ISSN 1068-3356, Bulletin of the Lebedev Physics Institute, 2017, Vol. 44, No. 3, pp. 53–55. © Allerton Press, Inc., 2017.
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Luminescence Properties of Nanoparticles Synthesized in Electric Discharge in Liquid under Ultrasonic Cavitation

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Received June 23, 2015

Abstract—The differences in the luminescence intensity of metal oxide nanoparticles synthesized in electric discharges in liquid media under intense ultrasonic vibrations in the absence and presence of cavitation are studied.

DOI: 10.3103/S1068335617030010

Keywords: ultrasound, cavitation, plasma, electric discharge, nanoparticles, luminescence.

Synthesis of nanoscale materials with controlled properties is an urgent fundamental scientific problem. Along with conventional chemical synthesis methods, attention of researchers is currently attracted to physical methods for influencing materials, such as electric discharges and ultrasonic cavitation [1–3].

One of the promising ways to produce nanoscale materials, including metal oxide powders, is the combined exposure of a liquid medium to high-intensity elastic ultrasonic vibrations and pulsed or steady electric fields. Such a plasma type, in addition to interest in it as to a new object of physical studies, has a number of advantages as a method for synthesizing nanomaterials, i.e., a relatively narrow size distribution of synthesized nanopowder particles, specific composition and properties of obtained nanomaterials, and high production [4–6].

To test the applicability of such discharge to directed production of optically active nanomaterials, properties of tungsten oxide and zinc oxide nanoparticles synthesized in the discharge in the presence of ultrasound, but without cavitation and under ultrasonic cavitation were studied.

The results of scanning electron microscopy show the presence of particles from 10 to 100 nm in size with various morphology in tungsten oxide samples. Particles with different spatial symmetry of the lattice are also observed. An analysis of the sample chemical composition showed that the tungsten-to-oxygen ratio for samples of particles synthesized without cavitation is close to 1/3; for particles synthesized under cavitation, this ratio varies from 2/5 to 1/3 [6]. This leads to the appearance of different symmetry types of the lattice and different morphologies of such particles.

Comparing the IR transmission spectra of large and small particles in Fig. 1, we can note significant differences in the range of 500–1000 cm^{-1} corresponding to W–O stretching vibrations. For the particles synthesized under ultrasonic cavitation, the intensity of W–O bond vibrations is appreciably higher; therewith, noticeable narrowing of vibration bands and an increase in their relative intensity are observed for small particles. We can see the difference in the dependences on the synthesis method for large and small particles.

In the case of intense exposure to ultrasound, it was possible to obtain narrow dimensional nanoparticle fractions, which is consistent with the results we obtained previously during synthesis and stabilization of particles of oxides of other metals [7–11].

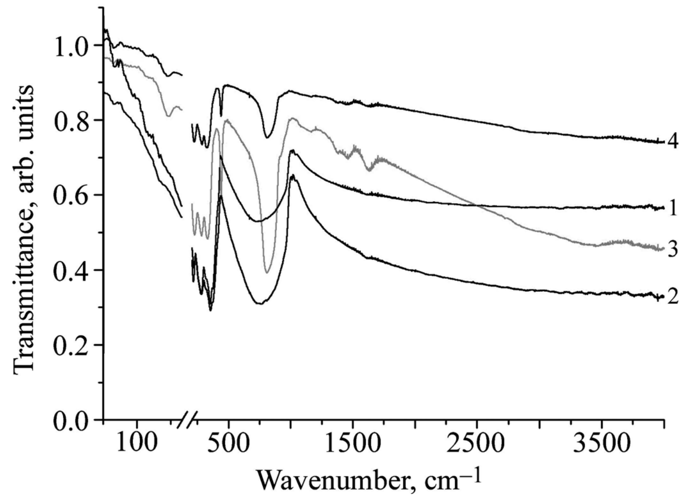

Fig. 1. IR spectra of tungsten oxide nanoparticles produced in the plasma discharge without and under ultrasonic cavitation: (1) large particles (50–100 nm) without ultrasound, (2) large particles with ultrasound, (3) small particles (10–30 nm) without ultrasound, and (4) small particles with ultrasound.

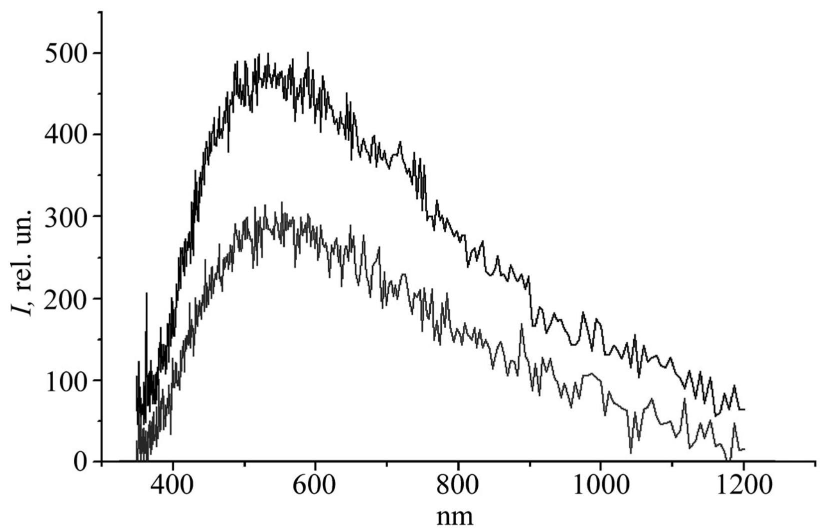

Fig. 2. Photoluminescence spectra of tungsten oxide nanoparticles produced in the plasma discharge under ultrasound. The lower and upper curves correspond to the ultrasound intensity below and above the cavitation threshold, respectively.

