

04.1

Activity of ZnO microstructures synthesized using microwave plasma in dinitrophenol photodegradation processes

© S.N. Antipov¹, A.E. Muslimov², A.A. Ulyankina³, A.D. Tsarenko³, M.Kh. Gadzhiev¹,
A.S. Lavrikov², A.S. Tyuftyaev¹

¹ Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia

² Shubnikov Institute of Crystallography „Crystallography and Photonics“ Russian Academy of Sciences, Moscow, Russia

³ Platov State Polytechnic University, Novocherkassk, Rostov oblast, Russia E-mail: antipov@ihed.ras.ru

Received July 18, 2023

Revised August 14, 2023

Accepted August 23, 2023

The activity of nitrogen-containing structures of ZnO synthesized using atmospheric-pressure microwave nitrogen plasma in the processes of photodegradation of 2,4-dinitrophenol under the exposure to sunlight was studied. It was shown that, during the plasma treatment of zinc microparticles, ZnO structures of various micromorphologies ranging in size from hundreds of nanometers to several micrometers are being formed. High photoactivity (rate constant of 0.036 min^{-1}) of synthesized ZnO structures during photodegradation of dinitrophenol under solar radiation was demonstrated. Photoactive ZnO structures synthesized using microwave nitrogen plasma can find application in the processes of mineralization of toxic organic compounds.

Keywords: photocatalytic activity, dinitrophenol, microwave plasma, zinc oxide, solar radiation.

DOI: 10.61011/TPL.2023.10.57058.19688

One of the most environmentally hazardous pollutants is phenol and its derivatives (hazard class II). Phenol-containing substances get formed in refining oil products and manufacturing paints, varnishes and pharmaceutical products. The phenol-containing substances are classified as compounds that are resistant to oxidation and possess toxic, carcinogenic and mutagenic properties. Conventional methods for wastewater treatment from organic pollutants comprise, above all, biological purification, and also a number of physical-chemical techniques, e.g. adsorption, ion exchange and reverse osmosis. As the disadvantages of these techniques, there may be regarded non-destructive nature of treatment, high power consumption and operation expenditures, low efficiency, and formation of a great amount of wastes in the form of sludge [1]. During recent years, advanced environmentally friendly and energy-efficient oxidation techniques have been intensely developed; among them, an important place is occupied by photocatalysis [2,3], that is, acceleration of chemical reactions with substances-catalysts getting activated under irradiation with light photons. A significant advantage of photocatalysis is the possibility of oxidation at relatively low pollutant concentrations [4], which is important in mineralizing toxic organic pollutants of low maximum permissible concentrations. It is evident that the Sun is an inexhaustible source of energy; therefore, the search for materials exhibiting a high photocatalytic activity under the solar radiation is a quite topical problem.

During last years, active investigations of photocatalysts based on zinc oxide (ZnO) are being conducted [5,6]. Preliminary investigations have demonstrated the efficiency of using ZnO microtetrapods obtained by carbothermal

synthesis in the reaction of photocatalytic degradation of antibiotic ciprofloxacin under UV irradiation [7]. Solving the issue of the photocatalytic wastewater treatment needs commercial production of ZnO tetrapods which can hardly be realized by using the method of carbothermal synthesis. In this connection, it is quite important to develop high-performance methods for synthesizing oxide microstructures. Due to their energy efficiency, plasma-synthesis methods (synthesis under the action of gas-discharge plasma) are regarded as belonging to those methods [8]. Of great interest is the atmospheric-pressure microwave discharge possessing a significantly higher charge density and, hence, a higher reactivity as compared with other discharges of the same power. Notice also that plasma of atmospheric-pressure discharges of some types (corona, spark and arc types) gets „contaminated“ with the material of internal discharge electrodes. This may be prevented by feeding energy to the microwave discharges induced in discharge chambers (for instance, in dielectric tubes) without a direct contact with metal electrodes. This property is of a fundamental importance for creating high-purity plasma. As a buffer plasma-forming gas for the plasma-synthesis techniques under development, nitrogen may be used; this makes possible nitridation of the zinc-oxide structures under formation. Paper [6] shows that doping with nitrogen ensures a significant increase in the ZnO photosensitivity under the solar radiation.

