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Influence of zinc oxide morphology on its photocatalytic properties

The rapid development of industry, in addition to the positive impact, has led to environmental problems. The release of polluting waste containing substances such as dyes, pesticides, heavy metals and pharmaceutical waste leads to contamination of water reservoirs, that has a negative impact on humans and aquatic organisms. In this regard, the development of an inexpensive, effective, environmentally friendly method of waste water treatment from organic pollutants is an urgent research priority. Zinc oxide (ZnO) is one of the most active semiconductor photocatalysts. In this paper, the influence of the morphology of nanostructured zinc oxide synthesized by effective methods on photocatalytic properties with respect to the rhodamine-B dye (RhB) was investigated, and the influence of the length-to-thickness ratio (aspect ratio AR) of ZnO samples on its structural and optical properties was studied. The results of the study showed that an increase in the annealing temperature of zinc acetate in the atmosphere leads to an increase in the size of zinc oxide crystallites, while an increase in the concentration of alkali in the growth solution (synthesis of ZnO by chemical deposition from 0.4 M to 0.7 M) makes it possible to synthesize thinner extended 2D plates. It is shown that an increase in the AR value of the synthesized samples makes it possible to increase their photocatalytic activity.

Keywords: chemical deposition, zinc oxide, calcination, optical and structural properties, photocatalyst, rhodamine-B.

Introduction

In recent years, the production and use of dyes has increased dramatically, for example, azo dyes, reactive, solvent and sulfur dyes are widely used in the textile, food, adhesive, cosmetic, construction, paint, cellulose, glass and ceramic industries [1, 2]. The release of organic dyes into the environment is a source of harmful pollution of the ecosystem [3].

These organic pollutants have high chemical stability and low biodegradability, which complicates the search for an appropriate method for the purification of wastewater and water reservoirs [4]. There are many different technologies that are used for wastewater disinfection, including such as electrodialysis [5], membrane filtration [6], precipitation [7], adsorption [8], electrochemical reduction [9] and electrodeionization [10]. But traditional chemical, physical and biological processes of wastewater treatment containing dyes have such disadvantages as high cost, high energy consumption and the formation of secondary pollutants during the treatment process [4].

However, the process of photocatalysis, as an advanced oxidation technology, attracts highest attention of researchers to the decomposition of organic dyes [11, 12]. Such processes are based on light amplification of highly reactive hydroxyl radicals generation, which oxidize organic substance in solution and completely convert it into water, CO_2 and harmless inorganic compounds.

During the photocatalysis reaction, electrons and holes are generated under the action of ultraviolet or visible light falling on the surface of semiconductors, which act as charge carriers. Heterogeneous semiconductor photocatalysts such as ZnO, ZnS, and TiO_2 are of particular interest to researchers [13-16]. Among the presented semiconductor compounds, zinc oxide attracts special attention as a photocatalyst due to the environmental friendliness of its production, optical properties, low cost synthesis, photosensitivity and high thermal stability [17-19].

One of the advantages of ZnO as a photocatalyst is the high mobility of electrons (200-300 $cm^2 \cdot B^{-1} \cdot s^{-1}$), which contributes to greater photodegradation efficiency of pollutants due to rapid electron transfer. Furthermore, the rate of recombination of photogenerated electron-hole (e^- / h^+) pairs is also large. It decreases their availability to the oxidation-reduction reactions with the surrounding material and increases the dissi-

pated energy as heat [13]. Zinc oxide, possessing a wide band gap (3.37 eV) and a high exciton binding energy (60 meV), can absorb most of the UV spectrum, effectively oxidizing and decomposing harmful organic substances in wastewater [20].

Zinc oxide, used as an effective photocatalyst for the decomposition of persistent organic pollutants, must have a high specific surface area to allow the diffusion of active particles and electron transfer. Previous studies of the photocatalytic activity of ZnO have shown high efficiency in the decomposition of dyes [21-23].

Traditionally, ZnO nanoparticles (NPs) are synthesized by various physicochemical methods, but many of these methods have such disadvantages as high cost, the need for high temperature, high pressure, specialized equipment, the use of toxic and environmentally hazardous chemicals, which leads to high energy consumption and the formation of a large amount of waste that is dangerous to the environment [24].

This innovative research used effective, one-step, environmentally friendly and inexpensive synthesis methods of ZnO nanoparticles. These methods make it possible to control the size and shape of nanoparticles, which is useful for improving their chemical, physical, and photocatalytic properties. The close relationship between the morphology and properties of ZnO nanoparticles provides a wide range of its scientific and practical applications [25-29].

