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PHYSICAL CHEMISTRY OF WATER  
TREATMENT PROCESSES

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## Photocatalysis with the Use of ZnO Nanostructures as a Method for the Purification of Aquatic Environments from Dyes

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Received October 15, 2020; revised February 22, 2021; accepted April 29, 2021

**Abstract**—The papers devoted to the purification of aquatic environments from industrial contaminants with the use of ZnO based nanosized photocatalysts in the period of 2018–2020 are analyzed. The data published in these papers have made it possible to determine the dye ( $\nu$ ) destruction rate used further as a photocatalytic activity criterion. As shown by the comparative analysis of the photocatalytic activity of the studied structures, the highest rates of water purification from industrial azodye contaminants are demonstrated by hybrid ZnO/Au structures. At a destruction rate of  $\nu = 10\%/min$ , the ZnO/Au structures are much better than all the other considered types of catalysts due to their morphology, low recombination rate of photogenerated electron-hole pairs, and nanoparticles with an absorption spectrum close to the solar spectrum. The review of literature data shows that the greatest attention of researchers in the considered time period is focused on the problem of the purification of water sources from industrial contaminants and, first of all, azodyes. Essential attention is also paid to the technological approaches applied by the authors to increase the photocatalytic activity of ZnO based nanostructures.

**Key words:** azodyes, zinc oxide, waste water, photocatalysis, destruction rate

**DOI:** 10.3103/S1063455X21040044

### INTRODUCTION

Zinc oxide is a broadband direct-gap semiconductor material with a bandgap width  $E_g$  of 3.37 eV at room temperature. Due to an advantageous combination of chemical inertness, transparency, low cost, manufacturability, and unique multifunctional properties, ZnO attracts the interest of researchers in the field of physics, material science, chemistry, biochemistry, and other sciences [1]. The study of ZnO based nanostructures is promising and important due to new opportunities of their application for the creation of light diodes, gas sensors, field-emission transistors, ultraviolet lasers, solar-energy photoconverters, and efficient photocatalytic materials [2, 3]. It is known that the doping of ZnO with accepting impurities (Li, Na, K, N, P, As, Sb, Cu, and some other elements) is studied to switch the electron type of conductivity in zinc oxide for hole conductivity [4]. Donating impurities (Al, Ga, In, etc.) are added to the zinc oxide lattice to reduce its specific resistance, and the doping with rare-earth elements is performed to change its optical absorption spectrum [5]. The doping of ZnO with nitrogen is used to improve the photoelectric properties of ZnO based UV detectors [6, 7]. ZnO is also doped with noble metals (Ag, Au, Pd, Pt) [8] to increase the intensity of photoluminescence and improve the photocatalytic activity due to the implementation of surface plasmon resonance [4].

At the present time, the photocatalytic properties of nanosized ZnO based structures are investigated along a wide front of studies, which open opportunities for the application of this material for the solution of such global-scale problems as air and water purification from contaminants and pathogenic microorganisms. Some detailed reviews of the papers devoted to the problems of photocatalysis with the use of ZnO based nanostructures are given in [9–11]. In these papers, the methods for the synthesis and modification of ZnO nanoparticles are considered alongside with catalysis mechanisms, and ZnO application prospects are estimated. In the present review, the papers devoted to studying the process of photocatalysis with ZnO nanostructures in the period of 2018–2020 are analyzed. The results obtained during the photocatalytic purification of water from contaminants with the use of different modification of ZnO nano-

structures are compared, and the problems facing the researchers of photocatalytic processes in the future are defined.

The contamination of natural water basins is an essential problem all over the planet. The most hazardous contaminants are complex compounds undegradable under natural conditions. Among them are azodyes, which amount up to a half of the industrial production of dyes [12]. Such dyes are widely applied in textile, printing, leather, coating, paper, rubber, plastic production industry. It has been proven that 15–20% of such dyes get into waste water in the process of their application and have a cancerogenic and mutagenic effect on living organisms [13].

The most efficient method for the purification of waste water from contaminants over this time period is heterogeneous photocatalysis, which is based on the principles of nanotechnologies and can remove a broad spectrum of organic compounds at a high rate under the influence of a renewable energy source, such as solar radiation [9, 10]. The comparative analysis of the photocatalytic activity of different nanocatalysts has shown the efficiency of ZnO based materials [11].

### PHOTOCATALYTIC ACTIVITY ESTIMATION METHOD

The photocatalytic destruction of organic contaminants on nanoparticles of an oxide semiconductor catalyst is described in [14]. The efficiency of this process depends on the properties of nanoparticles, such as their size, shape, crystallinity, crystal lattice type, doping impurities, and the method used for the deposition of nanoparticles on a substrate [9, 10]. These parameters influence the optical absorption of light, the recombination rate of electron-hole pairs, and the efficiency of the formation of  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$  radicals. Hence, the photocatalytic activity of nanoparticles is determined by the technology of their creation. The traditional techniques used for the synthesis of ZnO nanostructures are precipitation, coprecipitation, colloid methods, the sol-gel method, the water-oil method of microemulsions, hydrothermal synthesis, and also the solvothermal, sonochemical, and polyol methods. Some specific features inherent in the new supercritical antisolvent (SAS) precipitation method [13], which is an environmentally friendly technique based on the use of arabinose, a natural monosaccharide, have been recently demonstrated [15]. The studies on the properties of ZnO based nanostructures are aimed at searching for the ways of improving their catalytic activity, which cause the efficiency of their practical application.

