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STRUCTURE OF TUNGSTEN OXIDE NANOPARTICLES OBTAINED IN ULTRASONICALLY ASSISTED ELECTRIC DISCHARGE AS STUDIED BY IR AND PL METHODS

Lic. Mikhail O. Kaptakov
Moscow Aviation Institute (National Research University), Russia
ORCID: 0000-0001-8100-6495
mkaptakov@mail.ru
Lic. Victoria Kohlert
University of Stuttgart, Germany
ORCID: 0000-0003-3881-7262
tvictoria@yandex.ru

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Abstract

In this study, nanoparticles of tungsten oxide with controlled size and shape and narrow particle size distribution synthesized by plasma discharge in the presence of ultrasonic cavitation. Exploration of synthesized nanoparticles has demonstrated that the factor of ultrasonic cavitation during the synthesis substantially affects physical properties of nanoparticles. Defects of crystalline structure governs the luminescence characteristics as well as peculiarities of internal composition of nanoparticles as reflected from IR studies.

Keywords

Nanoparticles – Ultrasound – Plasma – Tungsten oxide

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Introduction

In previous studies it was found that combined excitation of electric arc discharge and acoustic cavitation in water and organic liquids was the effective method to create free hydrogen and various kinds of solid nanoparticles[1]. Chemical compositions, dimensions, morphologies, optical and other properties of these nanoparticles can be easily regulated by the plasma discharge parameters, materials of electrodes and liquids[2]. In other works, it was demonstrated that ultrasonic cavitation itself is a promising way for modification of properties of solid nano- and microparticles[3].

IR and PL examination of tungsten oxide nanoparticles

The research was started with the infrared spectroscopy studies of nanoparticles of tungsten oxide synthesized by electric discharge in the presence and absence of intensive ultrasonic cavitation[4]. The results of IR measurements of particles with various size are presented in the Figure 1.

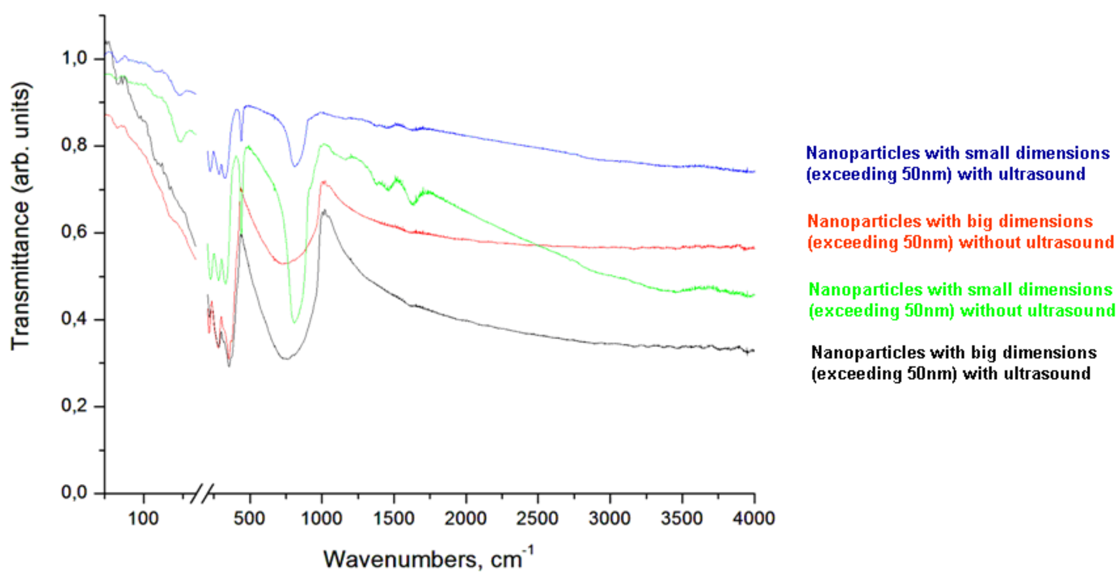

Figure 1
Infrared transmission spectra of nanoparticles of tungsten oxide created in the plasma discharge

[1] 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.
[2] 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.
[3] 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.
[4] 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.

The absorption bands between 500 and 1000 cm^{-1} are rather different for big and small nanoparticles (they correspond to vibrations in W–O bonds). For big particles these bands are wide and their center is shifted to lower frequencies. These features are explained by lower content of oxygen in comparison to WO_3[5].

Small particles (with dimensions in the range from 10 to 30 nm) are characterized by more strong and definite W–O bonds. In the spectral regions 1400 – 1750 cm^{-1} and 2800 – 3500 cm^{-1} several bands corresponding to vibrations of O–H and C–H are observed in the particles created under ultrasonic treatment[6]. So, we can assume that ultrasonic cavitation treatment promotes entrainment of hydrogen into tungsten oxide particles[7].

