

PHOTOLUMINESCENCE OF ZINC OXIDE NANOCRYSTALS OBTAINED BY CHEMICAL METHOD

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In this work, ZnO nanocrystals were synthesized by a chemical method. Optical absorption and photoluminescence spectra of the obtained nanocrystals were recorded. It was found that with an increase in the concentration of precursors, the fundamental absorption edge shifts to the region of lower energies. It was also shown that the ultraviolet radiation of colloidal zinc oxide nanocrystals is due to radiative transitions involving excitons bound on intrinsic defects, and visible radiation is within donor-acceptor pairs.

Keywords: ZnO nanoparticles, optical absorption, photoluminescence.

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Zinc oxide nanocrystals have found wide application due to their large band gap and biocompatibility, which determines their use in UV lasers and LEDs, luminescent sensors and biomedical imaging systems and antibacterial treatment [1, 2].

Chemical methods of synthesis, along with simplicity and low cost, have a number of disadvantages, the main one being the high dispersion of synthesized nanoparticles, which leads to the blurring of emission lines. Another disadvantage is the uncontrolled doping with precursor atoms.

In this work, an attempt was made to avoid these disadvantages by using precursors that are poorly integrated into the zinc oxide lattice (SO₄ and K). Effective visible radiation was obtained, the elementary lines of which do not depend on the size of the nanocrystallites in the range of 3-16 nm.

The size of the nanoparticles was estimated by the magnitude of the shift of the fundamental absorption edge in the effective mass approximation using the Wong formula [3]. For this purpose, the optical absorption spectra of ZnO nanocrystals were obtained in the presence and absence of a nanoparticle growth stabilizer, which was gelatin or polyvinyl alcohol. In both cases, it was found that with an increase in the concentration of precursors, the fundamental absorption edge shifts to the region of lower energies. This is associated with an increase in the size of the nanocrystallites.

The results of optical absorption calculations (Table 1) are in good agreement with scanning electron microscopy studies, which showed the formation of ZnO nanocrystals up to 15 nm in size.

Results of optical absorption calculations.

№.	ZnSO ₄ , KOH	Gelatin concentration	E _g , eV	ΔE _g , eV	R, nm
1.	10 %	5%	4.4	1.2	3.7
2.	20 %	5%	4.2	1.0	4.1
3.	50 %	5%	4.0	0.8	4.5
4.	10 %	0%	3.5	0.3	7.7
5.	20 %	0%	3.3	0.1	13

TABLE 1.

Photoluminescence spectra of ZnO nanocrystals have efficient photoluminescence in two spectral regions – ultraviolet and visible.

The radiation in the ultraviolet region is characterized by three narrow lines, the position of which correlates with the width of the forbidden band (Fig. 1). The position of the first two emission lines (3.8 eV and 3.6 eV) coincides with the energies of the second and third linear sections of the corresponding absorption spectra, which confirms their exciton nature.

The first emission line is associated [4] with excitons associated with neutral donors, which are

interstitial zinc atoms Zn_i^0 , with a depth of 0.40 eV from the bottom of the conduction band. The second emission line is due to radiative transitions involving excitons associated with neutral zinc vacancies V_{Zn}^0 , with a depth of 0.56 eV from the top of the valence band [5].

The third line of ultraviolet radiation the authors [6] attribute to recombination luminescence with the participation of deep (0.74 eV) donors which are interstitial zinc atoms in the charge state +2 (Zn_i^{+2}). The emission spectra in the visible region do not

correlate with the change in the width of the forbidden band of ZnO nanocrystals. Elementary emission lines are distinguished at 2.82 eV, 2.72 eV, 2.62 eV, 2.50 eV, 2.38 eV, 2.30 eV, 2.17 eV, 2.06 eV, 1.88 eV and 1.70 eV (Fig. 2). The absence of absorption in the visible region indicates the absence of impurity centers, and therefore, most likely, the observed emission lines are

due to optical transitions within transitions within donor-acceptor pairs, which include intrinsic defects. Since the emission line at 2.5 eV has the lowest emission intensity, it can be assumed that zinc vacancies, which are part of the $(Zn_i^0, V_{Zn}^0)^*$ centers, are filled at high precursor concentrations.

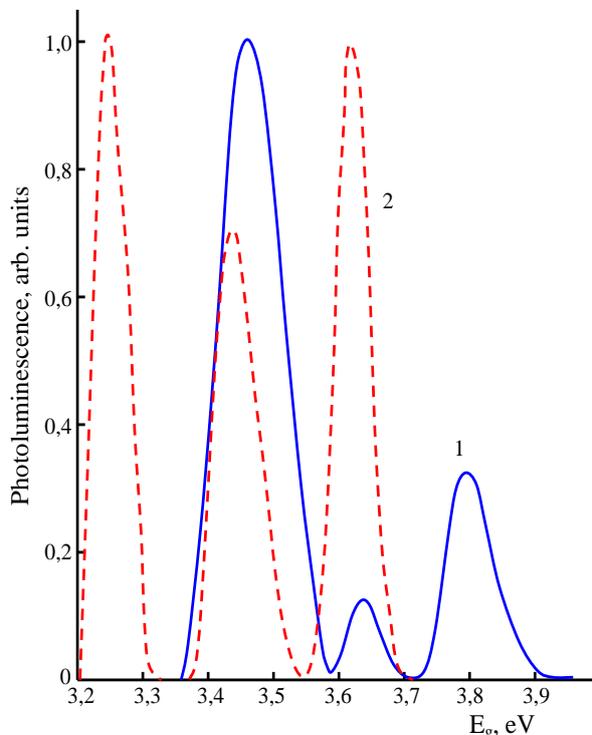


Fig. 1. Photoluminescence spectra in the UV region. Samples No. 2 (1), No. 3 (2). $T_{meas}=300$ K.