In all the considered papers, photocatalytic activity was estimated by calculating the degree of destruction  $D$  determined as the dye concentration change for the reaction time  $t$  as

$$D = \frac{C_0 - C_t}{C_0} \times 100, \quad (1)$$

where  $C_0$  and  $C_t$  are the initial and residual dye concentrations, %, respectively.

Since the reaction time  $t$  is specified in different ways, we used the destruction rate  $\nu$  representing the average relative change in the dye concentration per 1 min

$$\nu = \frac{C_0 - C_t}{C_0} \times 100 \frac{1}{t}, \quad (2)$$

as a criterion of objective comparison between the efficiencies of different catalytic activity improvement technologies.

### PHOTOCATALYTIC ACTIVITY OF ZnO BASED NANOSTRUCTURES

The highest photocatalytic activity at  $\nu = 10.00\%/min$  was attained in ZnO/Au nanostructures [16]. These nanostructures were synthesized by the coprecipitation of ZnO and Au from hydrogen tetrachloroaurate(III) ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), and KOH solutions. Au nanoparticles were included into a ZnO matrix. The morphology of ZnO/Au nanostructures was transformed with an increase in the Au concentration from nanowires to marigold-shaped flower-like structures. The absorption of nanostructures was observed to intensify in the visible spectral region (450–650 nm) due to the surface plasmon absorption of Au nanoparticles. The coincidence between the wavelength used for irradiation of photocatalysts and the wavelength of plasmon absorption by Au particles (550 nm) is one of the reasons for the fast oxidative destruction of sulforhodamine B with an initial concentration of  $90.12 \text{ mg/dm}^3$  by ZnO/Au nanostructures. The dye destruction rate grew with an increase in the Au concentration up to 4 mol %. Such an increase in the catalytic activity is provoked by a combination of several favorable circumstances: improved solar light absorption due to Au surface plasmons, a slight increase in

the bandgap width of ZnO with reduction of recombination between electron-hole pairs, an enlarged surface area of ZnO/Au nanostructures in comparison with undoped ZnO, and Schottky barriers formed at the Au/ZnO interface. The use of ZnO/Au nanostructures has provided 5-fold dye solution purification impossible for pure ZnO without efficiency loss.

A high destruction rate  $\nu = 3.36\%/min$  was demonstrated by spherical ZnO nanoparticles [15] at a radiation wavelength  $\lambda = 254\text{ nm}$  (irradiation with an UF-S bactericidal lamp)

And an initial dye concentration of  $11\text{ mg/dm}^3$ . The particles were synthesized by the simple and environmentally friendly method of mixing aqueous zinc nitrate  $Zn(NO_3)_2$  solutions with arabinose and further heating, evaporation, and calcination of reaction products at different temperatures. The nanoparticles had a hexagonal wurtzite structure. The size of crystals grew with an increase in the temperature from 400 to 700°C. Here, the absorption edge of ZnO nanoparticles shifted from 371 nm (400°C) to 381 nm (700°C) due to the formation of oxygen vacancies. A decrease in  $E_g$  from 3.20 to 3.16 eV also occurred. The photocatalytic activity of ZnO nanoparticles was estimated from the degree of mixture destruction in water with three dyes, such as methyl orange (MO), indigocarmine, and malachite green (MG). Decoloration in the aqueous solution of these dyes was monitored at  $\lambda = 616\text{ nm}$ . Spherical nanoparticles demonstrated the ability to provide the degree of destruction in the mixture of dyes at a level of 84% for 25 min of exposure.

High destruction rates  $\nu = 3.33\%/min$  were also attained for the hybrid ZnO/Ag nanostructures [17]. The synthesis of ZnO particles for these structures was performed by the method of an arc discharge in water between zinc rods. They were further bonded with Ag via the chemical reduction of salt  $AgNO_3$  in the presence of trisodium citrate. In these nanostructures, ZnO particles had a hexagonal wurtzite structure, and Ag particles had a face-centered cubic structure. As compared to pure ZnO, the absorption edge of hybrid ZnO/Ag structures shifted towards the visible spectral region due to the plasmon effect in Ag and the presence of defects in ZnO, which were promotive for more efficient absorption of visible light. ZnO defects in these nanostructures acted as electron traps, which hindered the recombination of electron-hole pairs. The combination of these factors in ZnO/Ag nanostructures provided an essential photocatalytic activity during the destruction of methylene blue (MB) at a level of  $\sim 100\%$  for 30 min of insolation. The surface oxidation of these nanostructures led to the formation of  $Ag_2O$  and an increase in the time of total destruction to 120 min of exposure.