Experimental

In this work, the synthesis of ZnO nanoparticles was carried out by two environmentally friendly methods: direct thermal decomposition route [30, 31] and chemical deposition from solution [22].

Direct calcination was performed at cheap zinc acetate salt $(CH_3COO)_2Zn\times2H_2O$ annealing in a muffle furnace in the atmosphere at temperatures of 400 °C and 700 °C. The annealing duration was 10 hours. During annealing zinc acetate salt was placed in a ceramic crucible covered with a ceramic lid. At the same time, the mass of the obtained ZnO NPs sample was (1/4-1/3) of the initial mass of zinc acetate. According to [32], the main weight loss occurs due to the combustion of acetone ($(CH_3)_2CO$) and carbon dioxide (CO_2) in the precursor. The sample # 1 (annealing at 700 °C for 10 hours) and sample # 2 (annealing at 400 °C for 10 hours) were synthesized by this method.

During low-temperature chemical deposition of ZnO, the growth solution contained zinc acetate dihydrate $(CH_3COO)_2Zn\times2H_2O$ and sodium hydroxide NaOH, dissolved in distilled water. The concentration of zinc acetate ($ZnAc_2$) was 0.1 M. Initially, salt and alkali were dissolved in water separately for 30 minutes. For the formation of zinc oxide nanoparticles (ZnO NPs) sodium hydroxide solution at room temperature was added dropwise into a beaker with a solution of zinc acetate. Then the entire solution was thoroughly stirred on a magnetic stirrer for 15 minutes. The synthesis of ZnO samples was carried out at room temperature at all stages. The resulting precipitate was washed with distilled water, separated by centrifugation, and then dried in an oven at 100 °C for 12 hours. The synthesized ZnO powders were finished annealing in a muffle furnace at 450 °C for an hour. The alkali concentration during the synthesis of the sample # 3 was 0.4 M, and for the sample # 4 it was 0.7 M NaOH.

Morphology (FESEM), X-ray diffraction analysis (XRD), optical properties and photocatalytic activity were studied for all synthesized ZnO NPs samples.

Results and Discussion

The morphology of synthesized samples was studied by Quanta 200i 3D scanning electron microscope (FEI Company). Figure 1 shows the morphology of synthesized ZnO nanoparticles. An electron microscopy analysis showed that at zinc acetate calcination at 400 °C and 700 °C, ZnO grows in the form of rods, the geometric parameters of which increase with longer annealing of $ZnAc_2$ (Fig. 1 a, b). The thermal decomposition route at 400 °C allows to obtain more thin long ZnO rods (Fig. 1 b) then at 700 °C (Fig. 1 a). The method of chemical deposition from a solution with 0.4M and 0.7M an alkali concentration in the growth solution makes it possible to synthesize ZnO in the form of thin 2D plates (Fig. 1 c, d). Commercial ZnO NPs (sample # 5, Sigma-Aldrich, USA) with high purity 99,999 % have an irregular rectangular form (Fig. 1e).

The physicochemical characteristics of all ZnO samples are presented in Table 1. Table 1 shows that ZnO NPs sample # 2, synthesized in the form of rods, and sample # 3, synthesized by chemical deposition from solution, possessed by highest aspect ratio.

