PHOTOCATALYTIC ACTIVITY OF NANOSIZED ZnO:HO FILMS DEPOSITED BY EXPLOSIVE EVAPORATION AT DEGRADATION OF TOLUENE IN AIR

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One of the most promising methods of air purification today is photocatalytic oxidation of gasphase and liquid-phase environmental pollutants of chemical and biological origin under the action of soft ultraviolet radiation to obtain non-harmous components of air: water and CO_2 . The photocatalytic properties of thickness-nanosized ZnO:Ho films obtained by electron beam explosive evaporation have been studied during degradation of toluene in air under ultraviolet (365 nm) irradiation. Methods for holmium doping of ZnO and explosive evaporation were chosen with a view to using them for air purification from volatile toluene compounds. The photocatalytic activity was studied depending on the following parameters: exposure time, temperature, humidity, initial toluene concentration in the air, and Ho content in ZnO. It was stated that the kinetics of photocatalytic decomposition of air toluene over film ZnO: Ho is close to the first-order reaction. The temperature dependence of the photocatalytic process is described by the Arrhenius equation. The rate and energy of adsorption activation of thermo- and photocatalysis of toluene on the ZnO:Ho film surface are calculated. The highest photocatalytic activity is achieved at the air humidity above 50%, initial concentration of toluene in the air below $2.5 \cdot 10^{-5} \frac{\text{mol}}{\text{L}}$, and the Ho content in ZnO of 3 at.%. As the Ho content in ZnO increases from 0 to 3 at.%, the rate of toluene degradation increases by 30%. The photocatalytic degradation of toluene over the ZnO:Ho film reaches the final stage with the formation of CO_2 gas.

Key words: photocatalytic activity, toluene, humidity, ZnO:Ho, concentration, CO₂.

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I. INTRODUCTION

Toluene is a volatile organic compound (VOC), dangerous for the human body, which adversely affects the central nervous system and muscle tissue to death in the case of high concentrations. As toluene is present in many substances used indoors (varnishes, paints, solvents, cosmetics, etc.) and outdoors (fuels and lubricants), air purification from it is an urgent problem. To solve it, various methods have been used, such as biological, adsorption, and others [1-3, 6, 7, 14]. The method of heterogeneous photocatalysis, which is based on the principles of nanotechnology and can rapidly destroy toxic organic substances under the action of a renewable energy source, in particular solar radiation, is recognized as the most effective of them [4-8]. The following works have been devoted to photocatalytic (FC) degradation of toluene in air due to using nanoparticles of different compositions [9–13] and BiVO₄:CuO [15], TiO₂:W [16], Pt:SrTiO_{3-x} [17]; TiO₂-CNT:B (carbon nanotubes) [18]; ZnO, TiO₂, WO_3 on a nickel foam deposited on an Ag substrate [19]; TiO₂:Mn [20]; in the model of a ring FC reactor [21]; TiO_2 on zeolite [22]; TiO_2 with microbial cellulose [23]; TiO_2 and TiO_2 :Pd [24, 25]; TiO₂:Pt [26]; immobilized TiO₂:SiO₂ on Al [27]; on combinations of TiO_2 UV, TiO_2 :UV:O₃ [28]; TiO₂:N:zeolite plus a biological process [29]. A review of FC air purification from a wide range of VOCs is given in [30].

The aim of this work is to study the activity of nanosized ZnO:Ho films deposited by electron beam explosive evaporation, depending on the experimental conditions such as exposure time, temperature, humidity, initial toluene concentration in the air, and Ho content in ZnO. We chose the rare earth element Ho for doping ZnO due to the fact that its presence provides a number of new properties, such as ferromagnetism [32], ferroelectricity [33], thermoelectricity [34], photoelectricity [34], photoluminescence [35], which expands the possibilities of influencing the FC activity of ZnO. Also, it is important to note that ZnO-based photocatalysts will have prospects of commercialization owing to ZnO's relatively low cost, non-toxicity, technological advantages, and resistance to radiation damage [36]. The method of explosive evaporation was chosen for rapid deposition of ZnO:Ho films, because, in contrast to the methods commonly used for ZnO (sol-gel treatment, sonochemical synthesis, solid-state reactions, thermal evaporation), which create equilibrium conditions for deposition, the proposed deposition method allows one to create an amorphized material structure appropriate for photocatalysis.

