

13.1

Influence of morphological and structural parameters of ZnO tetrapods on their activity in the reaction of photocatalytic degradation of ciprofloxacin

© A.E. Muslimov¹, A.D. Tsarenko², A.S. Lavrikov¹, A.A. Ulyankina², V.M. Kanevsky¹

¹ Shubnikov Institute of Crystallography „Crystallography and Photonics“, Russian Academy of Sciences, Moscow, Russia

² Platov State Polytechnic University, Novocheerkassk, Rostov oblast, Russia

E-mail: amuslimov@mail.ru

Received April 4, 2023

Revised May 17, 2023

Accepted May 30, 2023

The influence of morphological and structural parameters of microdimensional tetrapods ZnO on their activity in the reaction of photocatalytic degradation of ciprofloxacin under the influence of UV light has been studied. The greatest activity (reaction rate constant $25.5 \cdot 10^{-3} \text{ min}^{-1}$) was demonstrated by unalloyed ZnO tetrapods obtained in the presence of Au in the initial charge, which had the smallest geometric parameters. The photocatalytic activity of tetrapods is explained by the highly defective structure of their near-surface layers. Photoactive microsize tetrapods ZnO, synthesized by the carbothermal method, can be used in the mineralization of toxic organic compounds.

Keywords: photocatalytic activity, antibiotic, tetrapods, zinc oxide, microscopy, morphology, structure.

DOI: 10.61011/TPL.2023.08.56687.19577

The worsening contamination of water with medicinal drugs is a side effect of development of the pharmaceutical industry. Antibiotics [1], such as ciprofloxacin (CIP), hold a special place among them. CIP, which belongs to the group of fluoroquinolones, is a broad-spectrum antibiotic that has medicinal and veterinary applications. Fluoroquinolones are currently being examined as possible adjuncts in the treatment of pneumonia associated with SARS-CoV-2 [2]. However, as much as 90% of ciprofloxacin are eliminated out of the body in an unchanged form and enter sewage and soil. Within this context, the emergence of antibiotic resistance is regarded as one of the greatest problems of the world. Several methods for removal of antibiotics from water and reducing their concentration to safe levels have been proposed: membrane treatment, advanced oxidation techniques, such as ozone treatment, ultraviolet (UV) irradiation, photocatalysis (PC), etc. [3]. Photocatalytic processes, which ensure mineralization of toxic organic compounds with the formation of water and carbon dioxide in the presence of a photocatalyst, hold much promise due to their environmental friendliness and the possibility of application of solar radiation as a readily available and inexhaustible energy source [4]. Titanium dioxide (TiO₂) still remains the most extensively studied and widely used photocatalyst [4]. Active research into alternative photocatalysts (specifically, materials based on zinc oxide ZnO) has been conducted in the last few years [5–7]. It is known that the PC activity of semiconductor materials is the result of synergism of several factors such as the morphology, crystallinity, and surface area of particles [8] and the presence of centers inhibiting the recombination of photogenerated carriers. Within this context, tetrapod/multipod particles have an advantage over

spherical particles in providing an opportunity to suppress considerably their agglomeration in the process of photocatalysis [9]. ZnO tetrapods, which feature an enhanced surface area, are self-organized pseudo-three-dimensional nanostructures with four single-crystal rods extending from the vertices of a tetrahedron. These materials are easy to synthesize under nonequilibrium conditions [10–12]. Although tetrapods feature a perfect single-crystal core, their surface may, depending on the synthesis method, have an imperfect structure. The luminescent properties of a powder of ZnO tetrapods obtained by carbothermal pyrolysis have been reported in [10]. An intense green luminescence band, which is associated with surface defects in ZnO [13], was observed in the spectrum. Thus, ZnO tetrapods have a hierarchical structure with a single-crystal core and an imperfect surface layer that may act as an efficient sink for photogenerated carriers and suppress their recombination. However, it still remains difficult to produce ZnO tetrapods with the desired size and morphology [14]. A way to modify the shape and size of ZnO tetrapods by varying admixtures to the charge material has been proposed in [10]. Several research techniques have been applied to demonstrate that an admixture present in the charge material does not get incorporated (or substituted) into the matrix of ZnO tetrapods in the course of carbothermal synthesis. This allows one to state that the admixture concentration is negligible and has a much weaker effect on the properties of tetrapods than their morphological and structural properties.

