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SIZE AND OPTIC CHARACTERISTICS OF METAL OXIDE NANOPARTICLES OBTAINED BY ACOUSTOPLASMA TECHNIQUE

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Abstract

Nanoparticles of tungsten, copper, iron, and zinc oxides were synthesized in acoustoplasma discharge. Their size distribution was studied by electron microscopy and laser correlation spectroscopy. Water suspensions of zinc oxide nanoparticles showed photoluminescence in red and near infrared spectral ranges, which makes them a promising material for luminescent diagnostics of biological systems.

Keywords

Metal oxides – Plasma – Discharge – Nanoparticles

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Introduction

Obtaining of nanomaterials with desired physical and biochemical properties is an actual task of the modern science and technology. Nanoparticles (NPs) of the 3d metal oxides, particularly of the iron oxides, are widely used in biology and medicine[1]. So, nanomagnetite NPs are applied as active agents of magnetic hyperthermia in oncology. The interest in this method of treatment was increased owing to the lack of resistance[2]. The use of hyperthermia combined with other methods – chemotherapy and radiation therapy – can reduce the doses of drugs and radiation[3]. 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 cavitation[4]. One of the promising ways of the production of nanoscale materials, including metal oxide powder, is a method of combined impact on the liquid medium by high intensity ultrasonic oscillations and by pulsed or stationary electric fields[5]. The acoustic plasma discharge obtained in cavitation liquid medium is a new and poorly researched physical phenomenon[6]. This method has several advantages as the method of production of nanomaterials: a relatively narrow distribution of the particle size of the synthesised nanopowder, specific composition and properties of the resulting nanomaterials, high production rate[7].

Physical properties of nanoparticles

We have investigated the possibility of the controlled production of NPs of various materials in a liquid medium using the acoustic plasma discharge. The experiments were performed in water[8]. The use of the electrodes of a particular material (tungsten, iron,

[1] N. A. Bulychev; E. L. Kuznetsova; V. V. Bodryshev y L. N. Rabinskiy, “Nanotechnological Aspects of Temperature-Dependent Decomposition of Polymer Solutions”, Nanoscience and Technology: An International Journal, Vol: 9 num 2 (2018): 91-97.

[2] M. N. Kirichenko; L. L. Chaikov; I. S. Burkhanov; N. A. Bulychev y M. A. Kazaryan, “Interaction of aluminum oxide nanoparticles with human blood plasma thrombin (according to light scattering)”, Proceedings of SPIE, Vol: 11322 num 1Y (2019).

[3] Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, “Ultrasonic treatment impact on the stability of aqueous dispersions of inorganic and organic pigments in the presence of surfactants”, Revista Inclusiones, Vol: 7, num Especial (2020): 387-397.

[4] 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.

[5] 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.

[6] N. A. Bulychev y M. A. Kazaryan, “Application of Optical Spectroscopy for Study of Hydrogen Synthesis in Plasma Discharge in Liquid under Ultrasonic Cavitation”, Proceedings of SPIE, Vol: 11322 num 1A (2019).

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[8] 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): 700.

copper, zinc) leads to the oxidation in oxygen-containing liquids by plasma discharge and to the formation of the suspension of nanoparticles of metal oxides in liquid medium[9]. 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 surfaces[10]. The investigation of the size distribution of NPs was performed by the method of dynamic light scattering (DLS)[11]. The measurements were carried out with a Zetasizer Nano ZS device, Malvern Instruments Ltd[12].

The specific feature of the DLS method is its sensitivity to the shape of nanoparticles[13]. In the case of spherical particles, the hydrodynamic radius obtained by the Stokes-Einstein equation corresponds to the data produced by electron microscopy, in the case of deviations of the sphericity the method of DLS provides values in a wide size range[14]. The nanoparticles of zinc oxide are in the form of elongated cylinders and therefore the particle size distribution obtained by the DLS does not reflect the reality[15].

Figure 1 shows the DLS data for the NPs after the ultrasound treatment. It was experimentally confirmed that nanoparticles with a shape close to spherical, have size distribution consistent with that of electron microscopy[16]. In the data of the size distribution of such NPs in their aqueous suspensions shown in Figure 1 the maximum of the DLS spectrum of the test samples is around 9 nm for iron oxide with cavitation (Fe1), 220 nm for iron oxide without cavitation (Fe2), 20 nm for tungsten oxide (W) and 37 nm for copper oxide (Cu). For the zinc oxide owing to its elongated rod-shape the maximum of 100 nm corresponds to the longitudinal size of nano-object[17].

