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ZINC OXIDE AS A PROMISING ECOLOGICAL PHOTOCATALYST: PROPERTIES, SYNTHESIS AND APPLICATION

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Researching and understanding of the basic physical properties of zinc oxide is important for many reasons. For example, they are useful for the rational design of functional devices and for developing their potential as building blocks for future nanoscale devices. Due to its electrical properties, zinc oxide is very attractive for optoelectronic and electronic devices. For example, a device made of zinc oxide material has a high breakdown voltage, lower noise, and can operate at higher temperatures with greater operating power. The optical properties of zinc oxide nanostructures are related to both internal and external effects. Internal optical transitions occur between electrons in the conduction band and holes in the valence band, including exciton effects due to Coulomb interaction. External properties are associated with additives or defects that typically create discrete electronic states in the band gap, and therefore affect both optical absorption and emission processes.

There are two main methods used in the synthesis and production of zinc oxide nanostructures. These techniques are called «top-down» and «bottom-up». The top-down technique refers to a fabrication technique whereby an object is created by carefully removing pieces of a larger object, essentially carving out the desired object. The bottom-up approach, or sometimes referred to as the self-assembly approach, uses chemical or physical forces operating at the nanoscale to assemble basic units into larger structures.

In this work, the regularities of the photocatalytic decomposition of Congo red and methylene blue dyes under flowing (dynamic) conditions were studied using samples of zinc oxide of the wurtzite type synthesized by the sol-gel method. In a model photocatalytic process implemented in the presence of a synthesized ZnO sample of 2 and 3 g, an average of 75% dye decomposition was achieved in 3 hours of UV irradiation. Such experimental data indicate a greater influence of the duration of ultraviolet irradiation than the dose of the applied photocatalyst.

The study of the acid-base properties of the surface of the synthesized powder showed the presence of acidic Brønsted centers with a pK_a of 6.4 and basic Brønsted centers with a pK_a of 9.45. The study of the pH of the solutions of the studied dyes during photocatalytic decomposition in the presence of the synthesized photocatalyst showed that its value shifts to the acidic region for both dyes. *Key words:* zinc oxide, wurtzite, photocatalysis, Congo red, methylene blue.

Цинк оксид як перспективний екологічний фотокаталізатор: властивості, синтез та застосування. Іваненко І.М., Феденко Ю.М., Гуцул Х.Р., Кліменков О.М.

Дослідження та розуміння основних фізичних властивостей цинк оксиду є важливими з багатьох причин. Наприклад, вони корисні для раціонального проектування функціональних пристроїв та для розвитку їхнього потенціалу, як будівельних блоків для майбутніх нанорозмірних пристроїв. Завдяки електричним властивостям цинк оксид представляє велику привабливість для оптоелектронних та електронних пристроїв. Наприклад, пристрій, виготовлений з цинк оксиду, має високу напругу пробою, менший рівень шуму і може працювати при більш високих температурах з великою робочою потужністю. Оптичні властивості наноструктур цинк оксиду пов'язані як із внутрішніми, так і з зовнішніми ефектами. Внутрішні оптичні переходи відбуваються між електронами в зоні провідності та дірками в валентній зоні, включаючи екситонні ефекти внаслідок кулонівської взаємодії. Зовнішні властивості пов'язані з добавками або дефектами, які, як правило, створюють дискретні електронні стани в зазорі, і, отже, впливають як на процеси оптичного поглинання, так і на випромінювання.

Існує два основних метода, що використовуються при синтезі та виробництві наноструктур ZnO. Ці прийоми називаються «зверху вниз» і «знизу вгору». Техніка «зверху вниз» відноситься до технології виготовлення, за допомогою якої об'єкт створюється обережним видаленням шматочків більшого об'єкта, по суті вирізаючи бажаний об'єкт. Підхід «знизу вгору», або його іноді називають підходом до самозбирання, використовує хімічні або фізичні сили, що діють в наномасштабі, для збирання основних одиниць у більші структури.

