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**A COMPARATIVE STUDY OF ZNO NANOPARTICLES OBTAINED IN ELECTRIC DISCHARGE
IN THE ABSENCE AND PRESENCE OF ULTRASONIC CAVITATION**

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Abstract

In this work, nanoparticles zinc oxides were synthesized in electric discharge in liquid medium in the absence and in presence of ultrasonic cavitation. The size characteristics were studied by electron microscopy and dynamic light scattering techniques. Ultrasound was found to narrow significantly the size distribution width of zinc oxide nanoparticles as well as decrease the average size of nanoparticles. It can be explained by strong ultrasonically induced cavitation effect on the synthesized particles and desagglomeration of particles aggregates.

Keywords

Electric discharge – Ultrasonic cavitation – Nanoparticles – Zinc oxide

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Introduction

Formation of nanomaterials with desired physical and biochemical properties is an actual task of the modern science and technology¹. The production of nanoscale materials with controlled properties, along with traditional chemical methods of synthesis, is possible by applying physical methods, such as electrical discharge and ultrasonic cavitation². The experiments performed earlier have revealed that in the intensive ultrasonic field in a liquid above the cavitation threshold, there may exist a new form of electrical discharge, characterised by both volumetric glow throughout the space between the electrodes and by increasing the volt-ampere characteristics inherent to the abnormal glow discharge in gas³. New chemical reactions can potentially be implemented in this discharge⁴. The use of metal electrodes for the initiation and maintaining of such acoustic plasma discharge in the liquid phase allows the formation of the nanoparticles of the oxides of the metals of which the electrodes are made⁵.

Study of ZnO nanoparticles

The role of ultrasonic cavitation is not only in its impact on electrical-physical characteristics of the discharge, but also in its impact on the fragmentation of the associates of the obtained NPs and on the modification of their surfaces⁶. The investigation of the size

¹ I. S. Burkhanov; L. L. Chaikov; N. A. Bulychev; M. A. Kazaryan y V. I. Krasovskii, "Nanoscale metal oxide particles produced in the plasma discharge in the liquid phase upon exposure to ultrasonic cavitation. 2. Sizes and stability. Dynamic light scattering study", *Bulletin of the Lebedev Physical Institute*, Vol:41 num 10 (2014): 297-304 y A. V. Rudnev; N. G. Vanifatova; T. G. Dzherayan; E. V. Lazareva y N. A. Bulychev, "Study of stability and dispersion composition of calcium hydroxyapatite in aqueous suspensions by capillary zone electrophoresis", *Russian Journal of Analytical Chemistry*, Vol: 68 num 8 (2013).

² A. S. Averyushkin; A. N. Baranov; N. A. Bulychev; A. I. Erokhin y M. A. Kazaryan, "Ag nanoparticles suspensions for stimulated Rayleigh backscattering of single frequency 0.5 micron pulsed laser radiation", *Proceedings of SPIE*, Vol: 10614 num 1L (2018) y N. A. Bulychev; M. A. Kazaryan; E. S. Gridneva; E. N. Murav'ev; V. F. Solinov; K. K. Koshelev; O. K. Kosheleva; V. I. Sachkov y S. G. Chen, "Plasma discharge with bulk glow in the liquid phase exposed to ultrasound", *Bulletin of the Lebedev Physical Institute*, Vol: 39 num 7 (2012): 214-220.

³ N. A. Bulychev; M. A. Kazaryan; A. D. Kudryavtseva; M. V. Kuznetsova; T. F. Limonova; N. V. Tcherniega y K. I. Zemskov, "Anti-Stokes luminescence in nanoscale systems", *Proceedings of SPIE*, Vol: 10614 num 0N (2018) y Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "New approaches to stabilize aqueous soot suspensions in the field of ultrasound". *Revista Inclusiones*, Vol: 7 num 4 (2020).