The properties of ZnO:Ho (0-5 at.%) films deposited by explosive evaporation have been studied and described by us in [37]. It was shown that a rapid deposition of films of this composition on quartz glass substrates leads to amorphization of their structure and morphology, whose degree increases with an increase in the ligature content and is associated with the random introduction of Ho atoms into the ZnO crystal lattice. The amorphization is accompanied by a decrease in the size of ZnO crystallites from (20-27) nm to (10-13) nm, a shift of the ZnO absorption edge to the blue region of the spectrum from 388 to 400 nm, a reduction of the band gap from 3.2 to 3.1 eV, an increase in resistivity from $5 \cdot 10^2$ to $1.9 \cdot 10^6 \Omega \cdot m$, an increase in the lifetime of charge carriers from $7.0 \cdot 10^{-5}$ to $18.0 \cdot 10^{-5}$ s. All these changes are known to be favorable for the FC process.

II. EXPERIMENTAL METHODOLOGY

ZnO:Ho (0 - 5 at.%) films synthesis was presented by us in [37]. ZnO:Ho films were deposited under the following conditions: pressure in the working chamber was $5 \cdot 10^{-3}$ Pa, the substrate temperature was 40° C, the film growth rate was 90--100 nm/min. The rate of FC degradation of air toluene on the surface of the ZnO:Ho film was measured in the reactor shown in Fig. 1.

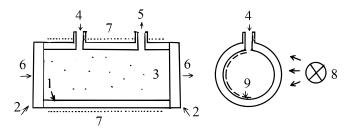


Fig. 1. Scheme of the reactor for measuring the rate of air toluene degradation on ZnO:Ho film. 1 -quartz tube, 2 -quartz windows, 3 -air with vapors of toluene and water and CO₂ gas, 4 -inlet, 5 -sensor hole, 6 -analysis light, 7 -heater, 8 -UV lamp, 9 -ZnO:Ho film

The reactor consists of a quartz tube 1, 7 cm long and 4 cm in diameter. The tube is covered on both sides with quartz windows 2. The reactor is installed in the cuvette unit of a spectrophotometer. The concentration of toluene is estimated by the intensity of two lines of its transmission in the UV region at a wavelength of 208 nm ($\varepsilon = 7.9 \cdot 10^3$) and 262 nm ($\varepsilon = 230$) according to the Lambert–Bouguer–Behr law [38]:

$$T = 10^{-\varepsilon Cl},\tag{1}$$

where T is the transmittance of luminous flux, ε is the extinction coefficient, C is the concentration, l is the thickness of the absorbing layer. The sensors determine temperature, humidity, and CO₂ content in the air. The coil heater 7 maintains the selected temperature in the reactor. Vapors of toluene and water are delivered into the reactor through hole 4 using a syringe needle.

A 100 nm thick ZnO:Ho film was deposited onto half the inner surface of the quartz tube. Irradiation was performed with a 40 watt UV lamp with maximal radiation at a wavelength of 365 nm through the quartz wall of the reactor.

The absolute $v_{abs.}$ and relative $v_{rel.}$ rates of decrease in the toluene concentration in the reactor air, which is a measure of the FC activity of ZnO:Ho films, were estimated by the expressions:

$$v_{\text{abs.}} = (C_0 - C_\tau) \frac{1}{\tau_{\text{exp.}}}$$
 and $v_{\text{rel.}} = \frac{C_0 - C_\tau}{C_0} \cdot \frac{1}{\tau_{\text{exp.}}}$, (2)

where C_0 and C_{τ} are the concentrations of toluene at the initial moment and after the exposure time $\tau_{\text{exp.}}$, respectively.

The change in toluene concentration was monitored using a SPECORD UV-VIS spectrophotometer. Temperature, humidity, and CO_2 gas concentration in the reactor were determined using TA 218 C and PTH-5 sensors.

III. RESULTS AND DISCUSSION

As we have reported in [39], due to the high boiling point of 110.6° C, toluene at a lower temperature exhibits the ability to be effectively adsorbed on any surface contacting air with its vapors. It is easily adsorbed even on chemically inert materials such as teflon. Therefore, the effect of its adsorption must be taken into account when controlling the change in its concentration during photocatalysis at room temperature.

