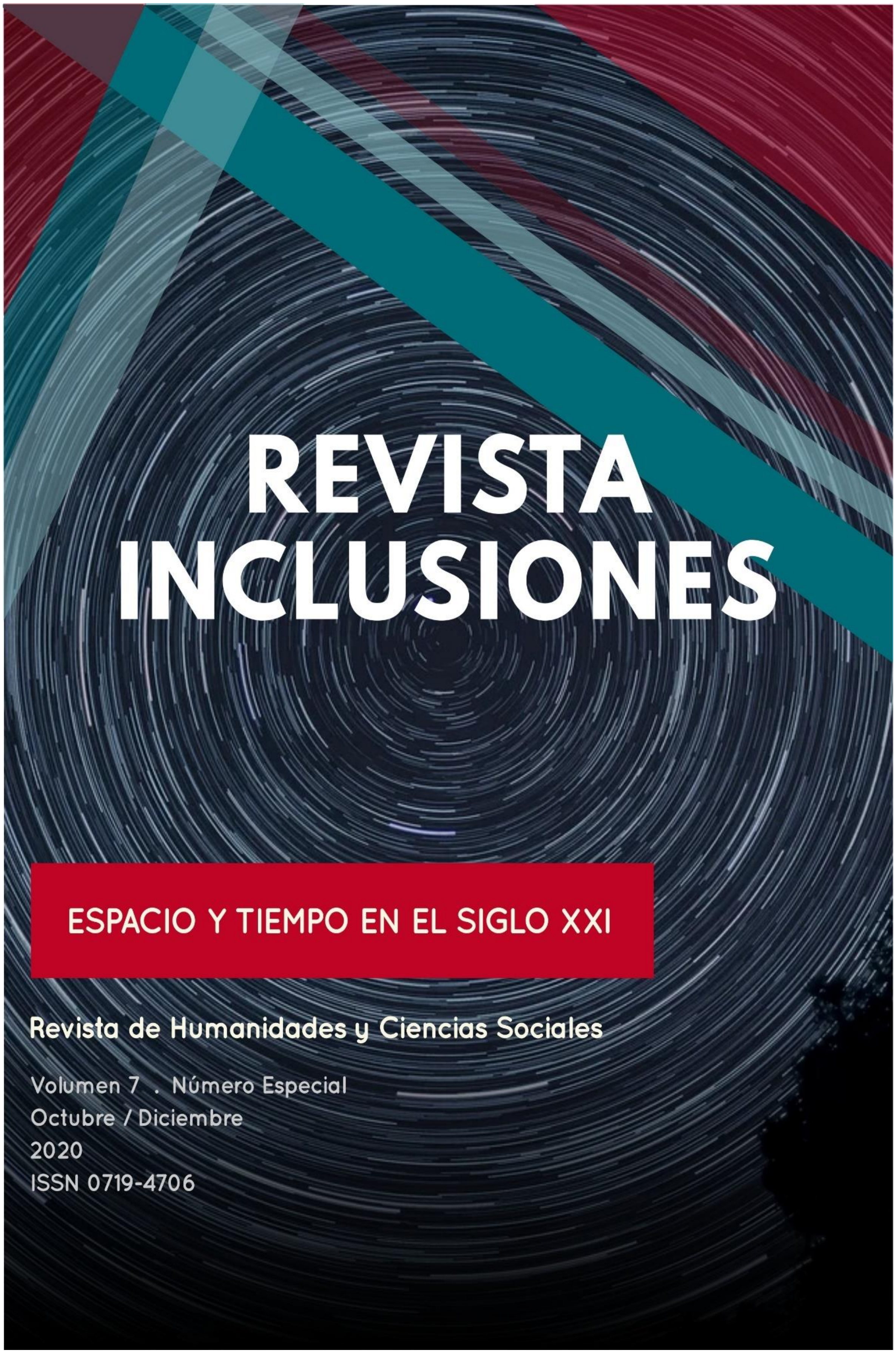

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OBTAINING OF TUNGSTEN OXIDE NANOPARTICLES IN ULTRASONICALLY ASSISTED ELECTRIC DISCHARGE

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Abstract

In this study, plasma discharge in a liquid at intensive ultrasonic field above the cavitation threshold has been proven to be of great interest for initiation of various physical and chemical processes. In such surcharge, nanoparticles of tungsten oxide with controlled size and shape and narrow particle size distribution have been synthesized. Further exploration of synthesized nanoparticles has demonstrated that the factor of ultrasonic cavitation during the synthesis substantially affects physical and chemical characteristics of nanoparticles. Similar procedure might be effective for compounds of tungsten and rare-earth elements.

Keywords

Nanoparticles – Plasma – Tungsten oxide – Ultrasound

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Introduction

The synthesis of nanoscale materials with controlled properties is an actual fundamental problem and becomes increasingly important in view of creation of novel functional and composite materials[1]. Along with traditional chemical methods of synthesis, some physical methods, such as electric discharges and ultrasound cavitation recently attracted a great deal of attention of many groups of researchers[2].