In the present study, we examine the influence of morphological and structural parameters of ZnO tetrapods on their activity in the reaction of PC degradation of ciprofloxacin under UV irradiation.

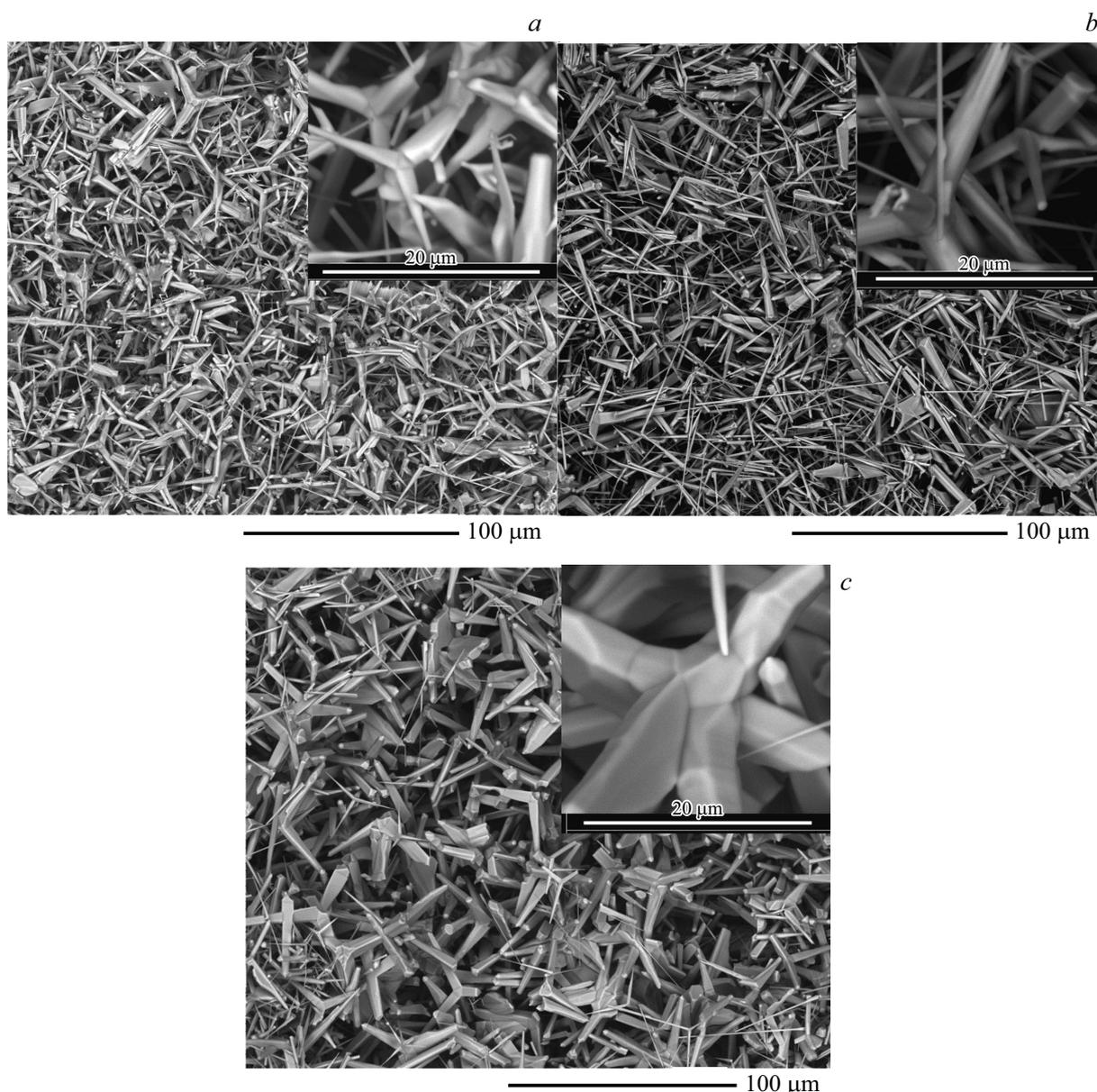


Figure 1. Microscope images of ensembles of ZnO tetrapods type I (*a*), II (*b*), and III (*c*). Enlarged fragments of the corresponding images are shown in the insets.

