sites for the photocatalytic reaction increasing the adsorption capacity and facilitating the transportation of the dye.

Keywords: zinc oxide, photocatalyst, porosity, wastewaters, polymer modification.

INTRODUCTION

Zinc oxide is known to be an excellent material for photocatalytic decontamination of wastewaters due to its high UV-light photosensitivity, nontoxic nature, and large band gap [1]. It has been demonstrated that the photocatalytic activity of ZnO is strongly dependent on its crystallite size, specific surface area, surface morphology, and texture. Various routes such as chemical bath deposition [2], thermal decomposition [3], vapour phase deposition [4], and hydrothermal process [5] have been applied to synthesize ZnO powders. The conventional hydrothermal method and its modifications such as electrochemically assisted, microwave-assisted, and surfactant-assisted versions have been developed as suitable methods for preparation of multifunctional ceramics materials. The surfactant-assisted hydrothermal synthesis of ZnO is an important phase method, which is used to prepare porous ZnO materials. Aimable *et al.* [6] have revealed that the size and morphology of precipitated ZnO can be tuned by addition of various anionic polymers, which cause reduction of the final particle size and lower the degree of agglomeration. Nanocrystalline mesoporous assembled TiO_2 photocatalyst has been synthesized using laurylamine hydrochloride, $CH_3(CH_2)_{11}NH_2.HCl$, as a structure-directing surfactant behaving as a mesopore-forming agent and tested in the photocatalytic degradation of monoazo dye [7].

Recent investigations have indicated that polymers could also be used as templates to direct the formation of mesoporous oxides having high specific area, large pore volume, and small pore size. Therefore, mesoporous oxide should be a more efective photocatalyst because it offers a greater number of active sites for carrying out catalytic reactions. The mesoporous structures allow rapid diffusion of various reactants and products and enhance the rate of photocatalytic reaction [8]. In view of this, mesoporous ZnO powders can be prepared *via* addition of definite quantity of triblock copolymer as structure-directing agent for organizing the network-forming ZnO species and for controlling the pore size.

The aim of this work was to prepare mesoporous ZnO powders using three-block copolymer named Pluronic (P123) to assist the hydrothermal method and to study the effect of polymer concentration on the structure and on the photocatalytic efficiency.

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EXPERIMENTAL

ZnO was synthesized by mixing zinc nitrate and P123 aqueous solutions. Zn^{2+} reactant solution was prepared by dissolving 2 g of Zn acetate in 200 ml deionized water. To prepare the P123-modified solutions, different quantities of tri-block copolymer Pluronic (P123, $EO_{20}PO_{70}EO_{20}$, Sigma-Aldrich) were diluted in small quantity of water and then added to the zinc acetate solution. Samples containing 2, 4, and 8 g of P123 were denoted as P1, P2, and P3, respectively. A sodium hydroxide aqueous solution was used to induce precipitation. For the sake of comparison, a reference sample was also obtained without any addition of polymer solution under the same preparation conditions (sample P0). The resulting mixture was transferred into an autoclave for thermal treatment at 140°C for 12 h. Then the autoclave was cooled down naturally to room temperature. The precipitates were washed several times with water and ethanol and dried in an oven at 60°C.

X-ray diffraction (XRD) patterns were recorded on a Bruker D2 Phaser diffractometer varying 2θ values between 25 and 75° and using Cu K_α radiation (λ = 0.154056 nm) at 40 kV. The single-point BET method has been applied to measure the specific surface area based on low-temperature adsorption of nitrogen. Method relative error amounts to about 8%. Specific surface area and pore-size distribution measurements were accomplished on an automated NOVA Win-CFR Quantachrom gas sorption system. The average pore diameter was evaluated by DFT assuming a cylindrical model of the pores. The total pore volume was estimated in accordance with the rule of Gurvich at a relative pressure of 0.96. For morphological characterization of the surface, a JEOL JEM-200CX scanning electron microscope (SEM) was used. The images were recorded at 80 keV accelerating voltage in secondary electrons image (SEI) mode. The samples were coated with a thin layer of carbon and gold for better conductivity prior to the investigation.

