POROUS ZINC OXIDE PLATE WITH MICRO- AND NANOELEMENTS OF THE SURFACE STRUCTURE FOR HETEROGENEOUS PHOTOCATALYSIS

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The zinc oxide porous plate with micro- and nanoelements of the surface structure was obtained by sintering metallic zinc powder, characterized and tested for the photodegradation of model organic dye (methyl orange) in water. The kinetics of dye photodegradation was studied via measurement of variation of the optical density at the maximum observed for the dye at 465 nm. After 30 min of illumination, the photodegradation efficiency of methyl orange was found to be about 100% when the ZnO plate with overall dimensions of 35 mm × 7 mm × 1 mm was used. The reaction rate constant calculated using the first-order approximation was equal to $2.7 \cdot 10^{-4}$ sec^{-1}. It is necessary to point out that the sample keeps its integrity after multiple experiments, which is important for practical applications. The obtained results evidently demonstrate the potential of the method of sintering metallic zinc powder for the production of efficient catalysts.

Key words: zinc oxide, heterogeneous photocatalysis, photodegradation, methyl orange, absorption spectroscopy.

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I. INTRODUCTION

A promising method of water purification from organic dyes is photocatalysis using semiconductor materials. This technology, unlike the classic ones, does not require energy costs, because the process of decomposition of chemical compounds is due to the irradiation of the photocatalyst with the light of the visible or ultraviolet range. Moreover, the complete oxidation of organic dyes is carried out at ambient temperature [1–4].

Zinc oxide is the cheapest alternative to the currently most efficient photocatalyst — titanium dioxide. Compared to the TiO_2 semiconductor, zinc oxide has a higher exciton binding energy, is more resistant to radiation, and is a multifunctional material with piezoelectric and — the case of impurities — also ferroelectric and ferromagnetic properties. In addition, it is important to note that controlled doping can reduce the effective band gap in ZnO, which will make it possible to use visible light for photocatalytic oxidation [1, 2, 5–7].

In recent years, among semiconductor materials in heterogeneous photocatalysis increasing attention has been paid to ZnO. It is known that there are zinc oxide photocatalysts in the form of a single crystal [8], arrays of micro- or nanorods on substrates [1, 4], nanopowders [9], hierarchical microspheres covered with nanoparticles [10]. However, they either have low photocatalytic activity or are difficult to separate from the solution.

In this paper, we report the data concerning fabrication, characterization, and photocatalytic properties of the zinc oxide porous plate with micro- and nanoelements of the surface structure obtained by sintering metallic zinc powder.

II. EXPERIMENTAL

The pure metallic zinc powder was taken as an initial material for sintering. The powder was put into a rectangular ceramic bath with overall dimensions of 10 mm × 10 mm × 70 mm. The ceramic bath was placed into a horizontal oven. The powder was heated to the temperature of about 673 K. After 1 h, the oven was switched off. After spontaneous cooling to room temperature, the plate formed from sintered zinc powder was removed from the ceramic bath. Then the plate was repeatedly placed in a horizontal oven and heated to the temperature of 723 K for the purpose of oxidation. After 1 h, the heating of the oven was turned off.

The morphology of the sample was examined using REMMA−102−02 Scanning Electron Microscope-Analyzer (JCS SELMI, Ukraine).

Methyl orange ($C_{14}H_{14}N_3NaO_3S$) was selected as the organic dye for testing the photocatalytic properties of the ZnO sample. The ZnO plate with overall dimensions of 35 mm × 7 mm × 1 mm was placed into a standard 3.5 mL quartz cuvette with aqueous solution of methyl orange (10 mg/L).

Prior to illumination, the sample was immersed in the methyl orange (MO) solution for about 20 h in darkness in order to achieve an adsorption–desorption equilibrium state. Then, the MO solution containing the sample was irradiated cyclically every 10 min over a period of 2 h by a DRT−125 Hg-quartz lamp (with the power of the UV–VIS source 125 W, among them ultraviolet was 70 W; with wavelengths of the irradiation 220–400 nm and light flow 1850 lm). The desired irradiation intensity can be achieved by the variation of a distance from the lamp. In this work,

the cuvette containing MO solution with a sample was placed at the distance of 10 cm from a source of light. The dye photodegradation kinetics was studied using its concentration change, which was determined using a portable fiber optic spectrometer AvaSpec-ULS2048L-USB2-UA-RS (Avantes BV, Apeldoorn, Netherlands) by measuring the optical density at the dye absorption maximum (465 nm). The detection of light in the spectrometer was carried out by a 2048 pixel CCD detector. The special software for automated computer control for this type of spectrometer and spectra processing was used (AvaSoft 8, Apeldoorn, Netherlands).