Next, photoluminescence studies of tungsten oxide nanoparticles have been carried out. The results are presented in the Figure 2.

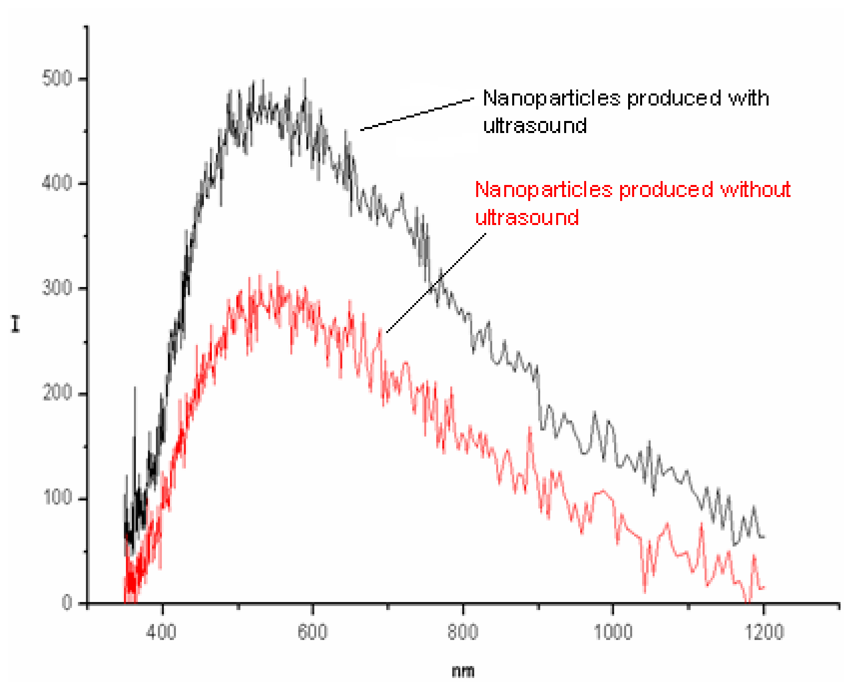

Figure 2
Photoluminescence of tungsten oxide nanoparticles excited by 308 nm xenon – chlorine pulsed laser

Photoluminescence spectra of tungsten oxide nanoparticles excited by xenon – chlorine laser (308 nm emission) differ significantly from the emission spectra of the same

[5] M. N. Kirichenko; L. L. Chaikov; I. S. Burkhanov; N. A. Bulychev y M. A. Kazaryan, "Effect of the pH of iron oxide nanoparticles solution on the rate of fibrin gel formation (according to light scattering data)", Proceedings of SPIE, Vol: 11322 num 1E (2019).

[6] 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.

[7] 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) y N. A. Bulychev; M. A. Kazaryan; L. S. Lepnev; A. S. Averyushkin; M. N. Kirichenko; A. R. Zakharyan y A. A. Chernov, "Luminescent properties of nanoparticles synthesized in electric discharge in liquid under ultrasonic cavitation", Proceedings of SPIE, Vol: 10614 num 13 (2018).

particles in plasma[8]. The emission maxima are observed at about 550 nm (instead of 650 nm for plasma discharge)[9]. Narrow emission lines corresponding to hydrogen and other gases (clearly seen in the plasma discharge) are not observed at all[10].

These spectra are observed for small particles which correspond to WO_3 composition[11].

The absence of hydrogen emission lines in the photoluminescence spectra does not reject the presence of hydrogen in tungsten oxide particles[12]. Their absence is explained by non- absorption of the laser light by hydrogen atoms[13].

Important feature observed is the pronounced difference between the luminescence intensity of particles obtained without ultrasonic treatment and particles obtained in plasma under ultrasonic treatment: higher intensity of particle in case of ultrasonic action during the synthesis can be attributed to the numerous defects in crystal structure and may be

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[8] 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 N. A. Bulychev; M. A. Kazaryan; A. S. Averyushkin; M. N. Kirichenko; A. R. Zakharyan y A. A. Chernov, "Dynamic characteristics of electric discharge in liquid under ultrasonic cavitation", Proceedings of SPIE, Vol. 10614 num 13 (2018).

[9] 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 y 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).

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[12] 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) y 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.

[13] 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 Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "Modification of the surface of carbon black with vinyl ether copolymers under ultrasonic treatment". Revista Inclusiones, Vol: 7 num 4 (2020).

advantageous in view of possible applications for creation of optically active and composite materials[14].

Conclusions

Acoustoplasma technique based on combination of a discharge in liquid with acoustic cavitation treatment provides an effective route for synthesis of solid nanoparticles of metals, oxides and semiconductors. In this study, the capabilities of this technique have been exemplarily performed for synthesis of WO_3 nanostructures. Nanoparticles, synthesized by acoustoplasma technique demonstrate good ability for hydrogen accumulation in the same process, which is much more safe than other methods, because it does not need high pressure of hydrogen.

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