The effect of adsorption can be eliminated by raising temperature of the air with toluene vapor above 110.6° C. Fig. 2 shows the dependence of the toluene concentration on the exposure time in the reactor with a ZnO:Ho (5 at.%) film in the absence of adsorption. To create such conditions, the air temperature in the reactor was chosen to be 114° C, i. e. higher than the boiling point of toluene.

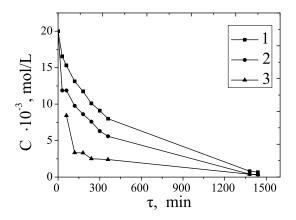


Fig. 2. Dependence of the change in the toluene concentration in the reactor air over the ZnO:Ho (5 at.%) film surface on the observation time τ : 1 — thermocatalysis, 2 — thermo- and photocatalysis, 3 — photocatalysis

Conditions for thermocatalysis were created by heating the reactor without UV irradiation, and for thermocatalysis and photocatalysis — under the simultaneous influence of heating and irradiation. Curves 1 and 2 were obtained

$$C_{\rm Ph}(\tau_{\rm exp.}) = C_{\rm Th}(\tau_{\rm exp.}) - C_{\rm ThPh}(\tau_{\rm exp.})$$

where C_{ThPh} , C_{Th} , C_{Ph} are the toluene concentrations in the reactor air under the combined influence of thermoand photocatalysis (C_{ThPh}), thermocatalysis (C_{Th}) and photocatalysis (C_{Ph}), respectively, at the moment of observation $\tau_{\text{exp.}}$. Irradiation of the ZnO:Ho (5 at.%) film with UV light accelerates the change in the concentration of toluene due to its FC degradation. The kinetics of the concentration change for all curves 1–3 is close to the kinetics of the first-order reaction:

$$C = C_0 e^{-k\tau}.$$
(3)

Such kinetics of the toluene degradation is characteristic of the photocatalysts of the $BiVO_4$: CuO composition [15]; TiO_2 -CNT:B (carbon nanotubes) [18], ZnO, TiO_2 , WO₃ on Ni foam and Ag substrate [19].

Figure 3 presents the curves of the final toluene concentration achieved from its initial value of $0.022 \frac{\text{mol}}{\text{L}}$ for a 24 h exposure to the air temperature over the ZnO:Ho (5 at.%) film during the action of thermocatalysis (1), thermo- and photocatalysis (2), and photocatalysis (3) up to a temperature of 110.6°C, which corresponds to the boiling point of toluene, is also influenced by the process of adsorption of this organic compound on the catalyst film. Above 110.6°C, no adsorption was observed.

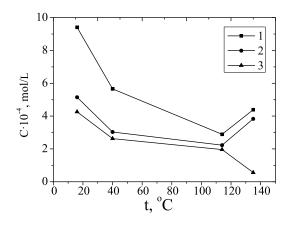


Fig. 3. Dependence of the final concentration of toluene on the temperature t of air during the action of thermocatalysis (1), thermo- and photocatalysis (2), and photocatalysis (3) with adsorption (up to 110.6° C) and without it (above 110.6° C)

In the temperature range $20 - 110.6^{\circ}$ C, when the decrease in the toluene concentration in the reactor is influenced by toluene adsorption, a decrease in curves 1-3 is observed with an increase in temperature, which can be described by the Arrhenius law.

$$v(T) = Ae^{-\frac{E_a}{RT}},\tag{4}$$

where E_a is the reaction activation energy, R is the universal gas constant, A is the molecules' collision frequency factor, v is the reaction rate, T is the absolute temperature.

Using formula (5) and Figs. 2 and 3, it is possible to calculate $v_{abs.}$, $v_{rel.}$ and E_a for adsorption, thermo- and photocatalysis processes on ZnO:Ho (5 at.%) film in air. Table 1 lists the values of these parameters.

For example, in [17] for the catalyst Pt:SrTiO_{3-x} during thermophotocatalysis of toluene in the temperature range $(30 - 90)^{\circ}$ C, E_a is equal to $1.06 \cdot 10^4 \frac{\text{J}}{\text{mol}}$, whereas in the interval (90 - 150)°C $E_a = 4.63 \cdot 10^4 \frac{\text{J}}{\text{mol}}$. For thermocatalysis $E_a = 5.36 \cdot 10^4 \frac{\text{J}}{\text{mol}}$.