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[9] 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.

[10] 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.

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[12] 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.

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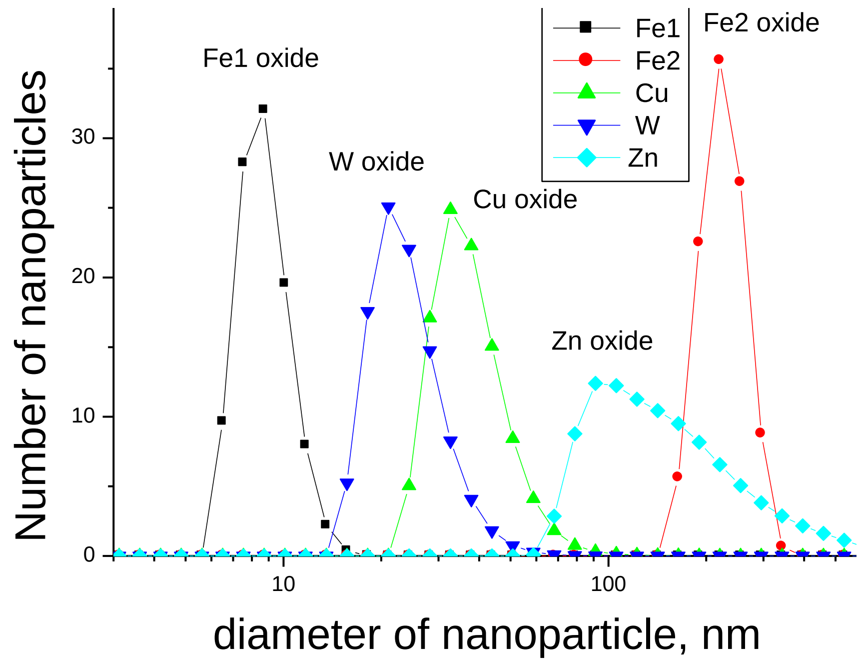

Figure 1
Size distribution of the metal oxide NPs in aqueous suspensions according to the DLS data

The obtained DLS data shows good correlation of the results of the size evaluation obtained through their direct SEM measurements. Figure 1 shows the spectra distribution of the particle size of the two types of iron oxide, Fe1 and Fe2, which differ by the synthesis method, particularly by the intensity of sonication. The synthesized particles differ by average sizes, depending on the intensity of ultrasonic field in the synthesis process: Fe2 corresponds to the intensity of ultrasound below the cavitation threshold, Fe1 – above the cavitation threshold, namely – 2 W/cm2. The maximum of the spectrum of DLS from the test samples is around 9 nm for iron oxide Fe1, 220 nm for iron oxide Fe2, the data that testifies to the decisive role of the intensity of ultrasound in the synthesis[18]. From the obtained data it is clear that the impact of ultrasound above the cavitation threshold in the synthesis shifts maximum range of DLS in the region of 9 nm. Such a change in the size indicates the strong interaction of nanoparticles which have a magnetic dipole-dipole interaction[19].

Photoluminescence spectrum of the aqueous dispersions of zinc oxide formed in the plasma discharge in the presence of ultrasonic cavitation are shown in the Fig. 2. The measurements were carried out with a Cary Eclipse spectrofluorimeter[20].

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18 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.

19 Yu. V. Ioni; S. V. Tkachev; N. A. Bulychev y S. P. Gubin, "Preparation of Finely Dispersed Nanographite", Inorganic Materials, Vol: 47 num 6, (2011): 597-602.