У даній роботі досліджувалися закономірності фотокаталітичного розкладання барвників Конго червоного та метиленового синього в проточних (динамічних) умовах із використанням зразків цинк оксиду типу вюрцит, синтезованого золь-гель методом. У модельному фотокаталітичному процесі, реалізованому у присутності синтезованого зразку ZnO масою 2 та 3 г, за 3 години УФ опромінення вдалось досягнути ступеня розкладання барвників в середньому 75%. Такі експериментальні дані свідчать про більший вплив тривалості дії ультрафіолетового опромінення, ніж дози застосованого фотокаталізатору.

Вивчення кислотно-основних властивостей поверхні синтезованого порошку показало наявність кислотних центрів Бренстеда з pK_a 6,4 та основних центрів Бренстеда з pK_a 9,45. Як показало дослідження pH розчинів досліджених барвників в ході фотокаталітичного розкладання у присутності синтезованого фотокаталізатора, його значення зміщується в кислу область для обох барвників. *Ключові слова:* цинк оксид, вюрцит, фотокаталіз, конго червоний, метиленовий синій.

Introduction. *Physical properties of wurtzite zinc oxide*. Researching and understanding of the basic physical properties of zinc oxide is important for many reasons. For example, they are useful for the rational design of functional devices and for developing their potential as building blocks for future nanoscale devices.

Table 1

Physical properties of wurtzite (at 300 K) [5]

Property	Value
a_0, nm	0.32495
c_0, nm	0.52069
a_0/c_0	1.602
U	0.345
Density, g/cm^3	5.606
Stable phase at 300 K	Wurtzite
Bond length, Å	1.977
Melting point, °C	1975
Thermal conductivity, W/cm·K	0.6–1.2
Static dielectric constant	8.656
Refractive index	2.008; 2.029
Band gap, eV	3.4
Knoop's hardness, N/cm^2	0.5
Bulk hardness, GPa	5.0±0.1
Ionicity, %	62
Heat capacity, J/mol·K	40.2
Jung's module, GPa	111.2±4.7
Involuntary polarization, S/m^2	-0.057

Table 1 shows a compilation of the main physical parameters for bulk zinc oxide. It is worth noting that there is still some uncertainty in these values. For example, several reports only mention the physical properties of the type of zinc oxide, and hence the hole mobility and effective mass are still under discussion [1, 2]. In addition, as the size of semiconductor materials continuously decreases to the nanometer or even smaller scale, some of their physical properties undergo changes known as «quantum size effects». Quantum confinement increases the band gap of zinc oxide nanowires, which has been confirmed by photoluminescence measurements [3, 4].

Mechanical properties. Direct measurement of the mechanical properties of individual ZnO nanostructures is a really difficult task. Therefore, there are very few experimental studies on the mechanical properties of ZnO nanostructures. In fact, the lack of experimental studies on ZnO nanostructures is mainly due to some problems arising from the characterization methods of nanoscale material, such as sample manipulation, alignment and gripping to achieve the desired boundary conditions, and the application and measurement of force and displacement with very high resolution [6]. According to Table 1, ZnO is a relatively soft material, with a hardness of 5 GPa at a plastic penetration depth of 300 nm (for a ZnO mass oriented on the c-axis). Some researchers have tried different techniques to measure the Young's modulus of ZnO nanostructures. Based on the resonant excitation caused by an electric field, the bending modulus of ZnO nanobelts was characterized using a transmission electron microscope (TEM) [7]. In this method, a special TEM sample holder was fabricated to apply an oscillating electric field between the ZnO nanobelt and a fixed electrode. This electric field drove the vibration of the nanobelt, and resonant oscillations were achieved by tuning the frequency of the motion. Following the classical theory of elasticity, the bending modulus was calculated and found to be 50 GPa.