Process	$v_{\rm abs.}, \frac{\rm mol}{\rm L\cdot h}$	$v_{\rm rel.}, \frac{\%}{h}$	$E_a, \frac{\mathrm{J}}{\mathrm{mol}}$
Adsorption	$8.77\cdot 10^{-4}$	3.99	$4.13\cdot 10^4$
Thermocatalysis	$9.05\cdot 10^{-4}$	4.11	$4.01 \cdot 10^4$
Photocatalysis	$9.13\cdot 10^{-4}$	4.15	$3.46 \cdot 10^4$

Table 1. The values of the absolute $v_{abs.}$ and relative $v_{rel.}$ reaction rates and the activation energy E_a of the processes of adsorption, thermo- and photocatalysis of toluene in air over the ZnO:Ho (5 at.%) film

The highest value of the activation energy and the lowest rate of decrease in the toluene concentration correspond to the process of adsorption on the ZnO:Ho (5 at.%) film, whereas the lowest E_a and the highest $v_{abs.}$ and $v_{rel.}$ do to the photocatalysis process. Thermocatalysis has average values of $v_{abs.}$, $v_{rel.}$ and E_a among these processes. The obtained values for ZnO:Ho (5 at.%) films are close to the corresponding values of other catalysts within the order of magnitude. For example, in [17] for the catalyst Pt:SrTiO_{3x} during thermophotocatalysis of toluene in the temperature range $30 - 90^{\circ}$ C, E_a is equal to $1.06 \cdot 10^4 \frac{\text{J}}{\text{mol}}$ and in the interval $(90 - 150)^{\circ}$ C to $E_a = 4.63 \cdot 10^4 \frac{\text{J}}{\text{mol}}$.

The proximity of the obtained values for different catalysts may be due to the same mechanism of the processes observed in them.

Figure 3 shows the role of adsorption in the processes of thermo- and photocatalysis. At temperatures above 110.6°C, when adsorption is absent, the process of thermocatalysis slows down (curve 1), whereas photocatalysis, on the contrary, accelerates (curve 2). This means that at temperatures below 110.6°C the adsorption promotes thermocatalysis, reducing the distance between the toluene molecules on the surface of the ZnO:Ho (5 at.%) film. On the other hand, adsorption inhibited photocatalysis. Apparently, the toluene molecules that settle on the catalyst surface prevent it from the H₂O and O₂ molecules which form the °OH and $^{\circ}O_2$ radicals, playing a major role in the decomposition of organic compounds.

The dependence of the rates of degradation of toluene $v_{\rm abs.}$ and $v_{\rm rel.}$ on the humidity of the air φ over the catalyst ZnO:Ho (5 at.%) film in the presence of UV radiation at 20°C is depicted in Fig. 4.

The curves of the dependence of the degradation rate of toluene vapor on the air humidity have a saturation region. With an increase in humidity up to 50%, the toluene degradation rates increase with accelerations of $\frac{\Delta v_{\rm abs.}}{\Delta \varphi} = 1.0 \cdot 10^{-5} \frac{\rm mol}{\% \cdot \rm L\cdot h}$ and $\frac{\Delta v_{\rm rel.}}{\Delta \varphi} = 0.043 \, \rm h^{-1}$. When the humidity reaches 50%, the increase in the rate of toluene degradation stops, and the curves of this dependence go to the stationary region values of $v_{\rm abs.} = 9.1 \cdot 10^{-4} \frac{\rm mol}{\rm L\cdot h}$ and $v_{\rm rel.} = 4.13 \frac{\%}{\rm h}$.

The dependence of the rate of the toluene degradation on the air humidity (Fig. 4) is in accordance with the general ideas about the mechanism of photocatalysis on the surface of semiconductors [40, 41]. Water molecules, meeting the charges photogenerated by UV irradiation of the ZnO:Ho film surface, yield one of the active forms of oxygen, namely •OH radicals, which cause the decomposition of toluene. As long as the quantity of photogenerated charges on the film surface is sufficient for the radicalization of all water molecules, the number of •OH radicals, i.e., the rate of toluene degradation, increases with an increase in humidity. This is the trend observed at low (to 50%) humidity in Fig. 4. When the number of water molecules exceeds the number of photogenerated charges on the catalyst film surface, then the increase in the formation of $^{\bullet}OH$ radicals with an increase in the air humidity, i.e., the rate of toluene degradation, stops. Figure 4 illustrates such a behavior at a humidity of above 50%.