The photocatalytic discoloration of Reactive Black 5 azo dye was evaluated using aqueous solution of initial concentration of 20 ppm under polychromatic UV-A lamp illumination (18 W) with maximum emission at wavelength 365 nm. A semi-batch photocatalytic reactor was used feeding continuously O_2 and creating large dissolved oxygen excess with respect to the stoichiometrically required amount for oxidation reaction. This allowed us to assume practically constant dissolved oxygen concentration and to include its value in the apparent rate constant, k_{app}. Therefore, the bimolecular reaction of Langmuir-Hinshelwood type of mechanism is reduced to a pseudo-first order kinetic equation following only the azo dye concentration decrease with time of illumination. The course of the oxidative discoloration reaction was monitored by a CamSpec M501 UV-Vis spectrophotometer within the wavelength range from 200 to 800 nm in absorbance mode. The samples were equilibrated in the dark (reaching adsorption-desorption equilibrium) for about 30 min before switching on the irradiation. The photocatalytic activity tests were carried out by taking sample aliquots of the suspension from the reaction vessel at regular time intervals and filtering them. After measuring the absorbance, the amount was placed back into the reactor to have constant volume operation.

RESULTS AND DISCUSSION

The X-ray diffraction patterns (Fig. 1) of both types of samples revealed narrow and sharp diffraction peaks, which proved a well crystallized phase identified as a hexagonal wurtzite type structure of ZnO (JCPDS 36-1451).

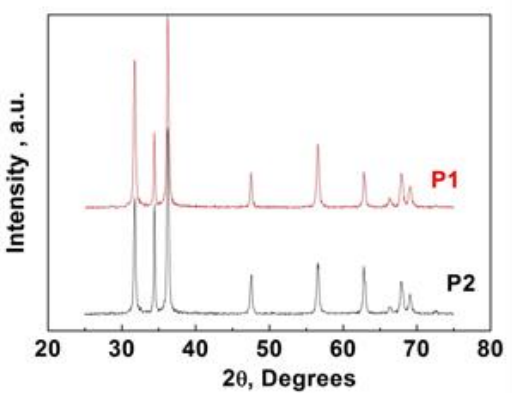

Fig. 1. XRD patterns of polymer modified samples.

The adsorption-desorption isotherms of the samples can be ascribed to type IV of the IUPAC classification, which shows the dominating presence of mesopores. The hysteresis loop could be interpreted as an H3 type. An almost horizontal section is observed, whereupon the hysteresis loop is shifted towards higher relative pressure (P/Po approximately 1), which implies the presence of cylindrical pores. A similar behaviour was observed with the dry pressed ZnO nanoparticles with elongated shape [9]. The pore size distribution of the P0 sample is shown in figure 2. Polymer modification of the zinc precursor solution increases the relative share of the mesopores at the expense of the share of micropores (Fig. 3). Increasing the Pluronic concentration up to a certain value leads to a larger share of the mesopores lowering the share of micropores. The ZnO powders P3 contain predominantly micropores, while the mesopore volume drops down abruptly.

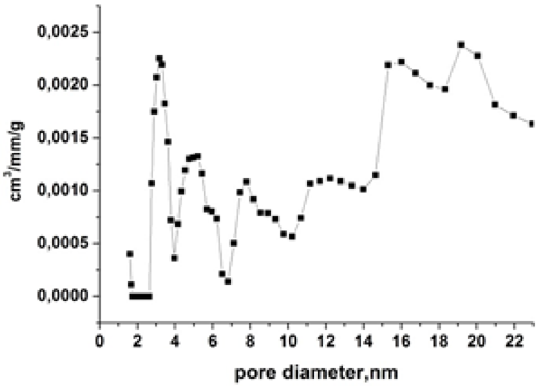

Fig. 2. Pore size distribution of P0 sample.

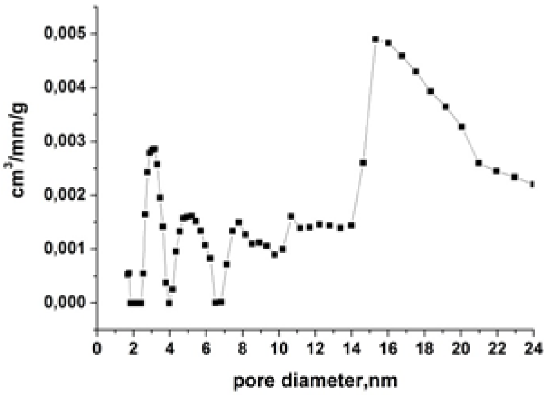

Fig. 3. Pore size distribution of P2 sample.