A lower values of  $\nu = 1.67\%/min$  were observed for ZnO nanoparticles synthesized via the thermal decomposition of zinc acetate (AcZn) nanoparticles at 300–600°C [13]. To decrease the size of AcZn particles used as an initial material for ZnO synthesis, the method of their precipitation in a supercritical antisolvent (SAS) was used. The used supercritical antisolvent was  $CO_2$ , and dimethylsulfoxide served as a solvent. The fast diffusion of  $CO_2$  into the liquid solvent led to oversaturation for dissolved AcZn and its precipitation in the form of nanoparticles with small sizes of  $\sim 54\text{ nm}$ . At the same time, AcZn untreated by the SAS method had much larger sizes of crystals. Zinc oxide obtained via the decomposition of untreated AcZn at 500°C had the morphology of irregular tetrapods with an average size of 81 nm, whereas the decomposition of AcZn treated by the SAS method resulted in regular nanoparticles with an average diameter of 65 nm. The size of particles grew with an increase in the calcination temperature due to the phenomenon of their sintering.

ZnO particles from treated AcZn had a smaller energy bandgap width  $E_g$  of 3.07–3.15 eV and a larger specific surface area of 3.3–6  $m^2/g$  in comparison with ZnO synthesized from untreated AcZn with 3.17 eV and 5  $m^2/g$ , respectively. This essentially improved the photocatalytic activity of ZnO nanoparticles synthesized from AcZn treated by the SAS method in comparison with untreated particles. The complete decoloration of crystalline violet dye under UV radiation occurred 60 min for nanoparticles from treated AcZn and 180 min, i.e., was twice slower for nanoparticles from untreated AcZn. An increase in the photocatalysis rate was promoted by the enlargement of the surface area of ZnO nanoparticles, the faster migration of charge from the volume to the surface in the photocatalyst with a smaller size, and the absence of organic impurities, which are not formed in the SAS technology.

Closer values of  $\nu = 1.63\%/min$  were obtained for spherical  $ZnFe_2O_4$  nanoparticles doped with rare-earth  $Sm^{3+}$ ,  $Eu^{3+}$ , and  $Ho^{3+}$  ions [18].  $ZnFe_2O_4$  nanopowder was synthesized from a mixture of  $Zn(NO_3)_2$ ,  $Fe(NO_3)_2$ , and oxides  $Sm_2O_3$ ,  $Eu_2O_3$ , or  $Ho_2O_3$  and calcined at 800°C for 15 h.  $ZnFe_2O_4$  particles had a cubic crystal lattice with a unit cell parameter  $a = 8.4\text{ \AA}$  and an average particle size within two ranges of 50–60 and 90–100 nm. The energy bandgap width of nanoparticles was 2.75 eV, being much higher than 1.9 eV typical for massive  $ZnFe_2O_4$  samples. Doping with  $Sm^{3+}$  has improved the uniformity of particle sizes, which were ranged within 40–60 nm. No appreciable uniformity of particles has been revealed after

doping with  $\text{Eu}^{3+}$  and  $\text{Ho}^{3+}$ . After doping  $\text{ZnFe}_2\text{O}_4$  with Sm, Eu, and Ho ions, their  $E_g$  shifts from 2.75 to 2.25, 2.15, and 1.7 eV, respectively, in agreement with the change in crystallite sizes. The degree of MG dye destruction during the irradiation of  $\text{ZnFe}_2\text{O}_4$  nanoparticles with visible light is 98% for 60 min of exposure. The possibility of repeated use was pointed out for this catalyst.

For the ZnO/Ag and ZnO/Co nanostructures, the obtained values of  $\nu$  are 1.63 and 1.00%/min, respectively [19]. The ZnO/Ag and ZnO/Co structures were synthesized as follows. At first, NaOH was added to the mixture of dissolved salts  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CH}_3\text{COOAg}$ , or  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  in ethanol. The colloid dispersions formed as a result of reaction by ZnO/Ag and ZnO/C nanoparticles were evaporated at 275°C for 1 h. The structure of ZnO corresponded to hexagonal wurtzite. The size of formed particles was 17.3 nm for ZnO/Ag and 7.2 nm for ZnO/Co. The energy bandgap width of ZnO, ZnO/Ag, and ZnO/Co was 3.47, 3.18, and 3.42 eV, respectively. A decrease in  $E_g$  for ZnO/Ag in comparison with pure ZnO is explained by surface plasmon resonance in Ag at 400 nm. The existence of oxygen vacancies on the surface of ZnO promoted the entrapment of electrons by these traps and reduced the recombination of electron-hole pairs. An increase in the efficiency of photocatalysis was promoted by the existence of ZnO/Ag Schottky barriers, which led to the efficient separation of charge carriers in hybrid nanostructures. The listed factors led to an increase in the photocatalytic activity of hybrid nanostructures. The activity of ZnO/Ag and ZnO/Co was estimated by the degree of destruction for Bismark brown Y dye under UV radiation for 1 h. The highest degree of dye destruction at a level of 98% was attained for ZnO/Ag. A lower activity of ZnO/Co structures is due to that the ZnO energy bandgap contains Co impurity levels, which accelerate the recombination of electron-hole pairs.