One of the most promising ways to obtain nanoscale materials, including metal oxide powders is the combined effect of the elastic oscillations of high intensity ultrasound or pulsed or steady-state electric fields in the liquid medium[3]. This type of plasma, being of great interest as a new object of physical study, has several advantages as a method for the synthesis of nanomaterials – a relatively narrow particle size distribution of the synthesized nanopowder, specific composition and the properties of nanomaterials[4].

Synthesis and examination of tungsten oxide nanoparticles

In this work, the capability of plasma combined with ultrasonic cavitation for synthesis of novel nanoparticles was exemplarily investigated on tungsten oxide nanoparticles. For this purpose, electric discharge in liquid medium was initiated using tungsten electrodes.

First, optical spectroscopy was applied for study of plasma at tungsten electrodes (Fig. 1).

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[1] N. A. Bulychev; M. A. Kazaryan; E. S. Gridneva et al., “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.

[2] 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; 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 y 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.

[3] 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); 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 y 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).

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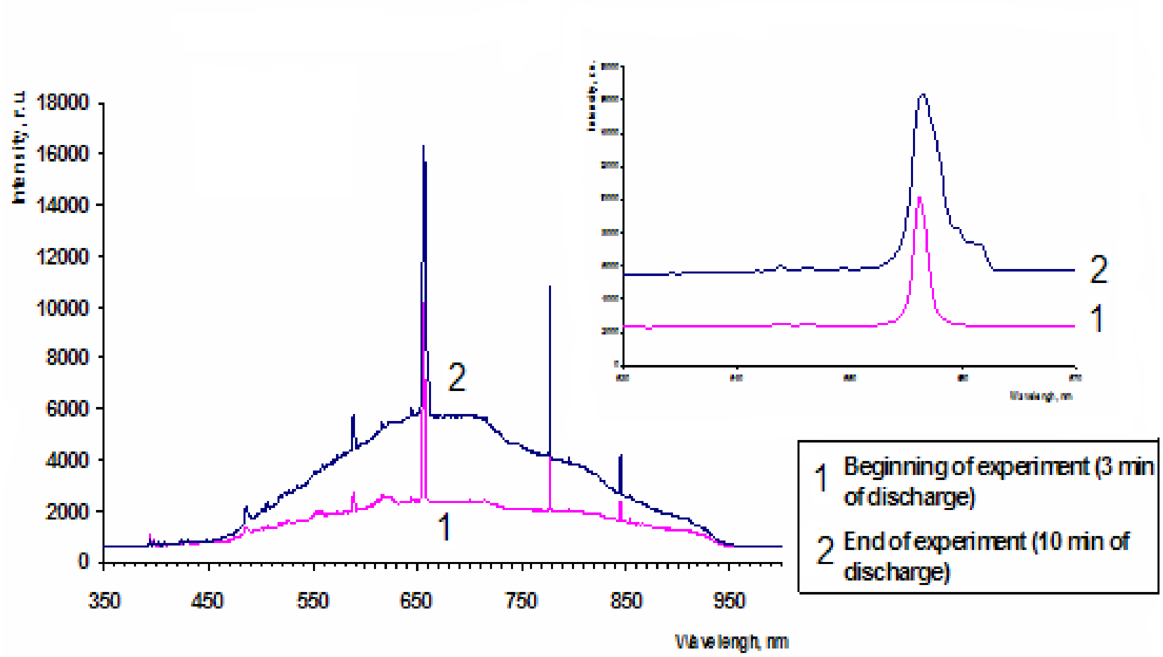

Figure 1
Optical spectra of plasma discharge in Optical spectra of plasma discharge at tungsten electrodes in water

At the initial stage of the plasma discharge, the light emission spectra consist from narrow lines of atomic emission of hydrogen and oxygen[5]. However, in the process of the discharge, a broad band corresponding to the thermal equilibrium emission of tungsten oxide grows monotonously. During the growth of the tungsten oxide band, the hydrogen line superposed onto this band is broadened. This broadening of the hydrogen line can be attributed to the partial capture of the hydrogen atoms by nanoparticles followed by corresponding deformations of the emission line[6].

The light emission spectra of the plasma discharge in water with tungsten and graphite electrodes demonstrate distinct differences both in the broad bands and in positions of hydrogen lines. Differences in the spectral positions of narrow lines for tungsten and graphite electrodes reveal active interactions of hydrogen and other ions created in the plasma discharge with the nanoparticles created in the process.

Further on, scanning electron microscopy pictures of synthesized nanoparticles were taken (Fig. 2). Electron microprobe analysis of the chemical compositions made simultaneously with scanning microscopy showed wide range of tungsten to oxygen ratios:

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[5] V. A. Pogodin; L. N. Rabinskiy y S. A. Sitnikov, “3D Printing of Components for the Gas-Discharge Chamber of Electric Rocket Engines”, Russian Engineering Research, Vol: 39 num 9 (2019): 797-799.