In this work, we have studied the activity of nitrogen-containing ZnO microstructures synthesized using atmospheric-pressure microwave nitrogen plasma in the processes of 2,4-dinitrophenol photodegradation under the solar radiation.

To generate the microwave plasma and synthesize ZnO microstructures, we used a waveguide-type microwave plasmatron with water load and trimming piston at the end of the waveguide duct. The design and operation principle of such a plasmatron are presented in detail in papers [9–11]. Here we give only their brief description. Operation of the microwave plasmatron is based on a typical low-power magnetron 2.45 GHz in frequency and enables creating atmospheric-pressure microwave discharges at wave H_{10} with the input power of ~ 1 kW. For this purpose, a quartz tube 3 cm in inner diameter was installed normally to the wide wall of the rectangular waveguide; in this tube, a stationary volume discharge was induced due to the microwave energy effect on the gaseous medium. As the plasma-forming gas, high-purity (99.998%) nitrogen was used, which was supplied into the tube with the flowrate of ~ 1 –10 l/min. From the results of spectral diagnostics of plasma of the microwave discharge in atmospheric-pressure nitrogen, which were obtained for similar experimental conditions, it is known that gas temperature T_g on the discharge tube axis is $\cong 5000$ –6000 K, while the concentration and temperature of plasma electrons are $n_e \sim 10^{13}$ cm $^{-3}$ and $T_e \sim 1$ eV, respectively [12,13]. Zinc powder with particle size of 30–40 μ m was poured into the discharge tube from the gas-supply end and passed together with the gas through the microwave discharge region inside the waveguide. Next, the particles of treated zinc powder were collected through the open end of the discharge tube into a quartz vessel.

Microscopic examination was performed using scanning electron microscope Quanta 200. The microscope was equipped with an energy-dispersive X-ray microanalyzer (EXM).

The X-ray phase analysis was carried out with diffractometer ARL X'TRA ThermoFisher using the $\text{CuK}\alpha$ -radiation (1.5405 Å). To study the photocatalytic activity of the synthesized materials, the ZnO powder (25 mg) was added to the aqueous solution of 2,4-dinitrophenol (DNP) 50 ml in volume, stirred in the dark for 30 min, and then irradiated with light under continuous agitation. As the source of light, a solar radiation simulator (xenon lamp, 100 mW/cm 2) was used. The DNP concentration was determined spectrophotometrically based on the absorption maximum at 358 nm (spectrophotometer Shimadzu UV-1800).

Fig. 1 illustrates the process of synthesizing the zinc oxide structures in the experiment with microwave plasma. The electron microscopy data (Fig. 2, *a*) shows that morphologically heterogeneous crystalline precipitate gets formed in the course of synthesis. Among individual components of the precipitate there are tetrapods, hexagonal rods. The structure sizes varied from hundreds of nanometers to several micrometers. The EXM data (see the Table) shows that, besides the basic components (zinc and oxygen), the powder contained nitrogen (atomic fraction of 4%), which confirms that the precipitate is nitrided. Diffraction reflections observed in the X-ray diffraction spectrum of the zinc oxide microstructure (Fig. 2, *b*) correspond to



Figure 1. Illustration of the process of ZnO microstructure synthesis in the microwave plasma experiment.

Elemental (atomic) composition of the ZnO structures as per EXM data

Element	Amount, %
Zn	27.56
O	68.32
N	4.12

the hexagonal (wurtzite) phase of ZnO (JCPDS card No 36-1451). The most intense reflections are observed at 31.68, 34.35 and 36.16°; they correspond to reflections from ZnO planes (100), (002) and (101) with a slight shift towards smaller angles. The shift may be caused by an increase in the ZnO lattice parameter due to partial nitrogen-for-oxygen substitution. Since the nitrogen atom radius (1.46 Å) is larger than that of oxygen (1.38 Å), the N-for-O substitution in ZnO leads to deformation of its lattice. The excess (over-stoichiometric) content of oxygen (see EXM data presented in the Table) is, probably, connected with the ability of the ZnO near-surface layers to absorb oxygen and water vapor.