III. RESULTS AND DISCUSSION

The surface monitoring of the photocatalyst based on ZnO, obtained by sintering metallic zinc powder, showed the presence of porosity and micro- and nanoelements of the structure (Fig. 1). Figure 1 clearly shows microgranules with a diameter of about 10 µm in diameter and aggregates of microgranules up to 30 µm in diameter. The surfaces of the spherical microgranules are coated with microneedles about 10 µm, long with the base and top diameters of about 1 µm and 100 nm, respectively.

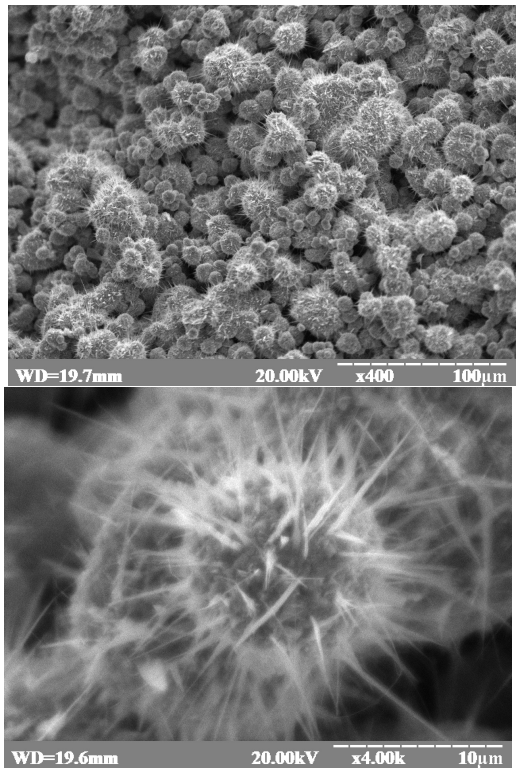

Fig. 1. Micrographs of the photocatalyst surface — a porous ZnO plate with micro- and nanoelements of the structure

Light–matter interactions during photocatalytic processes are critical and governed by the properties of the irradiated light and semiconductor material [11]. After reaching a critical thickness of approximately 89 nm for ZnO, the photocatalytic properties of the material mostly reach a plateau [11]. Therefore, the number of generated electron–hole pairs and, accordingly, the catalytic activity of the photocatalyst depend on the surface area of ZnO illuminated by a light source [2]. And our experimental sample had a developed surface.

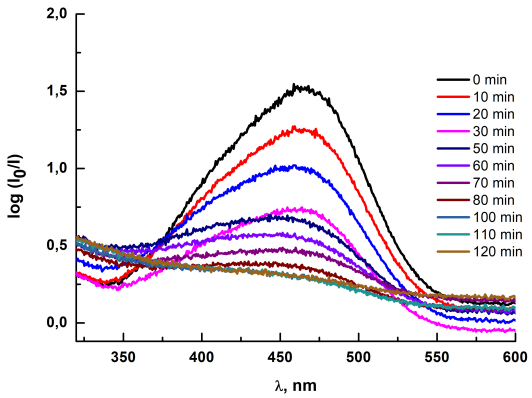

Fig. 2. Absorption spectra of an aqueous solution of MO taken at different intervals of irradiation with a DRT–125 lamp during the photocatalysis using a catalyst — porous ZnO plate with micro- and nanoelements of the structure

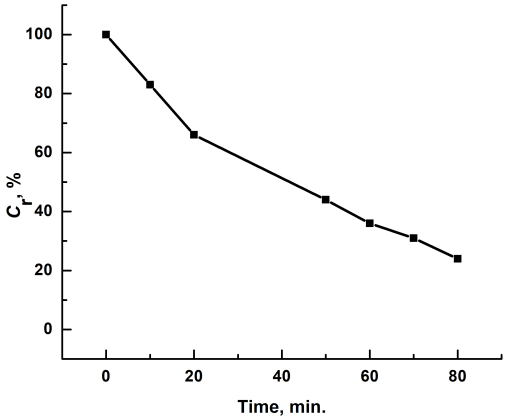

Fig. 3. Change in the relative concentration of MO with the time of irradiation during photocatalysis