In addition, atomic force microscope (AFM) experiments are popular methods for the mechanical characterization of ZnO nanostructures. Since the stiffness of the AFM tip is very small, the resolution of the force measurement is very high (nano-newtons). In this technique, a very soft spring (e.g., a cantilever beam) was used to bend the ZnO nanowire. Researchers have used this technique to measure the Young's modulus of ZnO nanowires [8, 9]. They reported different values of the Young's modulus of 29±8 and 97±18 GPa. On a massive scale, the Young's modulus of zinc oxide in the [001] direction is 140 GPa [10], which is significantly higher than the value of the modulus reported for ZnO nanostructures.

Electrical properties. Due to its electrical properties, ZnO is very attractive for optoelectronic and electronic devices. For example, a device made of ZnO material has a high breakdown voltage, lower noise, and can operate at higher temperatures with a large operating power. The background concentration of the ZnO carrier is typically 10^{16} cm^{-3}, and the effective electron mass of ZnO is 0.24 m_0 (m_0 is the mass of free electrons), while the effective hole mass is 0.59 m_0 [5]. In addition, studies of electrical transport after configuring individual ZnO nanowires as field-effect transistors confirm that the grown ZnO nanowires exhibit n-type behavior [11]. Typically, the field-effect mobility of grown nanowires is 20–100 cm^2/V·s [12]. Later, scientists reported an electron mobility of 1000 cm^2/V·s after coating the nanowires with a polyimide passivation layer to reduce scattering and trapping of electrons on the surface. Recently, it has been found that after coating ZnO nanowires with a SiO_2 layer followed by Si_3N_4 for surface state passivation, the mobility of ZnO nanowires can be significantly increased to over 4000 cm^2/V·s [13]. These results indicate that devices based on ZnO nanostructures have exceptional potential in high-speed electronics applications.

Optical properties. The optical properties of ZnO nanostructures have been widely studied due to their promising potential in optoelectronics. The optical properties of ZnO nanostructures are related to both internal and external effects. The internal optical transitions occur between electrons in the conduction band and holes in the valence band, including excitonic effects due to Coulomb interaction. External properties are associated with additives or defects that tend to create discrete electronic states in the band gap, and therefore affect both optical absorption and emission processes. ZnO is typically formed as an n-type semiconductor material in which electrical conductivity is due to excess zinc, presumably interstitially within the lattice and oxygen vacancies [14]. External defects,

such as hydrogen, are more often included as minor donors [15]. In general, ZnO is a wide semiconductor bandgap material (3.4 eV), making it potentially useful for efficient UV laser diodes and low power thresholds for room temperature pumping. It is also one of the promising materials for high temperature and high power devices. High-temperature operation requires a wide bandgap so that the internal carrier concentration remains. High-power operation is attractive for wide bandgap semiconductors because of the larger breakdown fields.

Materials and methods. *Synthesis of zinc oxide samples*. The synthesis of zinc oxide was carried out using the sol-gel method. To do this, 10 g of zinc acetate was dissolved in 300 cm^3 of ethanol at 80 °C and under constant stirring for 10 hours to obtain a clear solution. The resulting solution was then cooled to 0 °C and NaOH solution (0.225 mol/dm^3) was added dropwise to form a white gel. The resulting gel was left to age for 3 days. After that, the precipitate was separated on a vacuum filter and calcined for 3 hours at 500 °C [15].

The following dyes were used as research materials: Congo red and methylene blue. Congo red is an organic substance belonging to the class of azo dyes. In the literature, this substance may be referred to as: dinitrium salt of 4,4-bis(1-amino-4-sulfo-2-naphthylazo) biphenyl, congorot, kongorot. The formula is $C_{32}H_{22}N_6Na_2O_6S_2$. The molar mass is 696.665 g/mol [16]. Structural formula of Congo red is presented in Fig. 1.