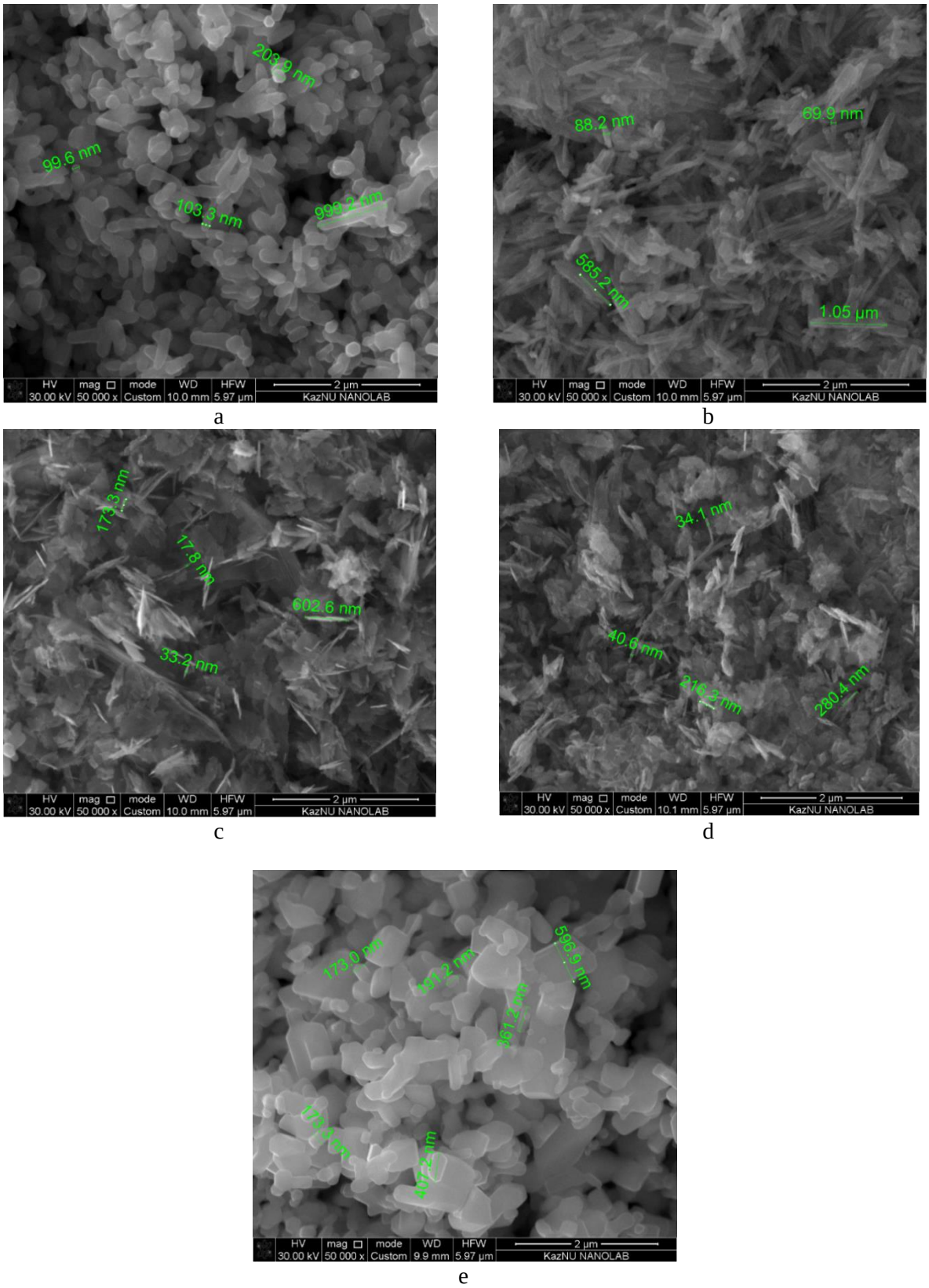

Figure 1. FESEM images of ZnO samples: a — # 1, b — # 2, c — # 3, d — # 4, e — # 5

Table 1

Physicochemical characteristics of ZnO samples

Sample	FESEM		Aspect ratio, l/d	Cell parameters, Å	
	Thickness d, nm	Length l, nm		a	c
# 1	140±20	670±50	4.8	3.243	5.197
# 2	70±20	900±50	12.9	3.245	5.200
# 3	25±5	520±5	20.8	3.253	5.209
# 4	33±5	270±5	8.2	3.251	5.208
# 5	170±20	390±50	2.3	3.251	5.208

The structural properties of the all ZnO samples were studied by X-ray diffraction analysis. X-ray diffraction measurements were performed under the same conditions for all samples on an X-ray diffractometer X'pert MPD PRO (PANalitical) (Fig. 2). The XRD peaks have been labelled according to the reference spectra (JCPDS Card No. 80-0075) of ZnO wurtzite structure with P63mc space group. We see that the (101) reflex is more intensive among all the others observed diffraction peaks that demonstrates a good crystalline quality of all considered samples. All ZnO samples show a slight difference in the intensity and width of the diffraction peaks, therefore the half-width of X-ray reflections (100), (002), and (101) was considered in more particular (Table 2).