The BET surface area (S) and average pore diameters of the samples are shown in table 1. BET measurements have revealed an enhancement of both specific surface area and average pore diameter of the Pluronic-modified powders (Table 1).

Table 1. BET surface area (S) and average pore size (d) of the samples

Sample	S [m^2/g]	d [nm]
P0	10	8.4
P1	13	9.2
P2	14	9.3
P3	14	8.4

XPS analyses of Zn2p$_{3/2}$ and ZnO1s spectra of the hydrothermally obtained samples disclosed similar features. The Zn2p$_{3/2}$ peak has a maximum at ~1021.7 eV that is typical of Zn^{2+} oxidation state. The O1s spectrum shows a mean peak at ~530.5 eV and a shoulder at ~532.0 eV, respectively. The former is assigned to lattice oxygen in zinc oxide while the latter is attributed to adsorbed hydroxyl groups. The Zn/O$_T$ atomic ratio was evaluated from the values of Zn2p$_{3/2}$ and O1s peak areas, normalized by corresponding photoionization cross-sections.

It has to be noted that all samples were non-stoichiometric. The values of Zn/O$_T$ atomic ratio are lower for samples P2 and P3 (Table 2).

Table 2. XPS chemical compositions of the samples

Sample	O [at.%]	Zn [at.%]	Zn/O$_T$
P0	54.7	45.3	0.83
P2	56.5	43.5	0.77
P3	57.6	42.4	0.74

The surface morphologies of the prepared ZnO samples were investigated by SEM (Figs. 4 and 5). As can be seen in the figures, in all cases oval nest-like units appear which consist of some non-uniform in size nanosheets and nanorods (Fig. 4). When Pluronic was added into the solution, the surface morphology of the product was slightly changed (Fig. 5). The number of nanorods decreases, but their length slightly increases. They have lengths in the range of 250–500 nm and diameters in the range of 30–60 nm. A further increase in the Pluronic concentration did not lead to any obvious changes in size and shape of the nanosheets and nanorods. A similar morphology of ZnO powders, obtained from PEG-modified solution of zinc acetate precipitated with NaOH, has been shown in the work of Adhyapak and co-workers [10].

Fig. 4. SEM photograph of P0 sample.

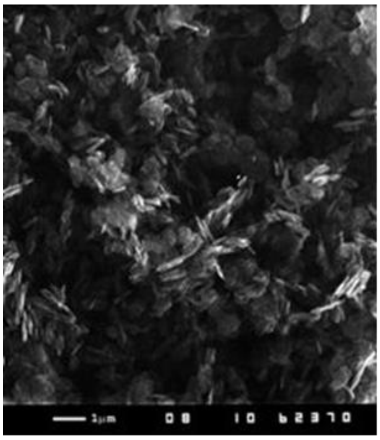

Fig. 5. SEM photograph of P2 sample.

The photocatalytic efficiencies of the samples were evaluated in the reaction of RB5 oxidative discoloration and the results are displayed in figure 6.

The reaction kinetics is represented by plotting the natural logarithm of the pollutant concentration ratio $–\ln(C/C_0)$ as a function of the illumination time interval t. The experimental results showed that the photocatalytic oxidative discoloration of the dye solution under UV-light irradiation follows a pseudo-first order reaction kinetics due to great excess of oxygen in the solution, and it is expressed by the equation:

$$\ln(C/C_0) = –kt\,, \tag{2}$$

where C_0 is the initial concentration of the dye, C is the concentration of the dye after irradiation for a certain time interval t, and k is the apparent rate constant. The latter was evaluated based on the slope of the straight linear dependence $–\ln(C/C_0)$ *vs* time.

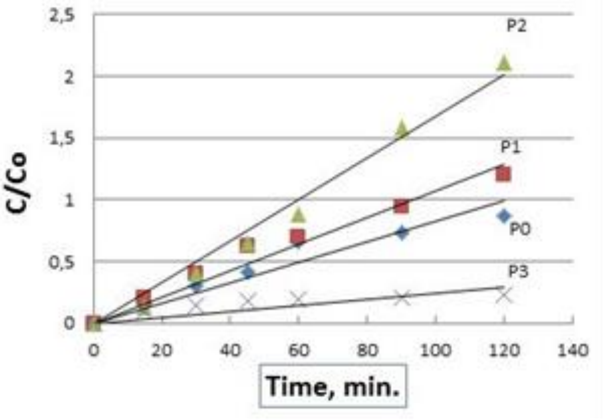

Fig. 6. Kinetic curves of dye discoloration on the samples, obtained by Pluronic modified hydrothermal method.