ZnO tetrapods have been synthesized from the charge material with various admixtures by carbothermal pyrolysis in [10]. The following three types of ZnO tetrapod samples with different admixture (atomic) concentrations were obtained: I (0.4% Au), II (4% Cu), and III (10% Cu). A Quanta 200 scanning electron microscope was used for microscopic examination of these samples. X-ray diffraction analysis (XRD) was performed using an X'TRA ThermoFisher diffractometer and $\text{CuK}\alpha$ -radiation (1.5405 Å). Emission spectra were examined by exciting cathodoluminescence (CL) at an accelerating voltage of 50 kV. In order to study the photocatalytic activity of synthesized materials, ZnO powder (25 mg) was introduced into an aqueous solution of CIP (50 ml) with a concentration of

5 mg/l, and the mixture was stirred in the dark for 30 min. The obtained suspension was illuminated by a UV lamp (Hamamatsu Photonics LC8) with its intensity maximum at 365 nm under constant stirring. The CIP concentration was determined using a Shimadzu UV-1800 spectrophotometer.

Figure 1 presents the images that were obtained using the scanning electron microscope and confirm the formation of particles in the shape of tetrapods in synthesized ZnO samples. ZnO tetrapods forming with admixed Au (type I) are the smallest in size (Fig. 1, *a*) with l (leg length) up to $20\ \mu\text{m}$ and d (leg diameter at the base) up to $3\ \mu\text{m}$. The low diffusion activity of „heavy“ Au atoms inhibits the growth of ZnO tetrapods. Powders forming in the presence of Cu (type II, Fig. 1, *b*) have

an inhomogeneous morphological composition: large ZnO tetrapods are observed alongside with rods and hollow structures. The dimensions are as follows: l up to $40\ \mu\text{m}$ and d up to $6\ \mu\text{m}$. The largest ZnO tetrapods (Fig. 1, *c*) form under an increased Cu concentration (type III). Their dimensions are as follows: l up to $20\ \mu\text{m}$ and d up to $10\ \mu\text{m}$. Multipods, which form as a result of coalescence of tetrapods (inset in Fig. 1, *c*), are also observed. Owing to a substantial morphological inhomogeneity of ZnO tetrapod ensembles, we provide only a rough estimate of parameters of structures. However, it may be noted that micrometer-sized tetrapods form in the course of carbothermal synthesis and that tetrapods grow larger in transition from type I to type III. Reflections in the XRD spectra of type I–III tetrapod samples correspond to the hexagonal wurtzite ZnO phase (JCPDS N 79-0205). The most intense reflections at 31.8 , 34.5 , and 36.4° correspond to reflections off planes (100), (002), and (101) ZnO. The wurtzite structure is specific in lacking a center of symmetry, which implies the presence of piezoelectric polarization along basal axis [001]. Planes (100) and (101) are nonpolar and semipolar, respectively. Ratio I_{101}/I_{002} of intensities of reflections off semipolar (101) and polar (002) planes was calculated for synthesized ZnO tetrapods based on XRD data: 2.45, 2.68, 3.18 for samples type I, II, and III, respectively. It follows that the fraction of the polar component is the greatest in samples type I and the smallest in samples type III. CL spectra of tetrapod samples of all three types were identical. The typical CL spectrum of ZnO tetrapod samples is shown in Fig. 2. The following two bands are seen in the CL spectrum: an intense broad (450–700 nm) defect luminescence band and a weak edge luminescence band. The luminescence spectra of identical batches of ZnO tetrapods examined earlier in [10] under X-ray excitation have also revealed a dominant defect luminescence band. It is known [15] that luminescence in the 450–700 nm region is associated with the energy levels of Zn_i , V_{Zn} , O_i , and V_O defects in the band gap. The shape and intensity equivalence of defect luminescence bands found in different tetrapod samples suggests the presence of the same defects with similar densities.