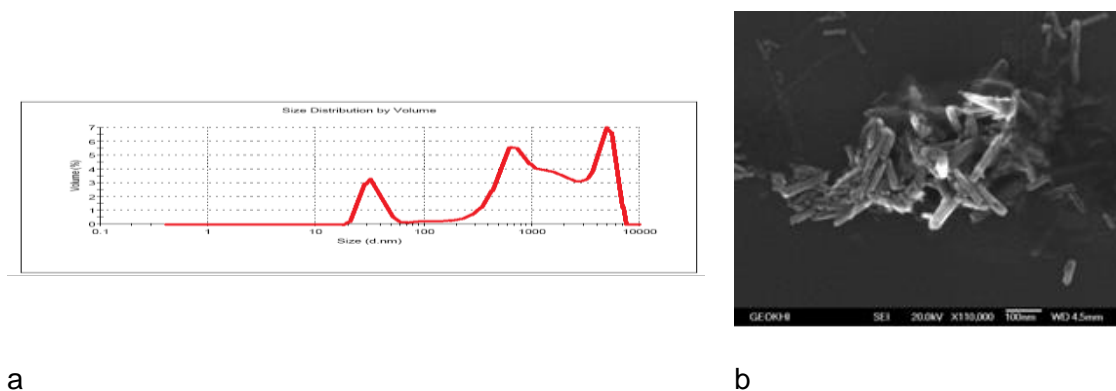
⁴ A. A. Asratyan; S. A. Ambrozevich; O. S. Andrienko; N. A. Bulychev; A. G. Grigoryants; M. A. Kazaryan; S. M. Kazaryan; N. A. Lyabin; R. G. Mkhitarian; G. A. Tonoyan; I. N. Shiganov y V. I. Sachkov, "Comparative analysis of parameters of pulsed copper vapour laser and known types of technological lasers", *Proceedings of SPIE* Vol: 10614 num 02 (2018).

⁵ A. V. Ivanov; V. N. Nikiforov; S. V. Shevchenko; V. Yu. Timoshenko; V. V. Pryadun; N. A. Bulychev; A. B. Bychenko y M. A. Kazaryan, "Properties of Metal Oxide Nanoparticles Prepared by Plasma Discharge in Water with Ultrasonic Cavitation", *International Journal of Nanotechnology*, Vol: 14 num 7/8 (2017): 618-626 y N. Bulychev; W. Van Camp; B. Dervaux; Y. Kirilina; K. Dirnberger; T. Schauer; V. Zubov; F. E. Du Prez y C. D. Eisenbach, "Comparative Study of the Solid-Liquid Interface Behaviour of Amphiphilic Block and Block-like Copolymers", *Macromolecular Chemistry and Physics*, Vol: 210 (2009): 287-298.

⁶ Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "Theoretical and experimental studies of the spectral characteristics of doped semiconductors using zinc oxide and sulfide", *Revista Inclusiones*, Vol: 7, num 3 (2020): 453-463.

distribution of NPs was performed by the method of dynamic light scattering (DLS)⁷. The measurements were carried out with a Zetasizer Nano ZS device, Malvern Instruments Ltd. Additionally the size and morphology on NPs were studied by means of the scanning electron microscopy (SEM)⁸.

By applying ultrasound with frequency of 44 kHz and intensity of 2 W/cm² in a mode of the developed cavitation (the threshold in pure water was about 0.05 W/cm²) the fractions of NPs with narrow size distribution could be obtained⁹. To investigate the effect of cavitation on the size of nanoparticles the experiments on zinc oxide were conducted¹⁰. Without applying cavitation, the agglomerates of the particles with broad size distribution (Fig. 1(a)) were obtained¹¹. The investigation of the precursor particles by the method of electron microscopy showed that, firstly, when plasma synthesis is applied the rod-shaped particles are produced, and secondly, during the aggregation process they did not grow larger, but could form constituent aggregations of several microns (Fig. 1(b))¹².



a – size distribution of NPs of zinc oxide obtained in the plasma discharge without cavitation. b – SEM image of an agglomerate of zinc oxide NPs.