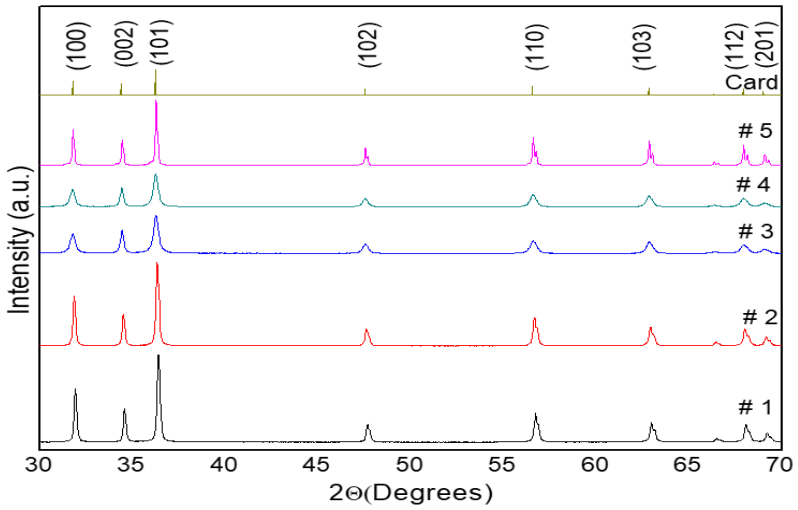

Figure 2. X-ray diffraction of ZnO samples

The results of the study showed that an increasing of the annealing temperature of zinc acetate in the atmosphere leads to an increasing in the size of zinc oxide crystallites along the (002) and (101) directions. It is noted that an increase in the concentration of alkali in the growth solution from 0.4 M to 0.7 M during the ZnO synthesis by chemical deposition makes it possible to obtain thinner extended 2D plates.

Table 2

Half-width of X-ray reflections of ZnO samples

Sample		FWHM	
	(100)	(200)	(101)
# 1	0,18	0,16	0,19
# 2	0,18	0,19	0,20
# 3	0,34	0,20	0,34
# 4	0,31	0,22	0,32
# 5	0,14	0,16	0,16

The ZnO crystallites sizes (d) were estimated based on the XRD analysis for the most intense peak (101) by employing the Scherrer's formula,

$$d = k\lambda / \beta \cos \theta, \qquad (1)$$

here k=0.89 is a dimensionless coefficient (Scherrer's constant), λ = 1.54 Å is the wavelength of CuKa radiation, θ is the diffraction angle, and β is the half-width of X-ray reflections in radians. The obtained results are consistent with the data of electron microscopy (Table 1).

The optical absorption spectra were measured by a double-beam UV / Vis Lambda 35 spectrophotometer (PerkinElmer). Figure 3 shows the absorption spectra in the UV-visible region of all considered ZnO samples. All samples are transparent in the visible spectrum and absorb light in the UV range. The maximum absorption is observed at a wavelength of 375 nm, that is corresponds to ~ 3,31 eV optical band gap according to Tauc's extrapolation [33].

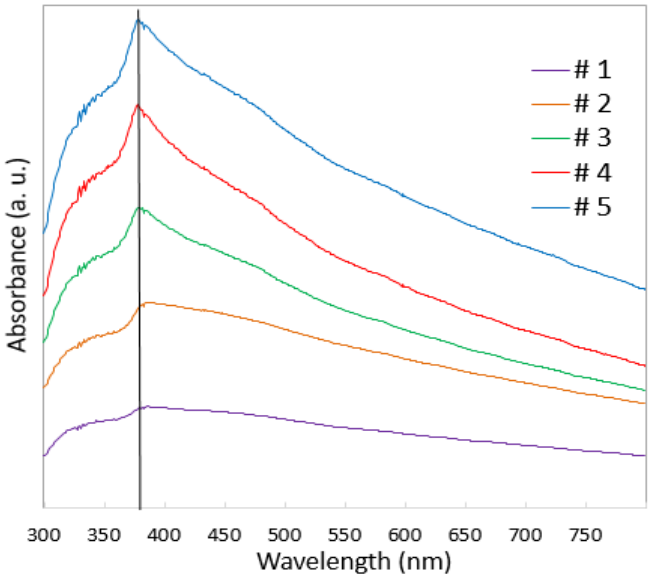

Figure 3. Absorbance spectra of synthesized ZnO samples

Photocatalysis is a change in the rate of chemical reactions under the action of catalytic substances that are activated at light irradiation, and participate in the reaction, but they are not included in the final products. Measurement of the photocatalytic activity of all synthesized ZnO NPs samples was carried out while observing the decomposition of the test substance, the dye rhodamine-B ($C_{28}H_{31}ClN_2O_3$, IMP, OAS "Reactive", Russia). Photocatalytic decomposition usually includes photoexcitation, charge separation and migration, and surface redox reactions [34]. Figure 4 is a schematic diagram illustrated the photocatalytic mechanism of dye decomposition in the presence of ZnO.