In the presence of Co-containing  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  nanoparticles ( $0.0 \leq x \leq 0.1$ ), the MB dye destruction rate ( $C_0 = 10 \text{ mg/dm}^3$ ) was  $\nu = 1.42\%/ \text{min}$  [20]. Co-doped ZnO nanoparticles were synthesized by a two-stage method. At the first stage, the method of coprecipitation from a zinc acetate and cobalt nitrate solution with addition of oxalic acid and ammonium hydroxide was applied. At the second stage, the resulting white precipitate was calcined in the air at 600°C for 5 h. The size of  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  nanoparticles ( $0.0 \leq x \leq 0.1$ ) was 17.4 nm at  $x = 0.1$ . The particles had a hexagonal wurtzite structure, and the unit cell parameters and size demonstrated the trend to grow with an increase in the parameter  $x$ . This indicates that  $\text{Co}^{2+}$  ions were incorporated into the ZnO lattice. The doped nanoparticles were more agglomerated than pure ZnO particles. It has been shown that the concentration of oxygen vacancies grows with an increase in  $x$ , and impurities may act as electron-hole recombination sites, thereby decreasing the photocatalytic activity of nanoparticles. When  $x$  grew from 0 to 0.08,  $E_g$  decreased from 3.2 to 2.6 eV. The doped samples exhibited the trend to ferromagnetism, demonstrating hysteresis loops at room temperature. Photocatalytic activity was estimated from the degree of MB dye destruction ( $C_0 = 10 \text{ mg/dm}^3$ ) during the irradiation of samples with a xenon lamp. When  $x$  grew from 0 to 0.1, the degree of destruction decreased from 99.3 to 78.8% for 70 min of irradiation due to the intensification of recombination between electron-hole pairs on the impurity. An increase in the degree of destruction to 99.4% was demonstrated by the composition with  $x = 0.04$  alone.

In the study [21], the destruction rate  $\nu = 1.27\%/ \text{min}$  was established for undoped ZnO nanoparticles. The nanoparticles were synthesized from zinc nitrate hexahydrate by the method of flame pyrolysis, in which  $\text{O}_2$  was used as an oxidizer, and petroleum gas was a fuel. ZnO particles had a hexagonal crystal structure and were composed of predominantly spherical nanoformations. Photocatalytic activity was estimated by the destruction of amaranth dye at a concentration of  $10 \text{ mg/dm}^3$  under insolation. Under optimal conditions, the degree of dye destruction was 95% under insolation for 75 min.

In the study [22], the photocatalytic activity of ZnO-Ag/polystyrene (PS) and ZnO/PS nanocomposites in the destruction of MB dye under UV radiation was investigated to develop a film photocatalyst, which would float over the surface of an aquatic environment and would not require any essential efforts on its removal from a water basin after use. The ZnO-Ag composite was manufactured from a suspension of ZnO nanoparticles with  $\text{AgNO}_3$  via the photoprecipitation of Ag ions onto ZnO under irradiation with an UV lamp. The reaction product, i.e., the ZnO-Ag composite or pure ZnO nanoparticles, was further mixed with a polystyrene solution in chloroform and dried with the formation of a film, where ZnO-Ag or ZnO were incorporated into a polymer matrix. ZnO particles had a hexagonal structure of wurtzite. The ZnO and metallic Ag phases were sharply separated, and the Ag amount was 2% in ZnO. ZnO-Ag and ZnO nanoparticles were strongly agglomerated, and ZnO-Ag/PS and ZnO/PS films had high roughness. IR spectra demonstrated the absence of interaction between ZnO and the functional groups of polystyrene. The presence of Ag on ZnO led to a decrease in the energy bandgap width of this semiconductor from 3.298 to 3.263 eV, thus confirming the role of Ag as a doping impurity. The lifetime of photoinduced electron-hole pairs is also observed to grow due to the transition of electrons from ZnO to Ag on the

Schottky barrier. The degree of MB dye destruction was monitored at a wavelength of 665 nm. During the exposure for 120 min to UV lamp radiation at attained  $\nu = 0.58\%/min$ , the degree of MB dye destruction was 97 and 70% for ZnO-Ag/PS and ZnO/PS, respectively. A rather high destruction rate  $\nu = 0.81\%/min$  for the ZnO-Ag/PS photocatalyst was explained by the authors by improved conditions for the creation of active oxygen forms in this composite. This film photocatalyst could be used up to three times at a small loss in its efficiency.