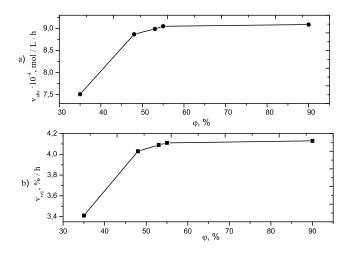


Fig. 4. Dependence of absolute $v_{\text{abs.}}$ (a) and relative $v_{\text{rel.}}$ (b) rates of toluene degradation on the air humidity φ in the presence of a ZnO:Ho (5 at.%) film under UV irradiation at 20°C

If the catalyst composition and experimental conditions change, the curves of the dependence of the toluene degradation rate on the air humidity may be more complex. For example, for Ag:ZnO,TiO₂, and WO₃ such a curve has one maximum [19], for Pt:SrTiO_{3-x} — two [17].

Figure 5 shows the dependence of FC degradation of toluene with a ZnO:Ho (0–5 at.%) film in the air of reactor on the concentration of holmium $C_{\rm Ho}$ in zinc oxide in the presence of UV irradiation at 20°C and humidity 40%. The exposure lasted 24 h.

The $v_{abs.}(C_{Ho})$ dependence curve has a maximum at $C_{Ho} = 3at.\%$, which may be due to the influence of various factors that accelerate or inhibit toluene degradation. The first of them includes a decrease in the band gap E_g and an increase in the lifetime of photogenerated carriers in ZnO:Ho with an increase in C_{Ho} [37]. The deceleration factor includes the above mentioned change in the morphology of ZnO:Ho nanoparticles in the direction of decrease in active centers on their surface, where the radicals •OH and •O₂ arise, which decompose toluene [37]. The total effect of these oppositely acting factors

gives rise to the maximum $v_{\rm abs.}$ at $C_{\rm Ho} = 3$ at.%. Figure 5 shows that with an increase in $C_{\rm Ho}$ from 0 to 3 at%, the rate of FC degradation of toluene increases by 30%, which is essential for the practical application of this catalyst. The dependence of the rate of changes in the toluene concentration in the reactor air during its FC degradation on the ZnO film surface on the initial concentration of toluene C_0 is given in Fig. 6. The experimental conditions are similar to those for Fig. 5.

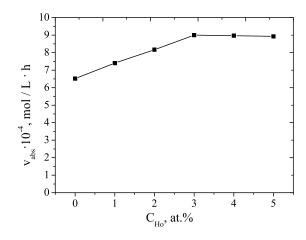


Fig. 5. Dependence of the absolute rate $v_{\rm abs.}$ of FC toluene degradation in the reactor with ZnO:Ho (0–5 at.%) film on the concentration of holmium $C_{\rm Ho}$ in zinc oxide

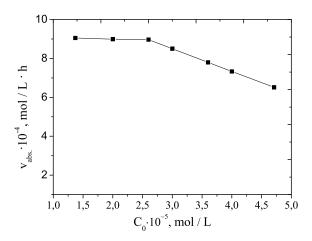


Fig. 6. Dependence of the absolute rate of change in toluene concentration $v_{\rm abs.}$ in the air of reactor with ZnO film under the action of UV radiation on the initial toluene concentration C_0

At low initial toluene concentrations C_0 , the rate $v_{abs.}$ is stationary. The degradation rate begins to decrease from $C_0 = 2.5 \cdot 10^{-5} \frac{\text{mol}}{\text{L}}$. The decrease in $v_{abs.}$ may be due to the fact that with an increase in C_0 , the number of formed radicals •OH and •O₂ is insufficient to decompose the increasing number of toluene molecules.

According to the literature [16, 18–20], FC degradation of toluene proceeds through intermediate stages with the formation of such products as phenol, benzaldehyde, benzoic acid, and benzyl alcohol. The decomposition products are CO_2 , CO, and H_2O . Thus, the presence of such concentration of these oxides that increases during the toluene photocatalysis is direct evidence of the complete decomposition of the VOC on the catalyst of the selected composition.