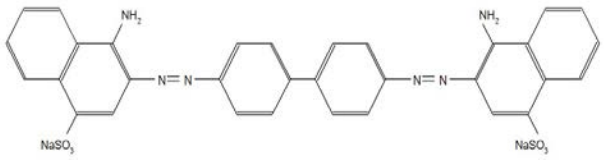

Fig. 1. Structural formula of Congo red

Methylene blue is an organic substance belonging to the class of azo dyes. In the literature, this substance can be called: methylene blue, methylenblau, methylthionii chloridum, N, N, N', N'-tetramethylthionine chloride trihydrate, 3,7-bisdimethylaminophenothiocyanine chloride [17]. Structural formula of methylene blue is presented in Fig. 2.

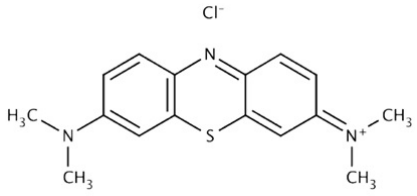

Fig. 2. Structural formula of methylene blue

To study the rate of photocatalytic activity of the synthesized zinc oxide, the following experiments were performed.

Photocatalytic decomposition of Congo red in a flow-through unit. A concentration of the dye of 5 mg/dm^3 was used to study the photocatalytic activity of the synthesized sample toward Congo red under dynamic conditions. The suspension consisting of zinc oxide and dye was exposed to ultrasound for 5 minutes. Then the suspension was quantitatively transferred to a vessel with a capacity of 5 dm^3 to the total volume of the dye solution. After that, the pump was turned on to pump the solution, and after 20 minutes, the UV lamp was turned on. Samples were taken every 5 min for 30 min, and then every 10 min for the next 150 min. The suspension was then filtered through a syringe membrane filter and the residual dye concentration was determined.

Photocatalytic decomposition of methylene blue in a flow-through unit. A methyl blue solution of 5 mg/dm^3 was used to study methyl blue under dynamic conditions. A suspension of the photocatalyst in a small volume of the solution of the dye under study was first exposed to ultrasound for 5 min. The resulting suspension was quantitatively transferred to a 5 dm^3 vessel to the total volume of the dye solution. Next, the pump was turned on to pump the solution and the UV lamp was turned on after 20 minutes. Samples were taken every 5 min for 30 min, and then every 10 min for 150 min.

Acid-base properties of the surface. The Hammett method was used to study the acid-base properties of the surface, namely the distribution of surface centers by acidity [18]. This method involves the use of 13 indicators with different pK_a values in the range from +0.80 to +12.8. The list of these indicators and their characteristics are presented in Table 2.

Table 2

Characterization of acid-base indicators

№	Indicator	pK_a	λ_{max}, nm
1	Crystal purple	+0.8	580
2	Diamond green	+1.3	610
3	Methyl orange	+3.46	460
4	Bromophenol blue	+4.1	590
5	Methyl red	+5.0	430
6	Chrysoidine	+5.5	448
7	Bromocresol purple	+6.4	540
8	p-Nitrophenol	+7.15	360
9	Bromothymol blue	+7.3	430
10	Thymol blue	+8.8	430
11	Pyrocatechin	+9.45	274
12	Tropheoline 00	+12.0	440
13	Indigocarmine	+12.8	610

Results and discussion. Experimental data on the photocatalytic decomposition of Congo red in a flow-through unit are shown in Fig. 3–4.

As can be seen from the histogram shown in Fig. 3, a solution of Congo red dye with an initial concentration of 5 mg/dm^3 of a volume of 3 dm^3 undergoes discoloration up to 75 % when the decomposition process with UV irradiation lasts for 180 min at a mass of ZnO of 2 g. In

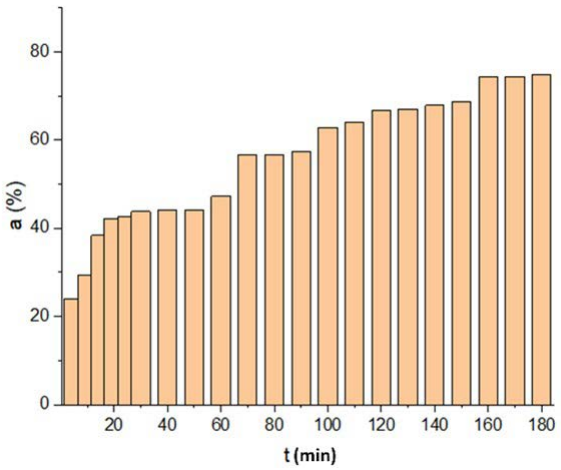

Fig. 3. The degree of photocatalytic decomposition of Congo red (m_{ZnO} = 2 g)