The authors [23] attained the MG dye destruction rate  $\nu = 0.66\%/min$  on ZnO nanoparticles. In this study, the calcined (annealed) and uncalcined ZnO forms as photocatalysts of dye destruction in an aquatic environment under UV radiation were compared. The process of calcination—the annealing of ZnO nanoparticles at 600°C for 4 h—led to their recrystallization and agglomeration with the formation of aggregates. Calcined ZnO particles had high dispersity and a size of up to 25 nm. The degree of destruction for calcined ZnO was 2% higher than for uncalcined ZnO due to an increased amount of nanocrystals formed in the process of annealing. Under optimal photocatalysis conditions, the degree of destruction was 98.48% for calcined ZnO and 96.31% for uncalcined ZnO at 150 min of exposure.

$La_xZn_{1-x}O$  nanoparticles, where  $x = 0.01, 0.05, \text{ and } 0.10$ , have demonstrated the MO dye destruction rate  $\nu = 0.57\%/min$  [24]. These nanoparticles were synthesized by the combustion of a gel prepared from a  $Zn(NO_3)_2 \cdot 4H_2O$  and  $La(NO_3)_3 \cdot 6H_2O$  solution in polyvinyl alcohol. The synthesized samples had a spherical morphology and a particle size, which was inversely proportional to the molar percentage of La and varied from 34.3 to 10.3 nm. The incorporation of La into the ZnO lattice led to a decrease in  $E_g$  from 3.1 to 2.78 eV. This argues that  $La_xZn_{1-x}O$  is promising for allocation as a photocatalyst for a solution with an initial dye concentration of 10 mg/dm<sup>3</sup> under visible light radiation. At  $x = 0.1$ , the degree of MO dye destruction in an aqueous solution was maximal and attained 85.86% after 150 min of exposure to visible light. The reaction rate constant for the  $La_xZn_{1-x}O$  samples with maximum  $x = 0.1$  was four times higher in comparison with pure ZnO. The authors explain the improvement of photocatalytic characteristics with an increase in the La content by a decrease in the size of nanoparticles, the bandgap width  $E_g$ , and the rate of recombination between electron-hole pairs.

In the presence of star-shaped ZnO nanoparticles doped with rare-earth metals Ce, La, and Ho the photocatalytic decomposition rate of Acid Red 88 dye was  $\nu = 0.43\%/min$  [25]. The particles were synthesized by the sonochemical method. In this case, a NaOH solution was added until pH of 10 to an aqueous  $Zn(NO_3)_2 \cdot 4H_2O$  and  $Ln(NO_3)_3 \cdot 6H_2O$  solution, where Ln is a lanthanide. The mixture was treated with ultrasound for 3 h. The synthesized product was centrifuged, washed, and calcined at 300°C for 3 h.

Doped ZnO particles had a hexagonal structure, a star-shaped morphology without agglomeration, and sizes ranged within 30–50 nm. After doping with Ce, the energy bandgap width  $E_g$  decreased from 3.2 to 2.8 eV. The Ce impurity has demonstrated the best photocatalytic activity in comparison with La and Ho. Photocatalysis was performed for an aqueous solution of reactive orange 29 dye ( $C_0 = 10 \text{ mg/dm}^3$ ) under the simultaneous effect of visible light and ultrasound. The combination of sonolysis and photocatalysis accelerated the formation of electron-hole pairs and active oxygen forms, which are necessary for dye destruction. The application of a membrane reactor with polypropylene membranes of hollow fibers combining sonophotocatalysis with filtration by the authors has provided the possibility to increase the degree of destruction of ZnO/Ce particles to 97.84% for 225 min of exposure.

The low value  $\nu = 0.33\%/min$  was obtained for nanosized ZnO/CO heterostructures [26]. These heterostructures were synthesized from copper acetate  $(CH_3COO)_2Cu$  and zinc nitrate  $Zn(NO_3)_2 \cdot 6H_2O$  solutions. Process conditions were created for the formation of first CuO and then ZnO or first ZnO and then CuO. Finer heterostructure particles (of less than 200 nm) were synthesized in the first case, and coarser particles (~400 nm) were formed in the second case. The particles were united into agglomerates of different sizes, which contained both ZnO and CuO. The degree of MO dye destruction under 100 min of exposure to UV radiation was 24 and 33% for ZnO/CuO with a particle size of 400 and 200 nm, respectively, which argues for the more advantageous use of finer particles. Under exposure to visible light, the degree of destruction was 12 and 6%, respectively. In this case, superiority was demonstrated by coarser particles due to a higher CuO amount on them. The lowest destruction rate  $\nu = 0.1\%/min$  was obtained for ZnO nanoparticles and the ZnO/zeolite composite based on them [27]. This composite was selected to make easier the recovery of the photocatalyst after use in water purification from the food dye tartrazine in comparison with ZnO nanoparticles. The ZnO/zeolite composite was synthesized by the chemical precipitation of ZnO onto clinoptilolite-type zeolite particles from 0.85 to 0.60 mm in size under boiling in a zinc acetate solution with addition of NaOH for 2 h. The product precipitate was washed, dried, and calcined at 300°C. ZnO nanoparticles were synthesized in a similar way, but without addition of a zeolite material. The structure of both individual ZnO nanoparticles and ZnO nanoparticles incorporated into

the ZnO/zeolite composite corresponded to the hexagonal wurtzite structure, and the zeolite structure was the same as for the clinoptilolite phase. The average size was 42.7 nm for both the ZnO nanoparticles incorporated the composite and individual ZnO particles. The agglomeration of ZnO particles in the formation of up to 2–10  $\mu\text{m}$  was observed. Such particles had a quasi-spherical shape. The energy bandgap width was 3.20 eV for individual particles and 3.23 eV for the particles incorporated into the ZnO/zeolite composite, thus arguing for similarity between the mechanisms of photocatalysis in these nanoformations. The degree of tartrazine destruction for 15 h of exposure to UV radiation was 87% for ZnO nanoparticles and 81% for the composite.