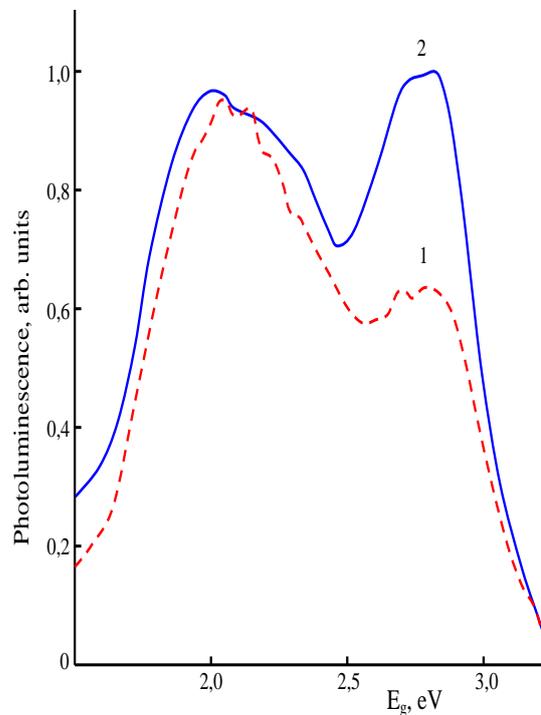


Fig. 2. Photoluminescence spectra in the visible region. Samples No. 2 (1) and No. 4 (2). $T_{meas}=300$ K.

In confirmation of this, we observed an increase in the intensity of the lines in the blue region of the spectrum (2.82 eV, 2.72 eV and 2.62 eV) (Fig. 2) with an increase in the concentration of zinc and oxygen precursors. These lines may be due to interstitial zinc and oxygen atoms. Comparison of the energy states of these centers in zinc oxide nanocrystals suggests that the lines at 2.82, 2.72 and 2.62 eV may be due to associative centers $(Zn_i^0, O_i^0)^*$ with different distances between donors and acceptors [7].

The yellow-green emission lines 2.3 and 2.38 eV

may be due to transitions within the centers $(Zn_i^+, V_{Zn}^-)^*$. The emission lines in the red-orange region with energies of 2.17 eV, 2.06 eV, 1.88 eV are caused by transitions within neutral association centers of the $(Zn_i^{+2}, O_i^{-2})^*$ with different distances between donors and acceptors. Thus, the conducted studies showed that the ultraviolet radiation of colloidal zinc oxide nanocrystals is caused by radiative transitions involving excitons bound on intrinsic defects, and the visible radiation is caused by transitions within donor-acceptor pairs.

[1] A. Wibowo, M.A. Marsudi, M.I. Amal, M.B. Ananda, R. Stephanie, H. Ardy, L.J. Diguna. ZnO nanostructured materials for emerging solar cell applications. RSC Adv.– 2020. – V. 10. – P. 42838 – 42859.
 [2] Z.-Y. Zhang, H.-M. Xiong. Photoluminescent ZnO Nanoparticles and Their Biological Applications. Mater. 2015. – V. 8. – P. 3101 – 3127.
 [3] B.K. Meyer, J. Sann, S. Lautenschläger,

M.R. Wagner, A. Hoffmann. Ionized and neutral donor-bound excitons in ZnO. Phys. Rev. B.– 2007. –V. 76.– N18. – P. 4120 – 4131.
 [4] J. Zhou, F. Zhao, Y. Wang, Y. Zhang, L. Yang. Size-controlled synthesis of ZnO nanoparticles and their photoluminescence properties. Journal of Luminescence.–2007.V. 122–123. P. 195– 197.
 [5] M. Willander, O. Nur, J. Sadaf, M. Qadir, Z. Saima, A. Zainelabdin, N. Bano, I. Hussain. Luminescence from Zinc Oxide Nanostructures

- and Polymers and their Hybrid Devices Materials. – 2010. – V. 3. – P. 2643 – 2667.
- [6] *A. Sharma, B.P. Singh, S. Dhar, A. Gondorf, M. Spasova.* Effect of surface groups on the luminescence property of ZnO nanoparticles synthesized by sol–gel route. Surface Science. – 2012. – V. 606. – L13 – L17.
- [7] *S. Vempati, J. Mitra, P. Dawson.* One-step synthesis of ZnO nanosheets: A blue-white fluorophore. Nanoscale research letters. – 2012. – V. 7. – P. 470.

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