The influence of morphological and structural features of synthesized ZnO tetrapods on their photocatalytic properties was examined in the process of CIP (antibiotic) photodegradation in an aqueous medium. Figure 3, *a* presents the dependences of C/C_0 on irradiation time with ZnO samples acting as photocatalysts. The efficiency of CIP photolysis was estimated for comparison. It can be seen that the depth of CIP photodegradation increased considerably following the addition of a photocatalyst. CIP photodegradation rate constant k was determined from the slope of linearized kinetic curves $\ln(C/C_0)-t$ (Fig. 3, *b*) with the use of the Langmuir–Hinshelwood model [16]. The CIP photodegradation rate was the highest for ZnO samples type I synthesized in the presence of Au (rate constant $k = 25.5 \cdot 10^{-3} \text{ min}^{-1}$). The PC activity of ZnO tetrapods increases in sequence from type III to type II

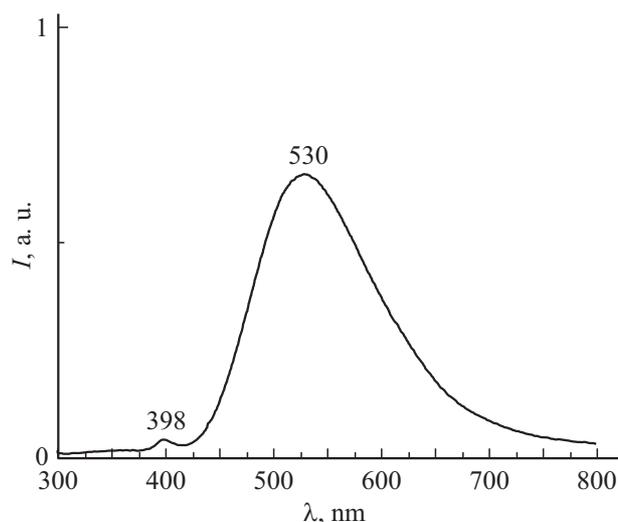


Figure 2. Typical CL spectrum of ZnO tetrapod samples.

to type I. Thus, the PC activity generally correlates with a reduction in the size of tetrapods and an increase in the active surface area. It should be noted that the structural conditioning of ZnO tetrapod photoactivity may also have an impact here. Calculated data [17] reveal that the electron energy for (101) ZnO is lower than the one for (100) ZnO. This implies that the PC activity of (101) ZnO should be increased. It is also known [18] that piezoelectric polarization along [001] in ZnO induces spatial separation of electrons and holes (quantum-dimensional Stark effect) and should enhance the PC sensitivity. However, the data reported in [19] reveal that the catalytic activity decreases as the polar component grows stronger and nanoscale ZnO tetrapods become smaller. It was concluded in [19] that the chemical state of the surface is more important than the surface area and structural features. The suppression of the polar component in transition from samples type I to samples type III does not explain a four-fold reduction in their PC activity. The chemical state of the surface of samples, which depends primarily on the synthesis conditions, is an important parameter. Since samples type I–III are synthesized under the same conditions, the specifics of synthesis also provide no explanation for the observed enhancement. The area (contribution of near-surface layers) decreases many-fold in transition from nanoscale tetrapods to microscale ones. However, microscale ZnO tetrapods synthesized in the present study exhibit high PC activity levels. The high density of near-surface defects, which are revealed by the CL data in Fig. 2, plays a leading part here. The intensity of the edge luminescence band of ZnO tetrapods (Fig. 2) is low, although the results of electron microscopic investigations [20] normally attest to a high degree of crystalline perfection of tetrapods. In carbothermal synthesis, the nucleation and growth of ZnO tetrapods proceed under strong supersaturation due to an excess concentration of zinc in the growth zone. This