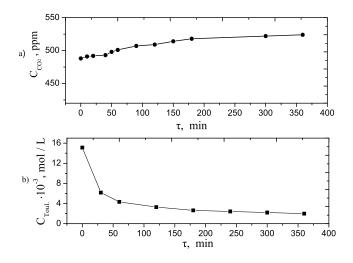


Fig. 7. Dependence of the concentrations of carbon dioxide(a) and toluene (b) in the air over the ZnO:Ho (5 at.%) film on the time of irradiation with a UV lamp

Figure 7,a shows the dependence of the increase in CO_2 concentration in the reactor with toluene vapor over the ZnO:Ho (5 at.%) film on the time of irradiation with a UV lamp. The simultaneous decrease in the toluene concentration is shown in Fig. 7,b. The temperature and humidity of the air were $12^{\circ}C$ and 60%, respectively.

Simultaneously with the decrease in the toluene concentration in the air over the ZnO:Ho (5 at.%) film,

an increase in CO_2 concentration is observed. The rate of change in toluene concentration is higher than that of CO_2 gas, especially in the initial period of irradiation, due to strong adsorption at low air temperature (12°C). Low temperature is also the reason for the absence of changes in air humidity, since the formed H₂O molecules condense on the inner surface of the reactor. The increase in CO_2 under UV irradiation is a confirmation of the achievement of the final stage of toluene decomposition in air over the surface of the ZnO:Ho (5 at.%) film due to the FC process.

IV. CONCLUSIONS

On the surface of the ZnO:Ho film deposited by explosive evaporation, the decrease in the toluene concentration in air under UV irradiation is regulated by the processes of adsorption, thermo-, and photocatalysis. The highest activation energy E_a and the lowest rate of change in toluene concentration correspond to the adsorption process, whereas the lowest Ea and the highest rate of C_o change correspond to photocatalysis.

At room temperature, the highest rate of air toluene degradation is reached at humidity above 50%.

The highest rate of FC degradation of toluene is observed at a Ho content in ZnO of 3 at.%. With the Ho content increasing from 0 to 3 at.%, the degradation rate increases by 30%.

Under stationary conditions of UV light irradiation, in the region of small values of the initial concentration of toluene, the rate of its FC degradation remains constant, and at over $2.5 \cdot 10^{-5} \frac{\text{mol}}{\text{L}}$ it decreases. The kinetics of the change in the concentration of

The kinetics of the change in the concentration of toluene on the ZnO:Ho film surface due to adsorption, thermo-, and photocatalysis is close to the first-order reaction. FC degradation of toluene over the ZnO:Ho film reaches the final stage with the formation of CO_2 gas.

- M. Gopinath, R. Dhanasekar, Afr. J. Biotechnol. 96, 16210 (2012); https://doi.org/10.5897/AJB12.2251.
- [2] M. Ghorbani, M. Omraei, M. Jafari, R. Katal, Asian J. Chem. 22, 8179 (2010).
- [3] Y. J. Tham, P. A. Latif, A. M. Abdullah, A. Shamaladevi, Y. H. Taufiq-Yap, Bioresour. Technol. 102, 724 (2011); https://doi.org/10.1016/j.biortech.2 010.08.068.
- [4] I. Ortiz, S. Revah, R. Auria, Environ. Technol. 24, 265 (2003); https://doi.org/10.1080/095933303093 85559.
- [5] R. Muñoz, S. Villaverde, B. Guieysse, S. Revahm, Biotechnol. Adv. 25, 410 (2007); https://doi.org/10.101 6/j.biotechadv.2007.03.005.
- [6] F. I. Khan, A. Kr. Ghoshal, J. Loss Prev. Process Ind. 13, 527 (2000); https://doi.org/10.1016/S0950-4230

(00)00007-3.

- [7] G. Gopinath, V. Archana, G. Saranya, V. Priscilla Pushparani, R. Dhanasekar, Int. J. Chem. Tech. Res. 5, 1401 (2013).
- [8] F. G. Shahna et al., Chin. J. Chem. Eng. 18, 113 (2010); https://doi.org/10.1016/S1004-9541(08)60331-6.
- [9] R. C. Harding, G. A. Hill, Y.-H. Lin, J. Chem. Technol. Biotechnol. 78, 406 (2003); https://doi.org/10.1002/ jctb.805.
- [10] A. B. Neal, R. C. Loehr, Waste Manage. 20, 59 (2000); https://doi.org/10.1016/S0956-053X(99)00297-4.
- [11] J. H. Song, K. A. Kinney, Appl. Microbiol. Biotechnol. 68, 554 (2005); https://doi.org/10.1007/s00253-005 -1956-8.
- [12] P. Jacobs, I. D. Bo, Kr. Demeestere, W. Verstraete, H. V. Langenhove, Biotechnol. Bioeng. 85, 68 (2004);

https://doi.org/10.1002/bit.10839.