The relative irradiated dye concentration C_r was calculated using the formula [4, 12]:

$$C_r = \frac{C(t)}{C_0} \times 100\,\% = \frac{A_t^{465}}{A_0^{465}} \times 100\,\%, \qquad (1)$$

where C_0 is the starting dye concentration; $C(t)$ — the dye concentration after irradiation for time t; A_0^{465} and A_t^{465} — dye solution optical densities at 465 nm before and after irradiation for time t. The dye degradation efficiency E_{eff} was calculated using the formula [1, 13]:

$$E_{\text{eff}} = [C_0 - C(t)/C_0] \times 100\,\%$$
$$= [A_0^{465} - A_t^{465}/A_0^{465}] \times 100\,\%. \qquad (2)$$

The reaction rate constant k, determined from the slope of the C_r dye concentration versus time, is used to quantify the photocatalytic activity of the sample. If the photodegradation reaction obeys first-order kinetics, then the solution of the kinetic equation can be represented as follows [1, 14]:

$$C(t) = C_0 \times \exp(-kt). \tag{3}$$

Thus, by plotting the dependence of $ln[C(t)/C_0]$ on time t, we can find the value of the reaction rate constant.

Figure 2 shows that for photocatalysis, the absorption maximum of the dye at 465 nm gradually decreases during the test time of 120 min. A permanent decrease in absorbance indicates a decrease in the concentration of MO, which is visually confirmed by the discoloration of the reaction solution.

Figure 3 shows changes in the relative concentration of the dye C_r as a function of degradation with the participation of the catalyst from the time of irradiation during photocatalysis.

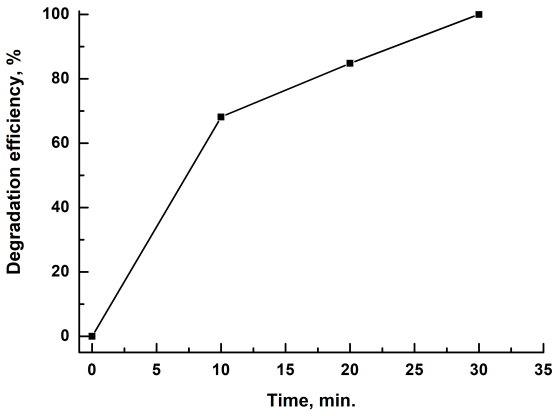

Fig. 4. Graph of the dependence of the MO degradation efficiency on the time of light irradiation using a photocatalyst a porous ZnO plate with micro- and nanoelements of the surface structure

Figure 4 presents the graph of the dependence of the MO degradation efficiency on time of light irradiation with using a photocatalyst a porous ZnO plate with micro- and nanoelements of the surface structure. After 30 min, 100 % of MO degraded.

The reaction order was determined graphically. If we plot a certain function of concentration along the ordinate axis, and time along the abscissa axis, then a straight-line dependence will indicate the correct reaction order. In our case, the obtained graphical dependence is linear in the coordinates $\ln[C(t)/C_0]$ on time, which corresponds to the first-order kinetics. Fig. 5 illustrates the results of the approximation of the photodegradation kinetics, using the first-order equation (3). The value of k for the porous ZnO plate with micro- and nanoelements of the surface structure is found to be $2.7 \cdot 10^{-4}$ sec^{-1}. The correlation coefficient for the kinetic curve of the reaction is $R = 0.9916$.

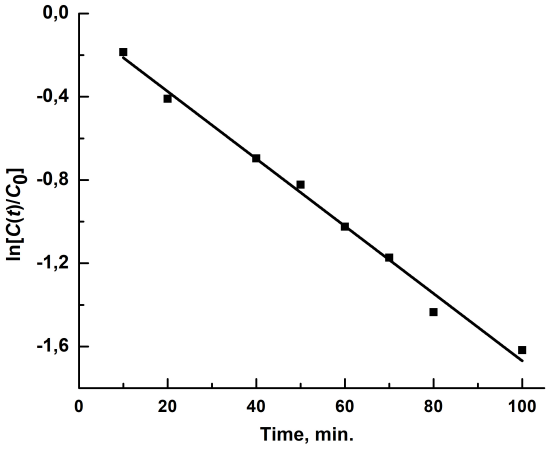

Fig. 5. The linear approximation of the kinetic curve of photocatalytic MO degradation with porous ZnO plate