It can be seen in the figure that the reference sample and sample P3 exhibit lower activities for dye discoloration than those of samples P1 and P2. The best photocatalytic activity is displayed by sample P2 (when 4 g of P123 were added into solution). Thus, this is the optimal Pluronic concentration in the zinc solution to obtain a highly active mesoporous photocatalyst. The apparent rate constants (k) are 1.5×10^{-3}.min^{-1}, 10.3×10^{-3}.min^{-1}, 15.8×10^{-3}.min^{-1}, and 2.5×10^{-3}.min^{-1} for the P0, P1, P2, and P3 samples, respectively. We have also estimated the ratio of rate constant to specific surface area (k/S) for polymer-modified samples in order to determine the photocatalytic activity related to unit of surface area. The k/S ratios are 0.0008, 0.014, and 0.00017 for samples P1, P2, and P3, respectively. As it was proved by BET measurements, the ZnO samples, produced by hydrothermal treatment of three-block copolymer containing precipitate, have slightly higher surface areas and possess more mesopores than the reference sample. It is well known that the photocatalytic activities are strongly dependent on the surface area of the photocatalysts, as the reacting molecules have to be first adsorbed on their surfaces. The presence of numerous nanosheets and nanorods ensures large surface, leading to the enhancement of dye adsorption and easier transportation. Higher values of surface area and pore volume for the polymer-modified samples provide a larger number of surface active sites for the photocatalytic reactions. In addition to this, the mesoporous channels also facilitated the diffusion of reactant molecules thereby increasing the reaction rate [11]. According to Barauch *et al*. [12], the mesoporous structure of ZnO can provide more active sites available for adsorption of reactive species due to the larger pore volume, which causes improvement in the photocatalytic activity. It is also possible that the Zn/O ratio influences the photocatalytic behaviour besides the surface area and particle size. The powders obtained from HT polymer-modified precipitate have a lower value of Zn/O_T ratio and a higher discoloration rate than those of the reference samples. It is worth mentioning that introducing P123 in the samples leads to creation of more oxygen vacancies on the surface of ZnO photocatalysts in comparison with those of the reference samples. These oxygen defects are adsorption sites, which result in an enhanced photocatalytic activity.

The results obtained indicate that the Pluronic-modified hydrothermal method can be used successfully to prepare highly effective photocatalysts representing well-crystallized mesoporous powders for oxidative dye discoloration.

CONCLUSIONS

Applied polymer-assisted precipitation, in combination with hydrothermal treatment, is beneficial in view of the effectiveness of the mesoporous ZnO photocatalytic material. The phase composition of all the samples represents a well-crystallized wurtzite phase. Typical of the ZnO samples are particles consisting of oval nest-like units, which contain some non-uniform nanosheets and nanorods. The polymer modification of zinc precursor solution with Pluronic (P123) results in an increased share of mesopores, which is accompanied by a decrease in the share of micropores. The superior photocatalytic performance in discoloration of azo dye by comparing modified samples with reference ZnO can be explained based on a larger share of mesopores enabling faster molecular diffusion and enhanced adsorption capacity as well as formation of a larger number of oxygen vacancies in the ZnO lattice.

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ХИДРОТЕРМАЛНО ПОЛУЧАВАНЕ НА ФОТОКАЛИЗАТОРИ ОТ ZnO С ПОМОЩТА НА КОПОЛИМЕР ПЛУРОНИК

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(Резюме)

Мезопорести прахове от ZnO бяха получени чрез хидротермална обработка на утайки, съдържащи триблоков съполимер. Получени са прахове от добре кристализирала вюрцитна фаза. Частиците са съставени от овални гнездовидни структури, съдържащи нееднакви нанолисти и нанопръчки. Увеличаването на концентрацията на Плуроник (P123) до определена стойност води до по-голям дял на мезопорите за сметка на микропорите. Образците от ZnO, получени от полимерно модифицирани хидротермално обработени утайки, проявяват по-висока фотокаталитична активност в реакцията на окислително обезцветяване на багрилото Реактивно Черно в сравнение с образеца за сравнение. По-високата специфична повърхност и по-големия обем на порите предоставят по-голям брой повърхностни активни центрове за фотокаталитичната реакция като повишават адсорбционния капацитет и улесняват транспорта на молекулите на багрилото.