Melting and evaporation points of the bulk zinc are 419.5 and 907°C, respectively. With decreasing size of particles, their thermodynamic characteristics also change, the melting and evaporation temperatures decrease. Under the conditions of a microwave discharge, the temperature of gas free of particles is 5000–6000 K. In the absence of active gases, the zinc particles in plasma had to undergo several phase transitions, transferring from the solid-particle

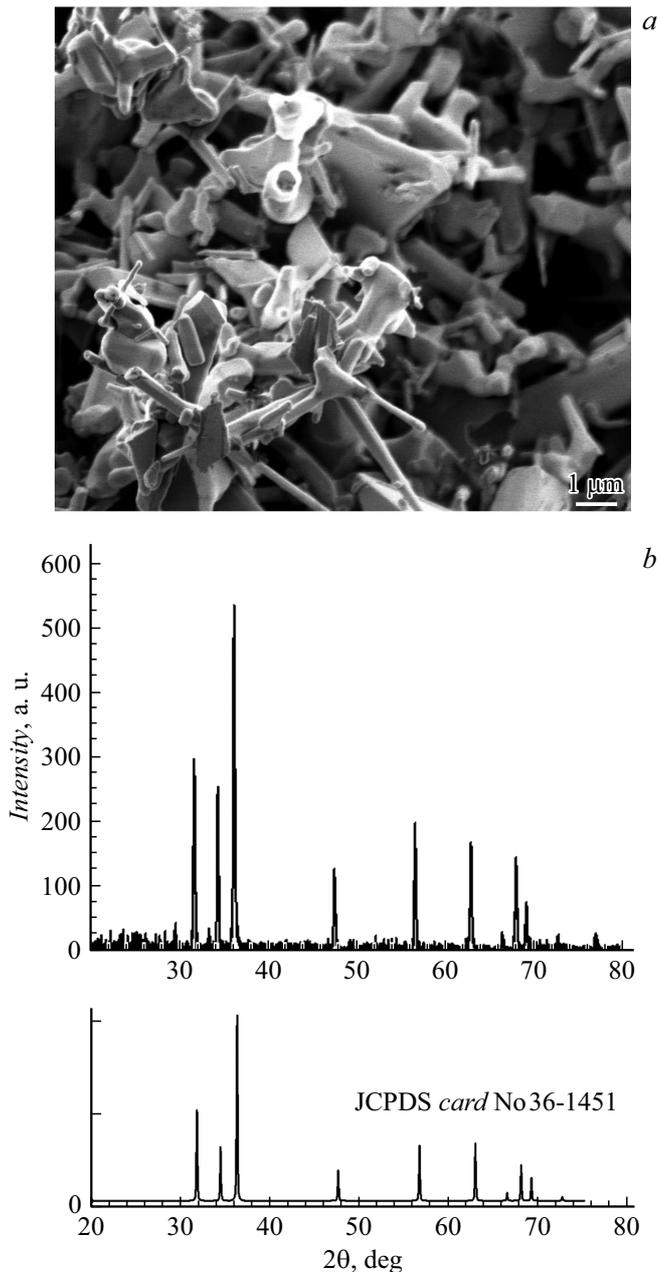


Figure 2. Microscopic image (a) and X-ray diffraction pattern (b) of the ZnO microstructures.

state to evaporation into plasma through the stage of melting. However, notice that in the discharge gap there exists active molecular and atomic nitrogen in the ionized state. In addition, oxygen is sucked into the discharge gap from the side of the quartz tube end and can get ionized due to high plasma electron temperature. The oxygen concentration and ionization degree are nonuniform: the oxygen concentration increases when approaching the outlet opening, while the ionization degree decreases with removing to the plasma periphery. It is possible to assume that, at the initial stage, metastable phases of zinc nitrides get formed on the zinc microparticle surfaces. Then, due