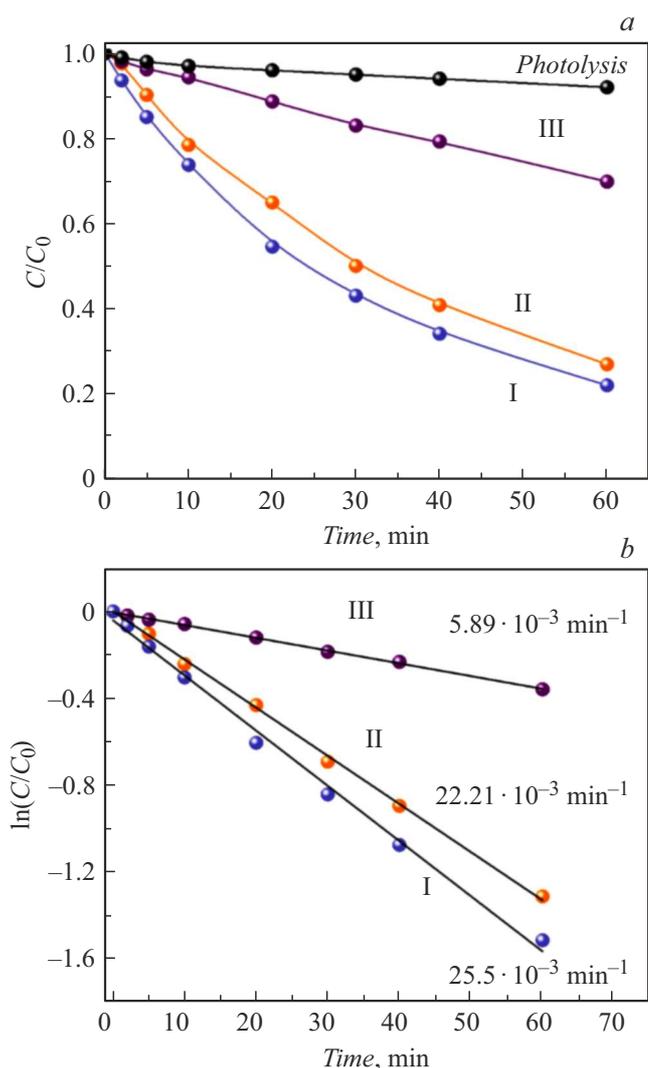


Figure 3. Curves of CIP photodegradation under UV irradiation (365 nm , 2 mW/cm^2) (a) and determination of the reaction rate constant (k , min^{-1}) (b) in the presence of ZnO tetrapods of different types. C — CIP concentration at time t elapsed from the start of UV irradiation; C_0 — initial CIP concentration (5 mg/l).

provides an opportunity to raise the synthesis rate, but the diffusion activity of adatoms decreases alongside with that, and the anion deficiency and the degree of imperfection of ZnO tetrapods increase.

The influence of morphological and structural parameters of ZnO tetrapods on their activity in the reaction of photocatalytic degradation of ciprofloxacin under UV irradiation was examined. It was demonstrated that microscale ZnO tetrapods form in the process of carbothermal synthesis. ZnO tetrapods with the smallest geometric dimensions synthesized in the presence of Au exhibited the highest activity in the reaction of photocatalytic degradation of ciprofloxacin (rate constant $25.5 \cdot 10^{-3} \text{ min}^{-1}$). The PC activity of ZnO tetrapods synthesized by carbothermal pyrolysis is governed by

their defect structure and an increased active surface area.

Funding

This study was carried out under the state assignments of FSRC „Crystallography and Photonics“ of the Russian Academy of Sciences (synthesis of tetrapod samples) and the Platov South-Russian State Polytechnic University (study of photocatalytic properties, code „FENN-2021-0008“).