- [13] M. M. Zahornyi *et al.*, J. Nano- Electron. Phys. 13, 05034 (2021); https://doi.org/10.21272/jnep.13(5) .05034.
- [14] O. E. Baibara, M. V. Radchenko, V. A. Karpyna, A. I. Ievtushenko, Phys. Chem. Solid State 22, 3 (2021); https://doi.org/10.15330/pcss.22.3.585-594.
- [15] W.-R. Zhao, W.-Y. Zeng, H.-P. Xi, X.-X. Yu, Acta Phys.-Chim. Sin. **30**, 761 (2014); https://doi.org/10.3866/ PKU.WHXB201402132.
- [16] L. Zhang, Y. Li, H. Xie, H. Wang, Q. Zhang, J. Nanosci. Nanotechnol. 15, 2944 (2015); https://doi.org/10.116 6/jnn.2015.9638.
- [17] J. Kong, Ch. Jiang, Z. Ruib, S. Liu, F. Xian, W. Ji, H. Ji, Chem. Engin. J **397**, 125485 (2020) ; https://doi.org/ 10.1016/j.cej.2020.125485.
- [18] V. B. Koli, Sh.-Ch Ke, A. G. Dodamani, Sh. P. Deshmukh, J.-S. Kim, Catalysts 10, 632 (2020); https://do i.org/10.3390/catal10060632.
- [19] Q. Zhang, F. Li, X. Chang, D. He, Mater. Manuf. Process. 29, 789 (2014); https://doi.org/10.1080/10 426914.2014.892616.
- [20] V. Binas, V. Stefanopoulos, G. Kiriakidis, P. Papagiannakopoulos, J. Materiomics 5, 56 (2019); https://do i.org/10.1016/j.jmat.2018.12.003.
- [21] V. Tomašić, F. Jović, Z. Gomzi, Catal. Today 137, 350 (2008); https://doi.org/10.1016/j.cattod.200 8.05.017.
- [22] H. Irvani, M.N. Pour, A. Vahidi, S. Arezoomandan, H. S. F. Abady, Med. Gas Res. 8, 91 (2018); https: //doi.org/10.4103/2045-9912.241074.
- [23] A. Rezaee, G. Pourtagi, H. Hossini, M. Loloi, J. Appl. Polymer Sci. 133, 43051 (2015); https://doi.org/10.1 002/app.43051.
- [24] T. M. Fujimoto, M. Ponczek, U. L. Rochetto, R. Landers,
 E. Tomaz, Environ. Sci. Pollut. Res. 24, 6390 (2017); https://doi.org/10.1007/s11356-016-6494-7.
- [25] C. Belver, M. J. López-Muñoz, J. M. Coronado, J. Soria, Appl. Catal. B 46, 497 (2003); https://doi.org/10.1 016/S0926-3373(03)00291-1.
- [26] G. Colón, M. Maicu, M.C. Hidalgo, J.A. Navío, A. Kuback, M. Fernández-García, J. Mol. Catal. A Chem. **320**, 14 (2010); https://doi.org/10.1016/j.mo lcata.2009.12.009.