to high activity of oxygen, preferable oxygen-for-nitrogen substitution occurs with the formation of zinc oxide. This is why the presence of nitrogen is observed in the synthesized ZnO structures. It is shown in [14] that the presence of the oxide film allows making the particles fully oxidized even at temperatures above the zinc melting point due to the oxygen diffusion through the growing oxide layer confining liquid zinc in the particle central parts. Nevertheless, this does not explain formation of a relatively small number of minor ZnO structures of various morphologies. The decisive role in the processes of synthesizing the ZnO structures is played by zinc vapors. For instance, to create pointed ZnO structures, zinc vapor concentration in the near-growth zone is typically reduced at the final stage. The ZnO formation enthalpy is about -350 kJ/mol , and, during the zinc oxidation, there occurs a release of energy inducing additional heating of plasma. Thus, conditions for the metallic zinc evaporation and ZnO nucleation can arise in some separate plasma regions. Sizes of the ZnO structures synthesized by using microwave nitrogen plasma are much less than those of the original zinc particles. It may be concluded that at the initial stages (after the zinc microparticles have got into plasma) the main processes are not nitridation and oxidation of zinc but evaporation of zinc microparticles. Later on, the processes of zinc vapor evolution proceed depending on the local thermodynamic parameters and composition of the plasma.

Fig. 3, a presents the 2,4-dinitrophenol absorption spectra for different times of irradiation in the presence of the synthesized ZnO used as photocatalyst. The obtained spectra evidence a significant decrease in the DNP concentration due to its photodegradation. The DNP photodegradation rate constant was calculated from the slope of the linearized kinetic curve $\ln(C/C_0)-t$ (Fig. 3, b) using the Langmuir–Hinshelwood model [15]; it appeared to be 0.036 min^{-1} . Photoactivity of the ZnO structures synthesized by using microwave nitrogen plasma under the solar radiation is comparable with that of composite nanoparticles in the similar process of the 2,4-dinitrophenol degradation [16].

In this work there was studied the activity of nitrogen-containing ZnO structures synthesized by using atmospheric-pressure microwave nitrogen plasma in the processes of 2,4-dinitrophenol photodegradation under the exposure to sunlight. It was shown that, during the plasma treatment of zinc microparticles, nitrogen-doped ZnO structures of different micromorphologies are being formed, their size ranging from hundreds of nanometers to several micrometers. Apparently, the main process is the primary evaporation of zinc microparticles within the plasma discharge, with subsequent formation of ZnO structures from the obtained vapor. The study demonstrated a high photoactivity (rate constant of 0.036 min^{-1}) of the synthesized ZnO structures in the process of the 2,4-dinitrophenol photodegradation under the solar radiation.

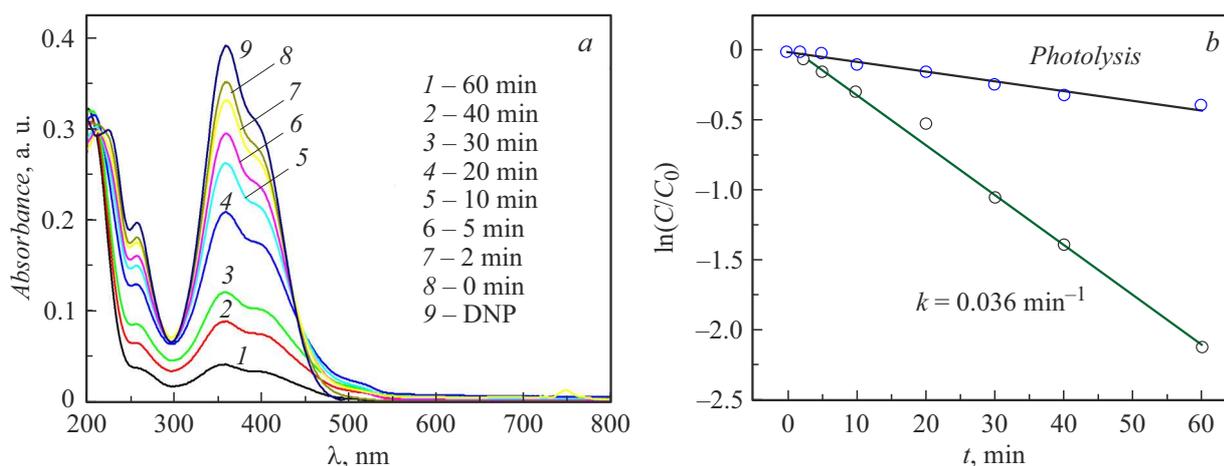


Figure 3. 2,4-dinitrophenol absorption spectra during its photolysis and photodegradation under the action of sunlight (100 mW/cm^2) (a) and determination of the reaction rate constant k (b) in the presence of ZnO. C is the DNP concentration at time moment t counted from the beginning of UV irradiation, C_0 is the initial DNP concentration (5 mg/l).