The results of studies on the photocatalytic activity of nanosized ZnO based structures were considered for the period of 2018–2020. The greatest number of papers was devoted to study of water purification from nitrogen-containing dye contaminants, bactericidal activity [25, 28, 29], and air purification from gaseous impurities of nitrogen oxides like  $\text{NO}_x$  [30]. The priority of this problem is reflected by the close attention of researchers to the purification of water sources for this period. However, the problem encountered with the pandemic of coronavirus COVID-19, which is generally spread by airborne transmission, allows us to presume that the attention of scientists will be turned soon to the purification of air from microbiological contaminants.

The bactericidal activity in an aquatic environment, as well as the activity in the purification of water from dyes, was highest for the ZnO/Au nanocomposite. In other words, the mentioned photocatalytic advantages of the ZnO/Au structure were more efficiently exhibited also in the neutralization of microorganisms. This allows us to presume that the ZnO/Au composite will also be highly efficient in the purification of air from contaminants.

The use of mathematical modeling in the study [28] for the photocatalytic purification of water from organic and bacterial contaminants opens a qualitatively new period in the investigations of photocatalysis, which will undoubtedly not only be promotive in solving the problems encountered the humanity, but also will increase the level of their solution.

## CONCLUSIONS

Hence, the highest photocatalytic activity was attained in the hybrid ZnO/Au and ZnO/Ag nanostructures. The advantage of these structures was provided by the combination of two principal factors favorable for photocatalysis, such as the intensive absorption of visible light due to the effect of Ag and Au surface plasmons and a decrease in the rate of recombination between electron-hole pairs due to the existence of Schottky barriers. In addition, the coincidence between the absorption maximum of Au surface plasmons and the maximum of solar radiation used in photocatalysis and an extremely developed flower-like morphology of particles have enabled the ZnO/Au structure to attain a record dye destruction rate (10.0%/min). It has been shown that the change in the technology used for the manufacturing of hybrid ZnO/Au nanostructures has an effect on the surface area of their particles. In the hybrid ZnO/CuO, ZnO/Co, ZnO/Ag<sub>2</sub>CO<sub>3</sub>, and ZnO/Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce heterostructures free from electron-plasmon interaction, the attained destruction rates are low (1%/min). The doping of ZnO with lanthanides Sm, Eu, Ho, La<sub>x</sub>Zn<sub>1-x</sub>O, Ce, La, and Co (Zn<sub>1-x</sub>Co<sub>x</sub>O), although enabling the use of visible light for photocatalysis, but also leads to low destruction rates ( $\leq 1.4\%$ /min).

Unfortunately, pure ZnO nanoparticles are active only under UV radiation, but demonstrate a low destruction rate even in this case ( $\leq 2.0\%$ /min).

Hence, it is possible to make a general conclusion that the flower-like ZnO/Au nanocomposite catalysts are most efficient for the practical purification of water from contaminants.

## FUNDING

This study was performed within the research project of the National Academy of Sciences of Ukraine “Development of Innovative Photocatalytic Nanostructural Materials on the Basis of ZnO and TiO<sub>2</sub>” in the Frantsevich Institute for Problems of Materials Science of the National Academy of Sciences of Ukraine.

## REFERENCES

1. Lashkarev, G.V., Shteplyuk, I.I., Ievtushenko, A.I., Khyzhun, O.Y., Kartuzov, V.V., Ovsiannikova, L.I., et al., Properties of solid solutions, doped film, and nanocomposite structures based on zinc oxide, *Low Temp. Phys.*, 2015, vol. 41, no. 2, pp. 129–140.  
<https://doi.org/10.1063/1.4908204>