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] Z. Maghsodian, A.M. Sanati, T. Mashifana, M. Sillanpää, S. Feng, T. Nhat, B. Ramavandi, *Antibiotics*, **11** (11), 1461 (2022). DOI: 10.3390/antibiotics11111461
- [2] I. Karampela, M. Dalamaga, *Arch. Med. Res.*, **51** (7), 741 (2020). DOI: 10.1016/j.arcmed.2020.06.004
- [3] J. Fu, Y. Zhao, O. Yao, O. Addo-Bankas, B. Ji, Y. Yuan, T. Wei, A. Esteve-Núñez, *Sci. Total. Environ.*, **838** (pt 3), 156427 (2022). DOI: 10.1016/j.scitotenv.2022.156427
- [4] O. Baaloudj, I. Assadi, N. Nasrallah, A. El Jery, L. Khezami, A.A. Assadi, *J. Water Process Eng.*, **42**, 102089 (2021). DOI: 10.1016/j.jwpe.2021.102089
- [5] D. Štrbac, C.A. Aggelopoulos, G. Štrbac, M. Dimitropoulos, M. Novaković, T. Ivetić, S.N. Yannopoulos, *Process Safety Environ. Protect.*, **113**, 174 (2018). DOI: 10.1016/j.psep.2017.10.007
- [6] M.I. Chebanenko, S.M. Tikhanova, V.N. Nevedomskiy, V.I. Popkov, *Inorganics*, **10** (12), 249 (2022). DOI: 10.3390/inorganics10120249
- [7] A.N. Matveyeva, S.O. Omarov, A.V. Nashchekin, V.I. Popkov, D.Y. Murzin, *Dalton Trans.*, **51** (32), 12213 (2022). DOI: 10.1039/D2DT02088B
- [8] W. Cen, T. Xiong, C. Tang, S. Yuan, F. Dong, *Ind. Eng. Chem. Res.*, **53** (39), 15002 (2014). DOI: 10.1021/ie502670n
- [9] Y.K. Mishra, G. Modi, V. Cretu, V. Postica, O. Lupan, T. Reimer, R. Adelung, *ACS Appl. Mater. Interfaces*, **7** (26), 14303 (2015). DOI: 10.1021/acsami.5b02816
- [10] I.D. Venetsev, A.E. Muslimov, L.A. Zadorozhnaya, A.S. Lavrikov, P.A. Rodnyi, V.M. Kanevsky, *Opt. Spectrosc.*, **128** (11), 1784 (2020). DOI: 10.1134/S0030400X20110272
- [11] K. Nishio, T. Isshiki, M. Kitano, M. Shiojiri, *Phil. Mag. A*, **76** (4), 889 (1997). DOI: 10.1080/01418619708214216
- [12] S.V. Avilov, A.V. Tuchin, A.N. Shebanov, E.P. Domashevskaya, *Cryst. Rep.*, **64** (2), 212 (2019). DOI: 10.1134/s1063774519020032
- [13] Z.G. Wang, X.T. Zu, S. Zhu, L.M. Wang, *Physica E*, **35** (1), 199 (2006). DOI: 10.1016/j.physe.2006.07.022
- [14] L. Shen, H. Zhang, S. Guo, *Mater. Chem. Phys.*, **114** (2-3), 580 (2009). DOI: 10.1016/j.matchemphys.2008.10.004
- [15] B.-J. Lee, S.-I. Jo, G.-H. Jeong, *Nanomaterials*, **9** (7), 942 (2019). DOI: 10.3390/nano9070942

- [16] A.V. Agafonov, A.A. Redozubov, V.V. Kozik, A.S. Kraev, *Russ. J. Inorg. Chem.*, **60** (8), 906 (2015). DOI: 10.1134/S0036023615080021
- [17] T. Zhou, M. Hu, J. He, R. Xie, C. An, C. Li, J. Luo, *CrystEngComm.*, **21** (36), 5526 (2019). DOI: 10.1039/c9ce01073d
- [18] A.E. Romanov, T.J. Baker, S. Nakamura, J.S. Speck, *J. Appl. Phys.*, **100** (2), 023522 (2006). DOI: 10.1063/1.2218385
- [19] S.-G. Heo, S.-I. Jo, G.-H. Jeong, *Current Appl. Phys.*, **46**, 46 (2023). DOI: 10.1016/j.cap.2022.12.004
- [20] M.C. Newton, P.A. Warburton, *Mater. Today*, **10** (5), 50 (2007). DOI: 10.1016/s1369-7021(07)70079-2

Translated by D.Safin