[6] V. V. Nigmatzyanov; V. A. Pogodin; L. N. Rabinskiy y S. A. Sitnikov, “The polymer-ceramic material for the manufacture of gas discharge chamber for the electric rocket engine”, Periodico Tche Quimica, Vol: 16 num 33 (2019): 801-808; L. N. Rabinskiy y S. A. Sitnikov, “Development of technologies for obtaining composite material based on silicone binder for its further use in space electric rocket engines”, Periodico Tche Quimica, Vol: 15 num 1 (2018): 390-395 y K. V. Pushkin; S. D. Sevruk; N. S. Okorokova y A. A. Farmakovskaya, “The most efficient corrosion inhibitors for aluminum anode of electrochemical cell used as a controlled hydrogen generator”, Periodico Tche Quimica, Vol: 15 num 1 (2018): 414-425.

from 2/5 to 1/3. Taking into consideration a wide set of crystalline symmetries of tungsten oxide resulting from variations of tungsten to oxygen compositions, we can assume that such a wide set of morphologies of the particles is a consequence of a wide dispersion of relative oxygen content[7].

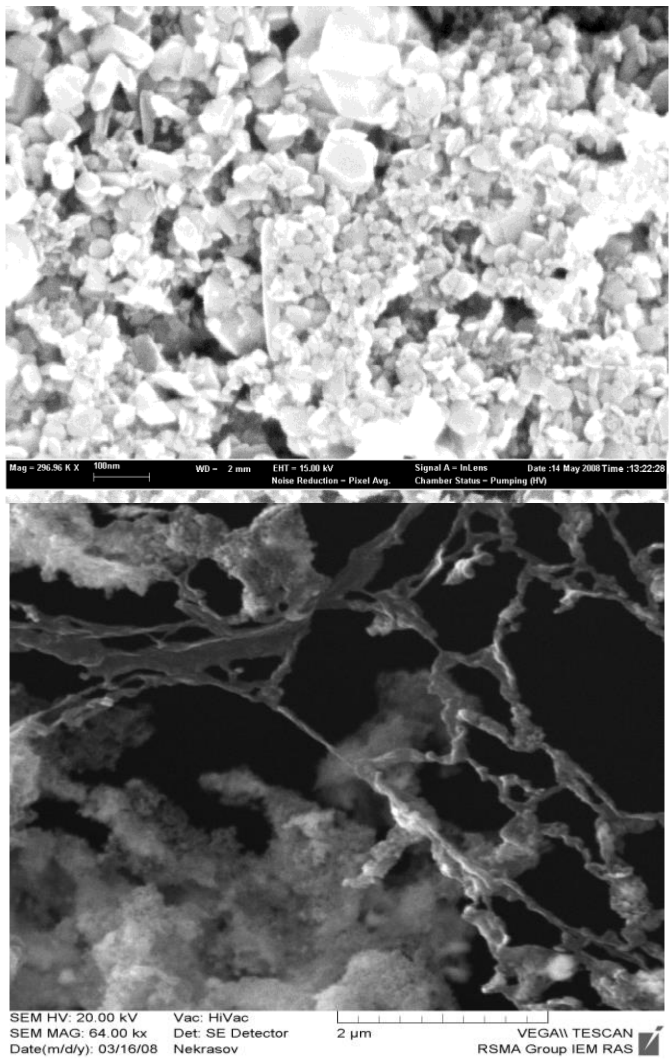

Figure 2
Various kinds of agglomerations of tungsten oxide particles

[7] Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "Surface modification of organic pigments by isobutyl vinyl ether copolymers under the action of ultrasonic", Revista Inclusiones, Vol: 7 num Especial (2020): 11-21; Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "The effect of ultrasonic treatment 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 y 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 on the example of zinc oxide and sulfide", Revista Inclusiones, Vol: 7 num 3 (2020): 453-463.

In most of structures here, tungsten oxide has oxygen content varied from WO2 to WO3. These variations of stechiometry result in a wide multitude of crystalline structures (hexagonal, cubic, orthorhombic, tetragonal, monoclinic, triclinic). This variety of atomic structures and corresponding morphologies of nanoparticles determines tremendous multitude of agglomerations, well revealed by scanning electron microscopy (hexagons, fibers, plates, etc.).

Scanning electron microscopy of the particles of tungsten oxide synthesized by plasma discharge using tungsten electrodes in water revealed their dimensions from 10 nm to more than 100 nm. Morphologies of these particles differ in a wide range. Well faceted particles having either rectangular or triangular symmetry are observed simultaneously with the particles having smooth ellipsoid – like geometries. The theoretical explanation as well as examination of such materials is referred[8].

Conclusions

Acoustoplasma technique based on combination of a discharge in liquid with acoustic cavitation treatment provides an effective route for synthesis of gaseous hydrogen and solid nanoparticles of metals, oxides and semiconductors. Chemical compositions, dimensions and morphology of nanoparticles can be easily modified for different applications, such as chemical catalyst, radiation detectors, solar cells, lasers, medical therapy etc.

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