2. Theerthagiri, J., Salla, S., Senthil, R.A., Nithyadharseni, P., Madankumar, A., Arunachalam, P., et al., A review on ZnO nanostructured materials: Energy, environmental and biological applications, *Nanotechnology*, 2019, vol. 30, 392001.  
<https://doi.org/10.1088/1361-6528/ab268a>
3. Ievtushenko, A., Tkach, V., Strelchuk, V., Petrosian, L., Kolomys, O., Kutsay, O., et al., Solar explosive evaporation growth of ZnO nanostructures, *Appl. Sci.*, 2017, vol. 7, no. 4, 383.  
<https://doi.org/10.3390/app7040383>
4. Ievtushenko, A., Karpyna, V., Eriksson, J., Tsiaoussis, I., Shtepliuk, I., Lashkarev, G., et al., Effect of Ag doping on the structural, electrical and optical properties of ZnO grown by MOCVD at different substrate temperatures, *Superlattices Microstruct.*, 2018, vol. 117, pp. 121–131.  
<https://doi.org/10.1016/j.spmi.2018.03.029>
5. Xiu, F., Xu, J., Joshi, P.C., Bridges, C.A., and Parans Paranthaman, M., ZnO doping and defect engineering—A review, in *Semiconductor Materials for Solar Photovoltaic Cells*, Springer Ser. Mater. Sci., vol. 2018, Cham: Springer, 2016, pp. 105–140.
6. Ievtushenko, A., Khyzhun, O., Shtepliuk, I., Bykov, O., Jakieła, R., Tkach, S., et al., X-ray photoelectron spectroscopy study of highly-doped ZnO:Al,N films grown at O-rich conditions, *J. Alloys Compd.*, 2017, vol. 722, pp. 683–689.  
<https://doi.org/10.1016/j.jallcom.2017.06.169>
7. Ievtushenko, A., Khyzhun, O., Karpyna, V., Bykov, O., Tkach, V., Strelchuk, V., et al., The effect of Zn<sub>3</sub>N<sub>2</sub> phase decomposition on the properties of highly-doped ZnO:Al,N films, *Thin Solid Films*, 2019, vol. 669, pp. 605–612.  
<https://doi.org/10.1016/j.tsf.2018.11.052>
8. Liu, H., Feng, J., and Jie, W., A review of noble metal (Pd, Ag, Pt, Au)—zinc oxide nanocomposites: Synthesis, structures and applications, *J. Mater. Sci.: Mater. Electron.*, 2017, vol. 28, pp. 16585–16597.  
<https://doi.org/10.1007/s10854-017-7612-0>
9. Kezhen, Q., Cheng, B., Yu, J., and Ho, W., Review on the improvement of the photocatalytic and antibacterial activities of ZnO, *J. Alloys Compd.*, 2017, vol. 727, pp. 792–820.  
<https://doi.org/10.1016/j.jallcom.2017.08.142>
10. Máynez-Navarro, O.D. and Sánchez-Salas, J.L., Focus on zinc oxide as a photocatalytic material for water treatment, *Int. J. Environ. Biorem. Biodegrad.*, 2018, vol. 106, pp. 1–8.  
<https://doi.org/10.29011/IJBB-106/100006>
11. Ong, C.B., Ng, L.Y., and Mohammad, A.W., A review of ZnO nanoparticles as solar photocatalysts: Synthesis, mechanisms and applications, *Renewable Sustainable Energy Rev.*, 2018, vol. 81, pp. 536–551.  
<https://doi.org/10.1016/j.rser.2017.08.020>
12. Azo dye, Chemistry and chemical technology, Handbook of Chemist 21. <https://chem21.info/tabmap/>
13. Franco, P., Sacco, O., De Marco, I., and Vaiano, V., Zinc oxide nanoparticles obtained by supercritical antisolvent precipitation for the photocatalytic degradation of crystal violet dye, *Catalysts*, 2019, vol. 346, no. 9, pp. 1–15.  
<https://doi.org/10.3390/catal9040346>
14. Soboleva, N.M., Nosonovich, A.A., and Goncharuk, V.V., Heterogeneous photocatalysis in water treatment processes, *J. Water Chem. Technol.*, 2007, vol. 29, no. 2, pp. 72–89.
15. Abdulkhair, B.I., Salih, M.E., Elamin, N.Y., Fatima, A.M.A., and Modwi, A., Simplistic synthesis and enhanced photocatalytic performance of spherical ZnO nanoparticles prepared from arabinose solution, *Z. Naturforsch.*, 2019, vol. 74, pp. 1–8.  
<https://doi.org/10.1515/zna-2019-0059>
16. Raji, R. and Gopchandran, K.G., Plasmonic photocatalytic activity of ZnO:Ag nanostructures: Tailoring the Plasmon absorption and interfacial charge transfer mechanism, *J. Hazard. Mater.*, 2019, vol. 368, pp. 345–357.  
<https://doi.org/10.1016/j.jhazmat.2019.01.052>
17. Ziashahabi, A., Prato, M., Dang, Z., and Poursalehi, R., The effect of silver oxidation on the photocatalytic activity of Ag/ZnO hybrid plasmonic/metal-oxide nanostructures under visible light and in the dark, *Sci. Rep.*, 2019, vol. 9, 11839.  
<https://doi.org/10.1038/s41598-019-48075-7>
18. Hakimyfard, A. and Mohammadi, S., ZnFe<sub>2</sub>O<sub>4</sub> and ZnO-Zn<sub>1-x</sub>M<sub>x</sub>Fe<sub>2</sub>O<sub>4+δ</sub> (M = Sm<sup>3+</sup>, Eu<sup>3+</sup> and Ho<sup>3+</sup>): Synthesis, physical properties and high performance visible light induced photocatalytic degradation of malachite green, *Adv. Powder Technol.*, 2019, vol. 30, no. 6, pp. 1257–1268.  
<https://doi.org/10.1016/j.apt.2019.04.005>
19. Martínez-Vargas, B.L., Durón-Torres, S.M., Bahena, D., Peralta-Hernández, J.M., and Picos, A., One-pot synthesis of ZnO–Ag and ZnO–Co nanohybrid materials for photocatalytic applications, *J. Phys. Chem. Solids*, 2019, vol. 135, pp. 109–120.  
<https://doi.org/10.1016/j.jpcs.2019.109120>