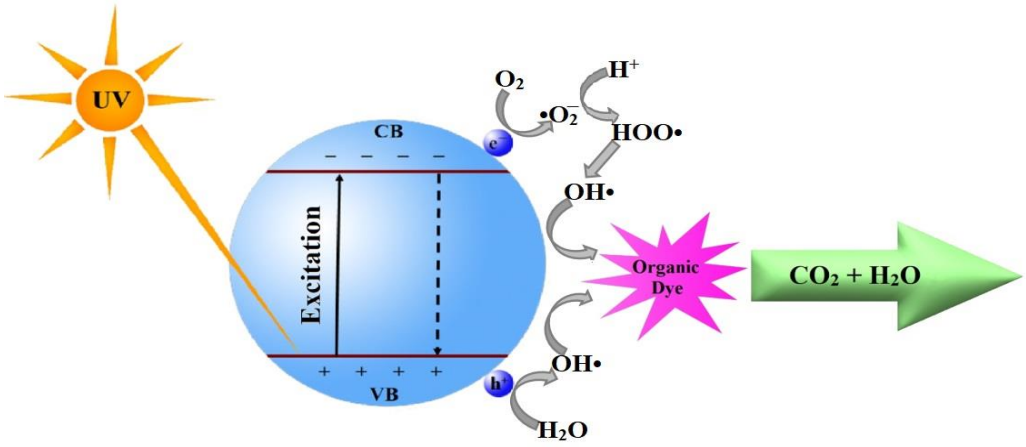

Figure 4. Scheme of the RhB decomposition mechanism on the ZnO NPs surface

Under UV light illuminated, an electron (e^-) from the ZnO valence band passes into the conduction band, and a hole (h^+) is formed in the valence band. The formed e^- (h^+) reacts with a water molecule (atmospheric oxygen), because of which hydroxyl radicals OH• and superoxide anions $•O_2^-$ are formed, and at the same time protonation gives HOO• radicals. The radicals are oxidized, leading to the production of intermediate compounds. The intermediate compounds eventually destroy the organic dye, forming CO_2 and H_2O as shown in Figure 4, while the following reactions are possible [35, 36]:

$$\begin{gathered}
ZnO + h\nu \rightarrow ZnO_{CB}\,(e^-) + ZnO_{VB}(h^+), \\
ZnO_{VB}(h^+) + H_2O \rightarrow ZnO + H^+ + OH•, \\
ZnO_{VB}(h^+) + OH^- \rightarrow ZnO + OH•, \\
•O_2^- + H^+ \rightarrow HOO•, \\
HO_2• + HO_2• \rightarrow H_2O_2 + O_2, \\
ZnO_{CB}\,(e^-) + H_2O_2 \rightarrow OH• + OH^-, \quad (2) \\
H_2O_2 + •O_2^- \rightarrow OH• + OH^- + O_2, \\
H_2O_2 + h\nu \rightarrow 2OH•, \\
\text{Organic pollutants} + OH• \rightarrow \text{Intermediates}, \\
\text{Intermediates} \rightarrow CO_2 + H_2O.
\end{gathered}$$

An aqueous dye solution, containing 0.08 mg RhB in 500g of distilled water was used at the investigation of the photocatalytic activity of the synthesized and commercial ZnO NPs under ultraviolet radiation. 9 mg of the ZnO sample was added to this solution. The prepared solution was treated in an ultrasonic bath for 30 min, followed by stirring on a magnetic stirrer at room temperature. A mercury arc lamp (LEH Germany UL Q 14 4P SE) with a power of 14 W, which was placed in a flask with a prepared dye solution, was used for ultraviolet illumination.

It was noted that with an increase in the exposure time, the absorption intensity of RhB gradually decreases in the presence of ZnO NPs, which indicates a decrease in the concentration of the RhB dye. The comparative concentration of RhB dye decreases with increasing exposure time, while for all the presented samples, RhB dye significantly decomposes on the ZnO NPs surface under the influence of UV illumination in the first 30 minutes of exposure and almost completely disappears after 150 minutes. Figure 5 is a photo of initial RhB solution and after each subsequent 30 minutes of UV exposure in the presence of a sample # 3.