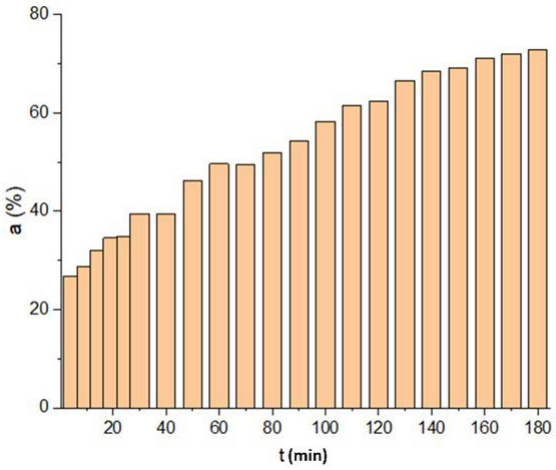

Fig. 5. Degree of photocatalytic decomposition of methyl blue (m_{ZnO} = 2 g)

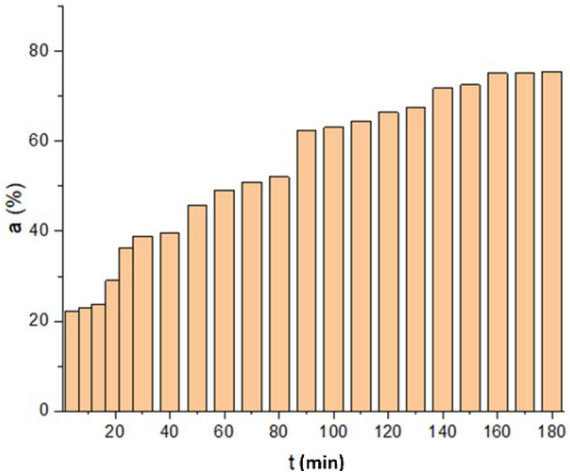

Fig. 4. The degree of photocatalytic decomposition of Congo red (m_{ZnO} = 3 g)

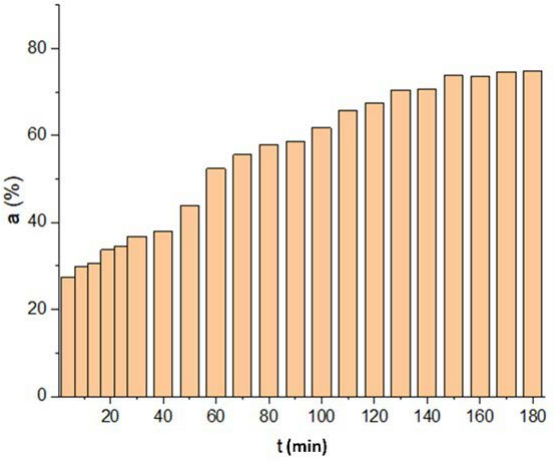

Fig. 6. Degree of photocatalytic decomposition of methyl blue (m_{ZnO} = 3 g)

the first 10 minutes, the degree of discoloration is 30 %, and in the next 60 minutes it rises to 57 %.

It is shown from the histogram in Fig. 4 that a solution of Congo red dye with an initial concentration of 5 mg/dm^3 of a volume of 3 dm^3 is subjected to discoloration only up to 76 %, with UV irradiation duration of 180 min at a mass of ZnO of 3 g. In the first 10 minutes, the solution is discolored by 23 % and after 60 minutes by 51 %.

Comparing the data of Figs. 3 and 4, it can be concluded that when implementing the photocatalytic decomposition process under dynamic conditions, the duration of UV irradiation has a greater effect on the degree of photocatalytic decomposition of Congo red than the weight of the photocatalyst used.