- [27] M. Tasbihi, M. Kete, A. M. Raichur, N. Novak Tušar, U. Lavrenčič Štangar, Environ. Sci. Pollut. Res. 19, 3735 (2012); https://doi.org/10.1007/s11356-012-0 864-6.
- [28] K.-P. Yu, G. W. M. Lee, Appl. Catal. B 75, 29 (2007); https://doi.org/10.1016/j.apcatb.2007.03.006.
- [29] Z. Wei, J. Sun, Zh. Xie, M. Liang, Sh. Chen, J. Hazard. Mater. 177, 814 (2010); https://doi.org/10.1016/j. jhazmat.2009.12.106.
- [30] J. Mo, Y. Zhang, Q. Xu, J. J. Lamson, R. Zhao, Atmospheric Environ. 43, 2229 (2009); https://doi.or g/10.1016/j.atmosenv.2009.01.034.
- [31] A. M. Kasumov et al., J. Water Chem. Technol. 43, 281, (2021); https://doi.org/10.3103/S1063455X210 40044.
- [32] G. L. Kabongo et al., Nanoscale Res. Lett 11, 418 (2016); https://doi.org/10.1186/s11671-016-1630-3.
- [33] S. Goel, N. Sinha, B. Kumar, Physica E 105, 29 (2019); https://doi.org/10.1016/j.physe.2018.09.002.
- [34] P. P. Pradyumnan, A. Paulson, M. Sabeer, N. Deepthy, AIP Conf. Proc. 1832, 110055 (2017); https://doi.or g/10.1063/1.4980679.
- [35] R. A. Mereu *et al.*, Ceram. Int. **39**, 5535 (2013); https: //doi.org/10.1016/j.ceramint.2012.12.067.
- [36] S. Golovynskyi et al., Vacuum 153, 204 (2018); https: //doi.org/10.1016/j.vacuum.2018.04.019.
- [37] A. M. Kasumov *et al.*, Semicond. Phys. Quantum Electron. Optoelectron. **24**, 139 (2021); https://doi. org/10.15407/spqeo24.02.139.
- [38] M. I. Bulanov, I. P. Kalinkin, Prakticheskoe rukovodstvo po fotokolorimetricheskim i spektrofotometricheskim metodam analiza (Khimija, Leningrad, 1972).
- [39] A. M. Kasumov, A. I. Dmitriev, K. A. Korotkov, V. M. Karavaeva, K. O. Vyshnevska, A. I. Ievtushenk, in Book of abstracts. Ukrainian Conference with International Participation "Chemistry, Physics and Technology of Surface", devoted to the 35th anniversary of the Chuiko Institute of Surface Chemistry of NAS of Ukraine 26-27 May 2021, Kyiv, p. 98.
- [40] C. B. Ong, L. Y. Ng, A. W. Mohammad, Renew. Sust. Energ. Rev. 81, 536 (2018); https://doi.org/10.1016/ j.rser.2017.08.020.
- [41] A. J. Jafari, R. R. Kalantari, M. Kermani, M. H. Firooz, Chem. Zvesti. 73, 635 (2019); https://doi.org/10.100 7/s11696-018-0621-5.

ФОТОКАТАЛІТИЧНА АКТИВНІСТЬ НАНОРОЗМІРНИХ ПЛІВОК ZnO:Ho, НАНЕСЕНИХ ВИБУХОВИМ ВИПАРОВУВАННЯМ, ПІД ЧАС ДЕҐРАДАЦІЇ ТОЛУОЛУ В ПОВІТРІ

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Одним із найбільш перспективних методів очищення повітря сьогодні є фотокаталітичне окиснення газофазних і рідкофазних забруднювачів екології хімічної та біологічної природи під дією м'якого ультрафіолетового опромінення до нешкідливих компонентів повітря: CO₂ та води. Досліджено фотокаталітичні властивості нанорозмірних за товщиною плівок ZnO:Ho, нанесених вибуховим випаровуванням, під час деґрадації толуолу в повітрі під час ультрафіолетового (365 нм) опромінення. Леґування ZnO гольмієм та метод вибухового випаровування були обрані з огляду на перспективність їх застосування для очищення повітря від леткої сполуки толуолу. Фотокаталітична активність вивчена залежно від таких параметрів: часу експозиції, температури, вологості, початкової концентрації толуолу в повітрі, вмісту Ho у ZnO. Установлено, що кінетика фотокаталітичного

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розкладу толуолу повітря над плівкою ZnO:Но близька до реакції першого порядку. Температурна залежність фотокаталітичного процесу описується рівнянням Арреніуса. Розраховано швидкість та енергію активації адсорбції, термо- та фотокаталізу толуолу на поверхні плівки ZnO:Ho. Найбільша фотокаталітична активність досягається за вологості повітря вище від 50%, початковій концентрації толуолу в повітрі нижче від $2.5 \cdot 10^{-5} \frac{моль}{\pi}$, умісту Ho y ZnO 3 ат.%. Зі збільшенням умісту Ho в ZnO від 0 до 3 ат.% швидкість деградації толуолу зростає на 30%. Фотокаталітична деградація толуолу над плівкою ZnO:Ho досягає остаточної стадії з утворенням газу CO₂.

Ключові слова: фотокаталітична активність, толуол, вологість, ZnO:Ho, концентрація, CO₂.