20. Pan, H., Zhang, Y., Hu, Y., and Xie, H., Effect of cobalt doping on optical, magnetic and photocatalytic properties of ZnO nanoparticles, *Optik*, 2020, vol. 208, 1640560.  
<https://doi.org/10.1016/j.ijleo.2020.164560>
21. Widiyandari, H., Umiati, N.A.K., and Herdianti, R.D., Synthesis and photocatalytic property of zinc oxide (ZnO) fine particle using flame spray pyrolysis method, *J. Phys.: Conf. Ser.*, 2018, vol. 1025, 012004.  
<https://doi.org/10.1088/1742-6596/1025/1/012004>
22. Naji, H.K., Oda, A.M., Abdulajeel, W., Abdilkadhim, H., and Hefdhhi, R., ZNO–Ag/PS and ZnO/PS films for photocatalytic degradation of methylene blue, *Indones. J. Chem.*, 2020, vol. 20, pp. 314–323.
23. Chijioke-Okere, M.O., Okorochoa, N.J., Anukam, B.N., and Oguzie, E.E., Photocatalytic degradation of a basic dye using zinc oxide, *Int. Lett. Chem., Phys. Astron.*, 2019, vol. 81, pp. 18–26.  
<https://doi.org/10.18052/www.scipress.com/ILCPA.81.18>
24. Nguyen, T.T., Nguyen, L.T.H., Duong, A.T.T., Nguyen, B.D., Hai, N.Q., Chu, V.H., et al., Preparation characterization and photocatalytic activity of la-doped zinc oxide nanoparticles, *Materials*, 2019, vol. 1195, no. 12.  
<https://doi.org/10.3390/ma12081195>
25. Sheydaei, M., Fattahi, M., Ghalamchi, L., and Vatanpour, V., Systematic comparison of sono-synthesized Ce-, La- and Ho-doped ZnO nanoparticles and using the optimum catalyst in a visible light assisted continuous sono-photocatalytic membrane reactor, *Ultrason. Sonochem.*, 2019, vol. 56, pp. 361–371.  
<https://doi.org/10.1016/j.ultsonch.2019.04.031>
26. Levkevich, E.A., Moshnikov, V.A., Yukhnovets, O., and Maximov, A.I., Photocatalytic properties of ZnO/CuO heterostructures, *Proc. 2019 IEEE Conf. of Russian Young Researchers in Electrical and Electronic Engineering (EIConRus)*, Red Hook, NY: Curran Assoc., 2019.  
<https://doi.org/10.1109/EIConRus.2019.8657316>
27. Alcántara-Cobos, A., Gutiérrez-Segura, E., Solache-Ríos, M., Amaya-Chávez, A., and Solís-Casados, D.A., Tartrazine removal by ZnO nanoparticles and a zeolite-ZnO nanoparticles composite and the phytotoxicity of ZnO nanoparticles, *Microporous Mesoporous Mater.*, 2020, vol. 302, 110212.  
<https://doi.org/10.1016/j.micromeso.2020.110212>
28. Murcia, J.J., Hernández, J.S., Rojas, H., Moreno Cascante, J., Sánchez Cid, P., Hidalgo, M.C., et al., Evaluation of Au–ZnO, ZnO/Ag<sub>2</sub>CO<sub>3</sub> and Ag–TiO<sub>2</sub> as photocatalyst for waste-water treatment, *Top. Catal.*, 2020, no. 11-14/2020.  
<https://doi.org/10.1007/s11244-020-01232-z>
29. Jin, S.-E., Jin, J.E., Hwang, W., and Hong, S.W., Photocatalytic antibacterial application of zinc oxide nanoparticles and selfassembled networks under dual UV irradiation for enhanced disinfection, *Int. J. Nanomed.*, 2019, vol. 14, pp. 1737–1751.  
<https://doi.org/10.2147/IJN.S192277>
30. Meroni, D., Gasparini, C., Di Michele, A., Ardizzone, S., and Bianchi, C.L., Ultrasound-assisted synthesis of ZnO photocatalysts for gas phase pollutant remediation: Role of the synthetic parameters and of promotion with WO<sub>3</sub>, *Ultrason. Sonochem.*, 2020, vol. 55, 105119.  
<https://doi.org/10.1016/j.ultsonch.2020.105119>

*Translated by E. Glushachenkova*