Experimental data on the photocatalytic decomposition of methylene blue in a flow-through unit are shown in Fig. 5–6.

As can be seen from the histogram in Fig. 5, a solution of methyl blue dye with an initial concentration of 5 mg/dm^3 of a volume of 3 dm^3 undergoes a decolorization of up to 73 % when the decomposition process with UV irradiation lasts for 180 min at a mass of ZnO of 2 g. In the first 10 minutes, the degree of decolorization is 29 %, and in the next 60 minutes it reaches 51 %.

From the histogram in Fig. 6 shows that a solution of methyl blue dye with an initial concentration of 5 mg/dm^3 of a volume of 3 dm^3 undergoes discoloration up to 75 % when the decomposition process with UV irradiation lasts for 180 min at a mass of ZnO of 3 g. In the first 10 minutes, the degree of discoloration is 30 %, and in the next 60 minutes it reaches 53 %.

Comparing the data of Figs. 5 and 6, it can be concluded that when implementing the photocatalytic decomposition process under dynamic conditions, the duration of UV irradiation has a greater effect on the degree of photocatalytic decomposition of methyl blue than the weight of the photocatalyst used.

Fig. 7 shows the distribution of surface centers by the degree of acidity of the synthesized zinc oxide.

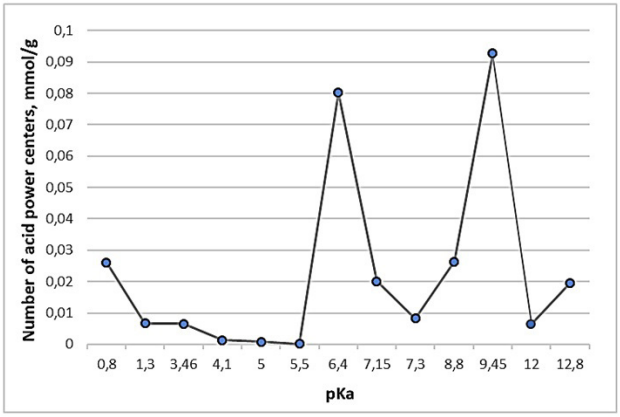

Fig. 7. Distribution of surface centers of synthesized ZnO by the degree of acidity

As can be seen in Fig. 7, to the left of the neutrality point (pH 7) are the acidic centers on which the basic indicators (pH < 7) adsorb. On the right are the basic centers on which acidic indicators (pH > 7) adsorb. At pH 7, the adsorbate molecules and surface centers have basic and acidic properties equally. The surface properties of the synthesized ZnO are determined by the presence of intense peaks in the weakly acidic (pK_a = 6.4) and weakly basic Brønsted regions (pK_a = 9.45). Therefore, the sample is characterized by low proton acceptor and proton donor properties. However, due to the presence of a peak in the neutral region, it is possible that the established equilibrium is shifted towards the manifestation of proton-acceptor or proton-donor properties by the centers.

Conclusions. In a model photocatalytic process implemented in a flow unit in the presence of a synthesized ZnO sample of 2 and 3 g, an average of 75 % of Congo red and methyl blue dyes decomposition was achieved in 3 hours of UV irradiation. Such an experimental data indicate a greater influence of the duration of ultraviolet irradiation than the dose of the applied photocatalyst.

The study of the acid-base properties of the surface of the synthesized powder showed the presence of acidic Brønsted centers with a pK_a of 6.4 and basic Brønsted centers with a pK_a of 9.45. The role of such centers is played by hydroxyl surface groups, which are differently attached to the surface of the synthesized zinc oxide crystals.

As shown by the study of the pH of the solutions of the studied dyes during photocatalytic decomposition in the presence of the synthesized photocatalyst, it shifts to the acidic region for both dyes. This indicates the destruction of the molecules of the model pollutants and is also indirect evidence of the formation of new compounds to which the studied dyes decompose because of photodegradation.

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