Financial support

The study was carried out in the framework of State Assignments for JIHT RAS as relevant to the sample synthesis, Physical Research Center „Crystallography and Photonics“ RAS as relevant to examining the samples structural-morphological characteristics, and Platov SPI (code „FENN-2021-0008“) as relevant to investigation of photocatalytic properties.

Conflict of interests

The authors declare that they have no conflict of interests.

References

- [1] A. Bibi, Sh. Bibi, M. Abu-Dieyh, M.A. Al-Ghouti, *J. Clean Prod.*, **417**, 137810 (2023). DOI: 10.1016/j.jclepro.2023.137810
- [2] S. Shurbaji, P.T. Huong, T.M. Altahtamouni, *Catalysts*, **11** (4), 437 (2021). DOI: 10.3390/catal11040437
- [3] G. Ren, H. Han, Y. Wang, S. Liu, J. Zhao, X. Meng, Z. Li, *Nanomaterials*, **11** (7), 1804 (2021). DOI: 10.3390/nano11071804
- [4] J.-M. Herrmann, *Catalys. Today*, **53** (1), 115 (1999). DOI: 10.1016/s0920-5861(99)00107-8
- [5] K.M. Mohamed, J.J. Benitto, J.J. Vijaya, M. Bououdina, *Crystals*, **13** (2), 329 (2023). DOI: 10.3390/cryst13020329
- [6] R. Kabir, M.A.K. Saifullah, A.Z. Ahmed, S.M. Masum, M.A.I. Molla, *J. Compos. Sci.*, **4** (2), 49 (2020). DOI: 10.3390/jcs4020049
- [7] A.E. Muslimov, A.D. Tsarenko, A.S. Lavrikov, A.A. Ulyankina, V.M. Kanevsky, *Pis'ma v ZhTF*, **49** (16), 8 (2023). DOI: 10.21883/PJTF.2023.16.55960.19577 (in Russian)
- [8] M.A. Hanif, Y.S. Kim, S. Ameen, H.G. Kim, L.K. Kwac, *Coatings*, **12** (5), 579 (2022). DOI: 10.3390/coatings12050579
- [9] V.N. Tikhonov, S.N. Aleshin, I.A. Ivanov, A.V. Tikhonov, *J. Phys.: Conf. Ser.*, **927** (1), 012067 (2017). DOI: 10.1088/1742-6596/927/1/012067
- [10] V.N. Tikhonov, I.A. Ivanov, A.V. Tikhonov, *Prikladnaya fizika*, № 4, 123 (2018). (in Russian)
- [11] V.M. Chepelev, A.V. Chistolov, M.A. Khromov, S.N. Antipov, M.K. Gadzhiev, *J. Phys.: Conf. Ser.*, **1556** (1), 012091 (2020). DOI: 10.1088/1742-6596/1556/1/012091
- [12] L.M. Baltin, V.M. Batenin, I.I. Devyatkin, V.R. Lebedeva, N.I. Tsemko, *Teplofizika vysokikh temperatur*, **9** (6), 1105 (1971). (in Russian)
- [13] C.J. Chen, S.Z. Li, *Plasma Sources Sci. Technol.*, **24** (3), 035017 (2015). DOI: 10.1088/0963-0252/24/3/035017
- [14] J.F. García, S. Sánchez, R. Metz, *Oxid. Met.*, **69** (5-6), 317 (2008). DOI: 10.1007/s11085-008-9099-9
- [15] K.V. Kumar, K. Porkodi, F. Rocha, *Catal. Commun.*, **9** (1), 82 (2008). DOI: 10.1016/j.catcom.2007.05.019
- [16] H. Wang, H.-L. Wang, W.-F. Jiang, Z.-Q. Li, *Water Res.*, **43** (1), 204 (2009). DOI: 10.1016/j.watres.2008.10.003

Translated by Solonitsyna Anna