It was found that synthesized tungsten oxide particles have optical characteristics depending on the ultrasonic field intensity during synthesis [5]. Figure 2 shows the photoluminescence spectra of aqueous dispersions of tungsten oxide, produced in the plasma discharge without and with ultrasonic cavitation. The normalization of the spectra is identical.

The difference in the luminescence intensity can probably be explained by different chemical compositions of formed tungsten oxide (WO_3 without cavitation and WO_{2-3} under cavitation). The presence of WO_2 promotes higher electron delocalization in molecules and, hence, a higher luminescence intensity. These results are consistent with the difference in the W–O bond vibration intensity detected by IR spectroscopy in particles produced without and with ultrasonic cavitation.

To confirm the dependence of the nanoparticle luminescence on the ultrasonic field intensity during synthesis, further experiments were performed with zinc oxide nanoparticles. To this end, the plasma discharge was initiated on zinc electrodes. The electron microscopy study of particles showed that, first, the rod-shaped particles are produced in the plasma synthesis and second, they are not enlarged,

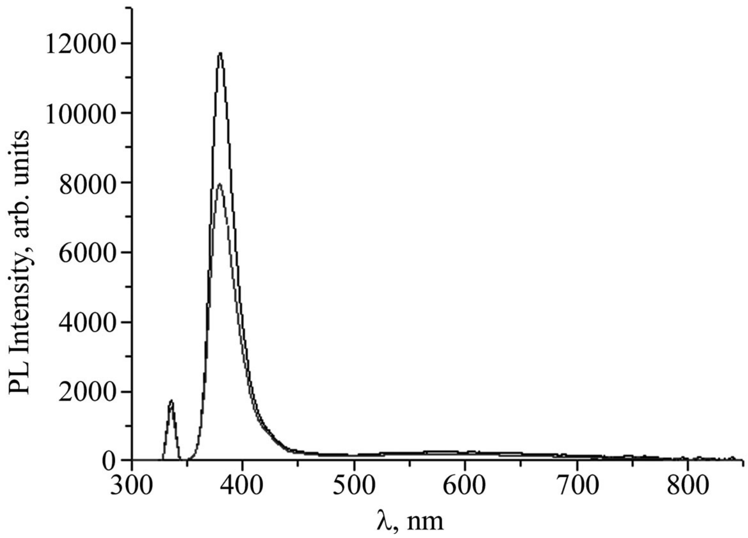

Fig. 3. Photoluminescence spectra of zinc oxide nanoparticles produced in the plasma discharge under ultrasound. The lower and upper curves correspond to the ultrasound intensity below and above the cavitation threshold. (Peaks of both curves near 340 nm almost coincide.)

but form composite aggregates [5]. In the synthesis under ultrasonic cavitation, stable suspensions of individual particles are formed.

The results of the study of luminescence properties of zinc oxide nanoparticles without and with cavitation are shown in Fig. 3.

An increase in the luminescence intensity of nanoparticles produced under ultrasonic cavitation can be explained by the defect formation in oxide nanocrystals under severe mechanical stress. In the synthesis, particles are subjected to not only electromagnetic fields, but also to impact loads during cavitation bubble collapse, which causes the formation of defect valence structures and electron delocalization.

Conclusions. It was found that the combined exposure of a liquid medium to the electric discharge and ultrasound above the cavitation threshold has a specific effect on materials. Metal oxide nanoparticles synthesized in such an acoustoplasma discharge have specific physicochemical and optical characteristics different from those which can be obtained without ultrasound or with ultrasound below the cavitation threshold.

ACKNOWLEDGMENTS

This study was supported in part by the Russian Foundation for Basic Research, projects nos. 15-02-03559-a, 14-02-00602-a, 14-02-92019 NNS_a.

REFERENCES

1. J. Ho Bang and K. S. Suslick, Adv. Mater. **22**, 1039 (2010).
2. H. Ghomi, M. Yousefi, N. Shahabi, and M. Khoramabadi, Radiat. Eff. Defects Solids **168**, 881 (2013).
3. A. Askarinejad, M. A. Alavi, and A. Morsali, Iran J. Chem. Chem. Eng. **30**, 75 (2011).
4. N. A. Bulychev, M. A. Kazaryan, E. S. Gridneva, et al., Kratkie Soobshcheniya po Fizike FIAN **39**(7), 39 (2012) [Bulletin of the Lebedev Physics Institute **39**, 214 (2012)].
5. N. A. Bulychev, M. A. Kazaryan, L. L. Chaikov, et al., Kratkie Soobshcheniya po Fizike FIAN **41**(9), 33 (2014) [Bulletin of the Lebedev Physics Institute **41**, 264 (2014)].
6. N. Klassen, O. Krivko, V. Kedrov, et al., IEEE Trans. Nucl. Sci. **57**, 1377 (2010).
7. R. F. Ganiev, N. A. Bulychev, V. N. Fomin, et al., Dokl. Akad. Nauk Khim. **407**(4), 35 (2006) [Dokl. Chem. **407**(2), 54 (2006)].
8. N. A. Bulychev, E. V. Kisterev, I. A. Arutunov, and V. P. Zubov, J. Balk. Tribol. Assoc. **1**(14), 30 (2008).
9. N. A. Bulychev, Neorg. Mater. **46**, 451 (2010) [Inorg. Mater. **46**, 393 (2010)].
10. N. Bulychev, B. Dervaux, K. Dirnberger, et al., Macromol. Chem. Phys. **9**, 971 (2010).
11. N. Bulychev, O. Confortini, P. Kopold, et al., Polymer **48**, 2636 (2007).