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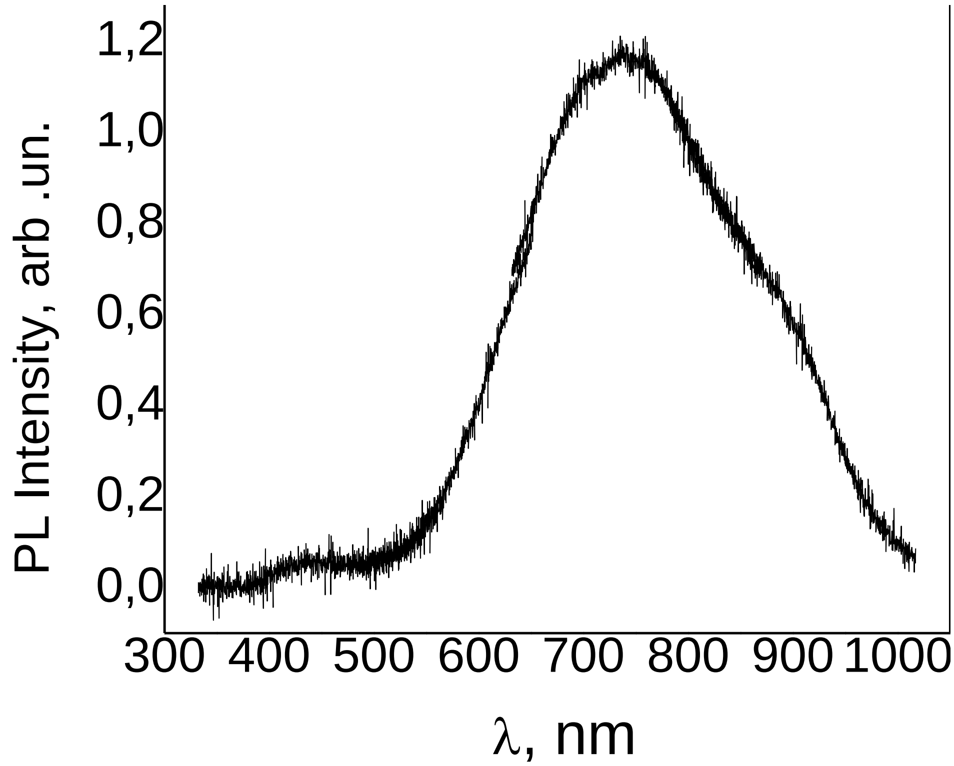

Figure 2
Photoluminescence spectrum of an aqueous suspension of ZnO NPs prepared in the plasma discharge with ultrasound cavitation. The PL was excited with wavelength of 337 nm at T = 300 K.

For the PL spectrum of the aqueous dispersion of zinc oxide NPs formed in the plasma discharge in the presence of ultrasonic cavitation it is evident that the dominant luminescence band corresponds to the wavelengths of 600–900 nm, i.e., it is in the range of red and near-infrared spectrum[21].

The appearance of this band can be explained by the contribution of radiative transitions involving deep level defects in the forbidden zone of ZnO (3.36 eV or 370 nm for the bulk crystalline phases). The presence of the PL in this spectral range allows to apply these nanoparticles as fluorescent labels in the diagnosis of the malignant neoplasms in the future[22].

Conclusions

Acoustoplasma discharge and cavitation in aqueous solutions were used to prepare metal oxide nanoparticles (NPs) based on tungsten, copper, iron and zinc. It was shown that the electrical discharge accompanied with ultrasound cavitation in aqueous

[21] N. A. Bulychev; A. I. Erokhin y M. A. Kazaryan, "A Comparative Study of Anti-Stokes Shift under Stimulated Rayleigh-Mie Scattering in Suspensions of Ag Nanoparticles Obtained in Plasma Discharge in Liquid under Ultrasonic Cavitation", Proceedings of SPIE, Vol: 11322 num 2G (2019).
[22] V. N. Nikiforov; N. A. Bulychev y V. V. Rzhevskii, "Elastic properties of HTSC ceramics", Bulletin of the Lebedev Physical Institute, Vol: 43 num 2 (2016): 74-79.

media can be applied to prepare nearly monodisperse nanoparticles of metal (W, Cu, Fe1 and Fe2) oxides. It was found that ultrasonic cavitation during the NP formation influenced strongly the size and physical properties of NPs, which were measured by means of the electron microscopy, dynamic light scattering (DLS) and photoluminescence (PL) techniques. The obtained results indicate good prospects of the prepared NPs for biomedical applications in the PL diagnostics of cancer and magnetic hyperthermia.

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