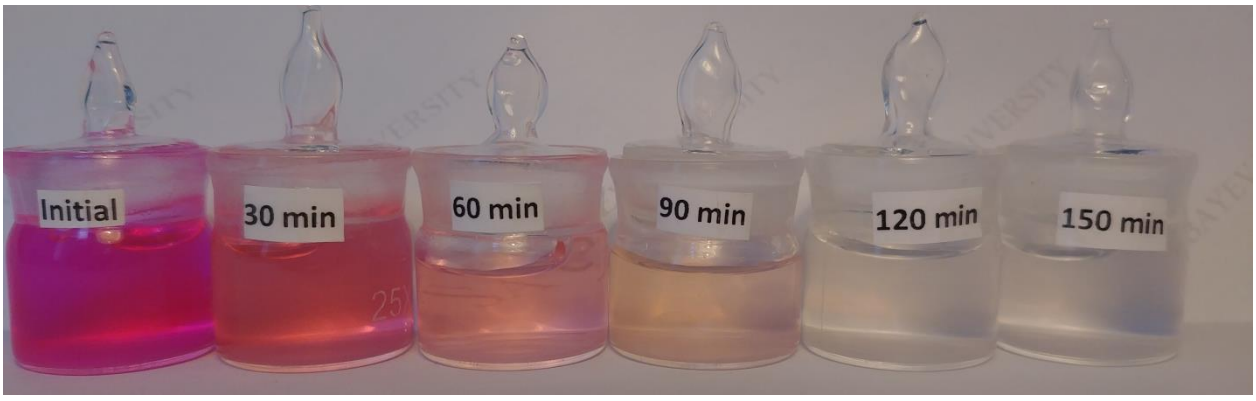

Figure 5. Photo of RhB solution in the presence of # 3 after each 30 min of UV exposure

In order to perform a quantitative analysis of the photocatalytic activity of all synthesized samples of ZnO NPs, the ratio $R = C / C_0$ was calculated as a function of the time of UV illumination (Fig. 6). In this ratio, C is the dye concentration after irradiation with UV radiation at the maximum intensity, C_0 is the initial concentration of the RhB dye.

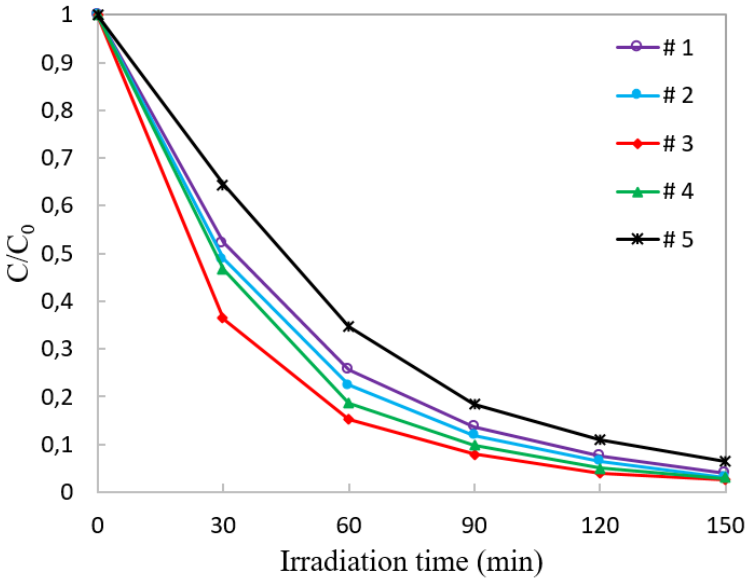

Figure 6. Photodegradation curves of RhB solution by using ZnO NPs as catalysts under irradiation with UV light

The Langmuir — Hinshelwood kinetic model was used to estimate the photodegradation rate k of ZnO NPs [36, 37]:

$$\ln (C_0 / C) = kt, \quad (3)$$

hence

$$k = \frac{lnR}{-t} = \frac{ln\,(C_0 / C)}{t}. \quad (4)$$

The dependence of $\ln(C_0/C)$ as a function of the UV illumination time is shown in Figure 7. The values of both the minimum k_{min}, maximum k_{max}, and the average degradation rate k_{av} of the dye in the presence of ZnO photocatalysts, calculated after each 30 minutes, are shown in Table 2. Based on the ratio R* = 100 (1 — R), the percentage of the decomposed RhB dye in an aqueous solution for 2.5 hours of exposure in the presence of considered ZnO samples was calculated.