Since we are dealing with reagents that are in different phases, the reaction rate will depend on the contact surface area of the phases. Substances that react in the adsorbed state must first be transferred to the surface, and then the reaction products must be desorbed from the surface. The sample created by us possessed high photocatalytic properties. For comparison, as reported in paper [8], after 180 min of illumination, the values of E_{eff} and k were found to be 48 % and $4.3 \cdot 10^{-5}$ sec^{-1} for a single ZnO crystal, respectively. For comparison, for the sample in the form of ZnO nanopowder, reported in paper [9], the values of E_{eff} and k were found to be 75 % and $8.1 \cdot 10^{-7}$ sec^{-1} in 80 min, respectively. Slightly higher than in our case, the values of the methylene blue dye degradation efficiency (100 % after 25 min of illumination) and the reaction rate constant ($3.6 \cdot 10^{-3}$ sec^{-1}) were obtained for a zinc oxide-based powder photocatalyst in the form of hierarchical microspheres with a diameter of 8–10 μm coated with nanoparticles larger than 20 nm [10]. However, a filter must be used to separate the powdered photocatalyst from the solution.

CONCLUSION

The porous zinc oxide plate with micro- and nanoelements of the surface structure was obtained by sintering metallic zinc powder and analyzed. The catalytic properties of the material in the photocatalytic degradation of MO dye were determined. Our catalyst had high catalytic activity and can be easily separated from the solution, which is important for commercial use [15].

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ГЕТЕРОГЕННИЙ ФОТОКАТАЛІЗ ПОРИСТОЇ ПЛАСТИНИ ZnO З МІКРО- ТА НАНОЕЛЕМЕНТАМИ НА ЇЇ ПОВЕРХНІ

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Пористу пластину з ZnO з мікро- та наноелементами структури поверхні отримано спіканням металевого порошку цинку, охарактеризовано та випробувано на фотодеґрадацію модельного органічного барвника (метилоранжу) у воді. Аналіз морфології поверхні фотокаталізатора на основі ZnO, отриманого спіканням порошку цинку, показав наявність пористості та мікро- і наноелементів структури. На поверхні зразка утворилися мікроґранули діаметром приблизно 10 мкм і аґрегати мікроґранул діаметром до 30 мкм. Поверхні сферичних мікроґранул покриті мікроголками довжиною приблизно 10 мкм, з діаметром основи та верхньої частини приблизно 1 мкм і 100 нм відповідно.

Для перевірки фотокаталітичних властивостей зразка ZnO використано органічний барвник метилоранж (МО) — ($C_{14}H_{14}N_3NaO_3S$). Отриманий зразок розмірами 35 мм × 7 мм × 1 мм поміщали в стандартну кварцову кювету об'ємом 3.5 мл з водним розчином метилоранжу (10 мг/л). Кювету з розчином МО зі зразком розміщували на відстані 10 см від джерела світла. Кінетику фотодеґрадації барвника вивчали за зміною його концентрації вимірюванням оптичної густини за максимуму поглинання барвника (465 нм) портативним волоконно-оптичним спектрометром AvaSpec-ULS2048L-USB2-UA-RS (Avantes BV, Апелдорн, Нідерланди).

Під час фотокаталізу максимум поглинання барвника (за 465 нм) поступово зменшувався. Уже після 30 хв опромінення фотокаталізатора ефективність розпаду барвника (E_{eff}) досягла 100 %. Постійне зниження поглинання свідчить про зменшення концентрації МО, що візуально підтверджується зміною кольору реакційного розчину. Для кількісної оцінки фотокаталітичної активності зразка використано константу швидкості реакції k, яку визначено з нахилу залежності концентрації барвника C_r від часу. Значення k для пористої пластини ZnO з мікро- та наноелементами структури поверхні становило $2.7 \cdot 10^{-4}$ с$^{-1}$.

Отриманий фотокаталізатор мав високу каталітичну активність, легко відділявся від розчину та зберігав свою цілісність після багаторазових експериментів, що важливо для комерційного використання.

Ключові слова: оксид цинку, гетерогенний фотокаталіз, фотодеґрадація, метилоранж, абсорбційна спектроскопія.