⁷ Yu. O. Kirilina; I. V. Bakeeva; N. A. Bulychev y V. P. Zubov, "Organic-inorganic hybrid hydrogels based on linear poly(N-vinylpyrrolidone) and products of hydrolytic polycondensation of tetramethoxysilane", Polymer Science Series B, Vol: 51 num 3-4 (2009): 135.

⁸ Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "Organic pigments surface modification by isobutyl vinyl ether copolymers under the action of ultrasonic", Revista Inclusiones, Vol: 7, num Especial (2020): 11-21.

⁹ Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "The effect of surface mechanical activation of inorganic pigments on the stability of their aqueous dispersions in the presence of ethyl hydroxyethyl cellulose". Revista Inclusiones, Vol: 7 num 4 (2020).

¹⁰ Y. A. Dyakov; M. A. Kazaryan; M. G. Golubkov; D. P. Gubanova; N. A. Bulychev y S. M. Kazaryan, "Laser-induced dissociation processes of protonated glucose: dehydration reactions vs cross-ring dissociation", Proceedings of SPIE, Vol: 10614 num 17 (2018).

¹¹ N. A. Bulychev; M. A. Kazaryan; A. Ethiraj y L. L. Chaikov, "Plasma Discharge in Liquid Phase Media under Ultrasonic Cavitation as a Technique for Synthesizing Gaseous Hydrogen", Bulletin of the Lebedev Physical Institute, Vol: 45 num 9 (2018): 263-266.

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In the ultrasonic cavitation mode, the agglomerates of NPs disintegrated to the primary particles and the width of the distribution peak was substantially tapered, i.e., the system became almost monodisperse one (Fig. 2(a)). It was also shown in previous studies¹³. The SEM image of these NPs is shown in Fig. 2(b).

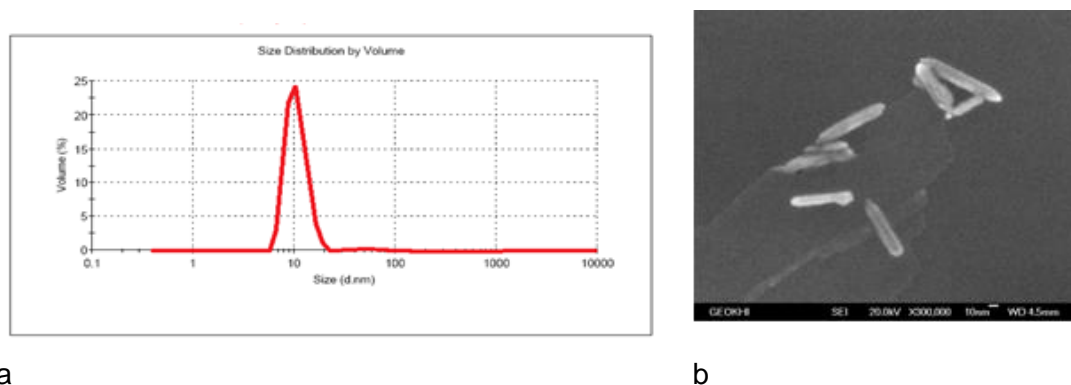


Figure 2

a – size distribution of zinc oxide NPs obtained in the plasma discharge under cavitation. b – SEM image of the corresponding zinc oxide NPs.

In addition to size characteristics it is possible to conclude that the total surface area of such nanoparticles is increased as a result of ultrasonic cavitation, that makes these nanoparticles more favorable in view of production of composite materials, dispersions and functional materials¹⁴.

Conclusions

It was found that ultrasonic cavitation during the nanoparticle formation influenced strongly the size and physical properties of nanoparticles, which were measured by means of the electron microscopy, dynamic light scattering techniques¹⁵. The obtained results indicate good prospects of the prepared nanoparticles for preparing composite materials and high-stable dispersions¹⁶.

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