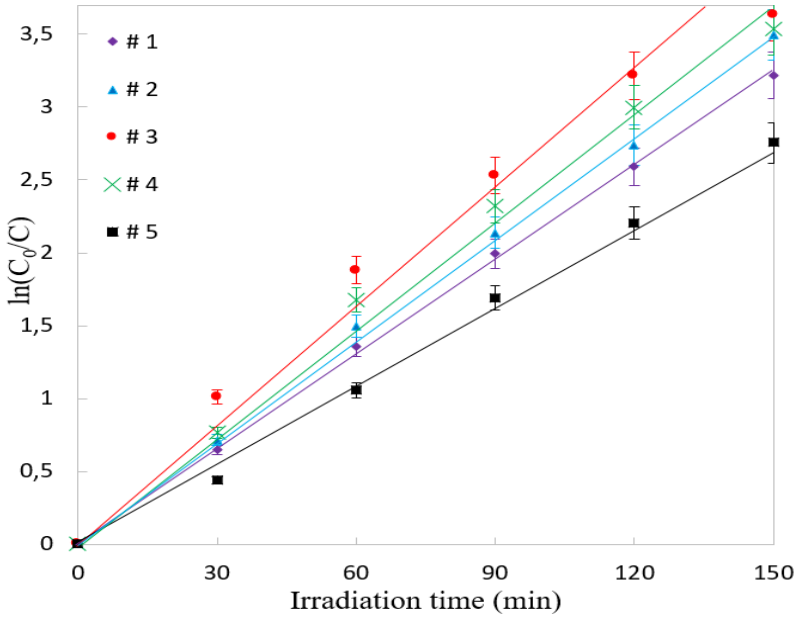

Figure 7. Plots of $\ln(C_0/C)$ as function of UV light irradiation time for the degradation of RhB dye in the presence of ZnO samples as photocatalyst

Figures 6 and 7 show that all studied samples have high photocatalytic activity. It was noted that the highest activity corresponds to samples # 3 that has the highest AR of considered ZnO samples (Table 1). Others ZnO samples demonstrate a slightly less photoactivity. The smallest photoactivity has commercial ZnO sample #5 with smallest AR.

Table 3

Photocatalytic efficiency of ZnO samples

Sample	R* after 150 min, %	k, min^{-1}		k_{av}, min^{-1}	k_{av}, hr^{-1}
		min	max		
# 1	95.9888	0.0214	0.0226	0.0219	1.3131
# 2	96.9607	0.0228	0.0249	0.0237	1.4241
# 3	97.3601	0.0242	0.0337	0.0289	1.7312
# 4	97.0830	0.0236	0.0280	0.0256	1.5331
# 5	93.6376	0.0146	0.0188	0.0176	1.0534

As follows from Figure 7 and Table 3, in the presence of all considered ZnO samples, a high rate of RhB decomposition in an aqueous solution under UV radiation is observed. The average degradation rate of the dye varies from 0.0176 min^{-1} (for the commercial ZnO sample) to 0.0289 min^{-1} (for the sample # 3). It was noted that ~ (94 — 97) % of the initial dye concentration in the aqueous solution decomposes after 150 minutes of exposure in the presence of these samples. The highest percentage of RhB decomposition corresponds to the sample # 3 (~ 97.4 %) with k_{max} = 0.0337 min^{-1}, synthesized at room temperature by a low-cost chemical deposition from a water grow solution with 0.4M NaOH.

Conclusions

The effect of the morphology of ZnO NPs samples synthesized by simple, low-cost, environmentally friendly synthesis methods: direct thermal decomposition route and chemical deposition, on their optical and photocatalytic properties with respect to the degradation of the rhodamine-B dye in an aqueous solution under the action of UV radiation was studied. It is shown that during thermal decomposition of zinc acetate in the atmosphere at 400 °C and 700 °C for 10 hours, ZnO particles are formed in the form of rods of different diameters. The used parameters of chemical deposition from solution at an alkali concentration of NaOH in the growth solution of 0.4 and 0.7 M make it possible to grow ZnO in the form of thin 2D plates. The results of X-ray diffraction, analysis of the half-width of X-ray reflections, as well as consistent with them scanning electron microscopy data of synthesized ZnO samples showed that the determining factor for photocatalytic activity is the value of the AR parameter. Thus, an increase in the aspect ratio of ZnO NPs makes it possible to obtain more photocatalytically active ZnO samples. All studied samples demonstrate high photocatalytic activity. Within 2.5 hours of UV exposure in the presence of these samples ~ (94 — 97) % of the initial concentration of dye in the aqueous solution decomposes. The highest percentage of RhB decomposition corresponds to the sample # 3 synthesized at room temperature by a low-cost chemical deposition from a solution with 0.4 M NaOH in the growth solution. This sample has the highest value of the AR parameter. In the presence of all the considered samples of ZnO NPs, a high rate of degradation of the RhB dye in an aqueous solution under the influence of UV radiation is noted (0.0176 min^{-1} — 0.0289 min^{-1}). Hence, all considered methods used for the synthesis of ZnO NPs with the indicated parameters make it possible to obtain highly active photocatalysts for the decomposition of organic dyes under UV radiation. These methods are economical, easy to implement, do not require complex expensive equipment, and are appropriate for large-scale production.

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Мырыш оксиді морфологиясының оның фотокаталитикалық қасиеттеріне әсері

Өнеркәсіптің қарқынды дамуы оң әсерін тигізумен қатар экологиялық мәселелерді де тудырды. Құрамында бояғыштар, пестицидтер, ауыр металдар және фармацевтикалық қалдықтар сияқты заттары бар ластаушы қалдықтардың шығарылуы судың ластануына әкеліп соғады, бұл адамдар мен су организмдеріне кері әсерін тигізеді. Осыған байланысты ағынды суларды органикалық ластаушы заттардан тазартудың арзан, тиімді, экологиялық таза әдісін жасау ғылыми зерттеулердің өзекті міндеті болып табылады. Мырыш оксиді (ZnO) — ең белсенді жартылай өткізгіш фотокатализаторлардың бірі. Мақалада тиімді әдістермен синтезделген наноқұрылымды мырыш оксидінің морфологиясының родамин-В (RhB) бояғышына қатысты фотокаталитикалық қасиеттерге, сондай-ақ ZnO үлгілерінің ұзындық пен қалыңдық (Ar) қатынасының оның құрылымдық және оптикалық қасиеттеріне әсері зерттелген. Зерттеу нәтижелері атмосферадағы мырыш ацетатының күйдіру температурасының жоғарылауы мырыш оксиді кристаллиттерінің мөлшерінің ұлғаюына әкелетінін және өсу ерітіндісіндегі сілтілік концентрациясының жоғарылауы (ZnO химиялық ыдырау әдісімен 0,4 М-ден 0,7 М-ге дейін синтезделуі) жұқа, ұзартылған 2D пластиналарды алуға мүмкіндік беретінін көрсетті. Синтезделген үлгілердің AR мәнін арттыру олардың фотокаталитикалық белсенділігін арттыруға мүмкіндік беретіні анықталған.

Кілт сөздер: химиялық тұндыру, мырыш оксиді, термиялық ыдырау, оптикалық және құрылымдық қасиеттері, фотокатализатор, родамин-В.

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Влияние морфологии оксида цинка на его фотокаталитические свойства

Бурное развитие промышленности, помимо положительного влияния, привело к экологическим проблемам. Выброс загрязняющих отходов, содержащих такие вещества, как красители, пестициды, тяжелые металлы и фармацевтические отходы, приводит к загрязнению водоемов, что оказывает негативное воздействие на человека и водные организмы. В связи с этим разработка недорогого, эффективного, экологически чистого способа очистки сточных вод от органических загрязнителей является актуальной задачей научных исследований. Оксид цинка (ZnO) является одним из наиболее активных полупроводниковых фотокатализаторов. В статье исследовано влияние морфологии наноструктури-

рованного оксида цинка, синтезированного эффективными методами, на фотокаталитические свойства по отношению к красителю родамина-B (RhB), а также изучено влияние соотношения длины к толщине (AR) образцов ZnO на его структурные и оптические свойства. Результаты исследования показали, что повышение температуры отжига ацетата цинка в атмосфере приводит к увеличению размеров кристаллитов оксида цинка, а увеличение концентрации щелочи в ростовом растворе (синтез ZnO методом химического осаждения от 0,4M до 0,7M) позволяет получать более тонкие протяженные 2D пластины. Доказано, что увеличение значения AR синтезированных образцов позволяет повышать их фотокаталическую активность.

Ключевые слова: химическое осаждение, оксид цинка, термическое разложение, оптические и структурные свойства, фотокатализатор, родамин-B.

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