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Acoustoplasma Technique for Obtaining of Metal-Based Nanostructures

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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 discharge, nanoparticles of tungsten and zinc oxides 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.

1. Introduction

In recent years, approaches to synthesis of nanomaterials and nanopowders in particular have been of increasing interest and have attracted a great deal of attention of many groups of researchers [1-3]. A range of techniques, including sol-gel method, high-energy dispersing, nanoscale biosynthesis have been being applied for several decades already that enabled to obtain nanoparticles of titania, silica, mica, carbon black and other materials. Along with traditional chemical methods of synthesis, some physical methods, such as electric discharges and ultrasound cavitation became increasingly important in view of creation of novel functional and composite materials.

One of the new promising ways to obtain nanoscale materials, including metal oxide powders is the combined effect of the elastic oscillations of high intensity ultrasound and pulsed or steady electric fields in a liquid medium. 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 [4-7].

More specifically, the traditional arc discharge in aqueous electrolytes, which is widely used in engineering, is the most well-known form of stationary plasma discharge in liquid media. For many years, such discharge is used in physicochemical studies and in the synthesis of various materials. The specific feature of arc discharge in liquid media is the localization of plasma region near the electrode ends and “falling” form of volt-ampere characteristics.

However, when ultrasonic cavitation is applied to a liquid, phase composition and physical properties of the liquid change abruptly, and this effect can lead to some specific features of the formation of electric discharges in the liquid. In the region of intensive cavitation, the fraction of gas-vapor component in the liquid has a significant value, therefore it can be assumed that the conditions of electric breakdown in the cavitation region should become easier, which can result in the initiation of different forms of discharges. Varying the parameters of ultrasonic field, it is apparently possible to exert an influence on the processes of plasma glow in a cavitating liquid. Furthermore, in this configuration, ultrasonic cavitation will interact with micro- and nanoparticles obtained in plasma and

affect their physical properties and surface characteristics. The objective of the present work is to check this hypothesis and, moreover, to analyze the features of such acoustoplasma discharge and possible chemical conversions that can occur under its excitation in water and water-hydrocarbon mixtures.

2. Methods and materials

2.1. Plasma discharge in a cavitating liquid

Acoustoplasma technique involves the initiating of an electric discharge in a liquid that goes along with ultrasonic power assisted cavitation. In general, the specially designed acoustoplasma reactor includes a reservoir with two immersed electrodes and ultrasonic cavitator. Cavitation bubbles in the liquid phase provide the outstanding characteristics of a discharge and these characteristics have been proven to be governed by the regimes of ultrasonification [4-7]. Furthermore, ultrasonic power prevents the secondary agglomeration of nanoparticles being synthesized from metal electrodes in electric discharge. The scheme of experimental setup is shown in the figure 1.

The setup consists of a reaction chamber, where discharge electrodes and an ultrasonic irradiator are introduced, a generator of high-voltage pulses for discharge initiation, a power supply of discharge in liquid, an ultrasonic generator and blocks of control of electric and acoustic characteristics. The chamber is provided with quartz windows for the observation of dynamic processes and registration of optical spectra of visible discharge glow.

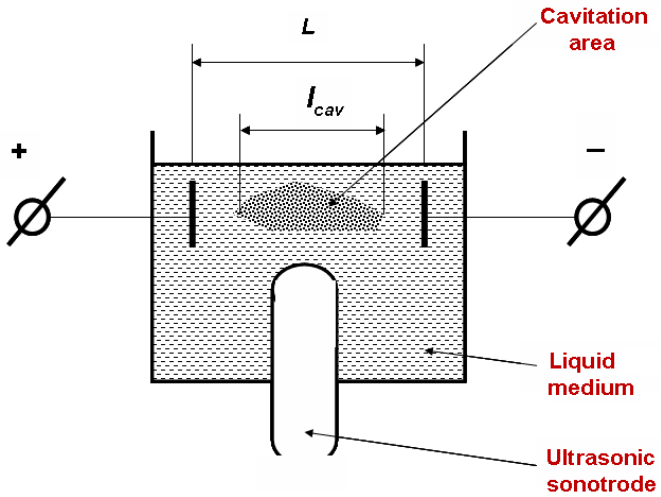

Figure 1. Scheme of experiment. L means the distance between the electrodes; Lcav means the size of cavitation zone.

The ultrasonic generator with a piesoceramic transducer provides the output acoustic power up to 2 kW in the frequency range 27-44 kHz. The parameters of acoustic equipment allow one to implement the intensity of an ultrasonic field in the volume of liquid up to 10 W/cm^2 and to vary cavitation regime in a wide range.

2.2. Synthesis of nanoparticles by acoustoplasma

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. 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. In other works, it was demonstrated that ultrasonic cavitation itself is a promising way for modification of properties of solid nano- and microparticles [8-12].

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

3. Results

First, optical spectroscopy was applied for study of plasma at tungsten and zinc electrodes (figure 2 and 3).

At the initial stage of the plasma discharge, the light emission spectra consist from narrow lines of atomic emission of hydrogen and oxygen. 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.

The light emission spectra of the plasma discharge in water with tungsten and zinc 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 zinc 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 (figure 4).

In the most of structures here, tungsten oxide has oxygen content varied from WO_2 to WO_3. 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.).

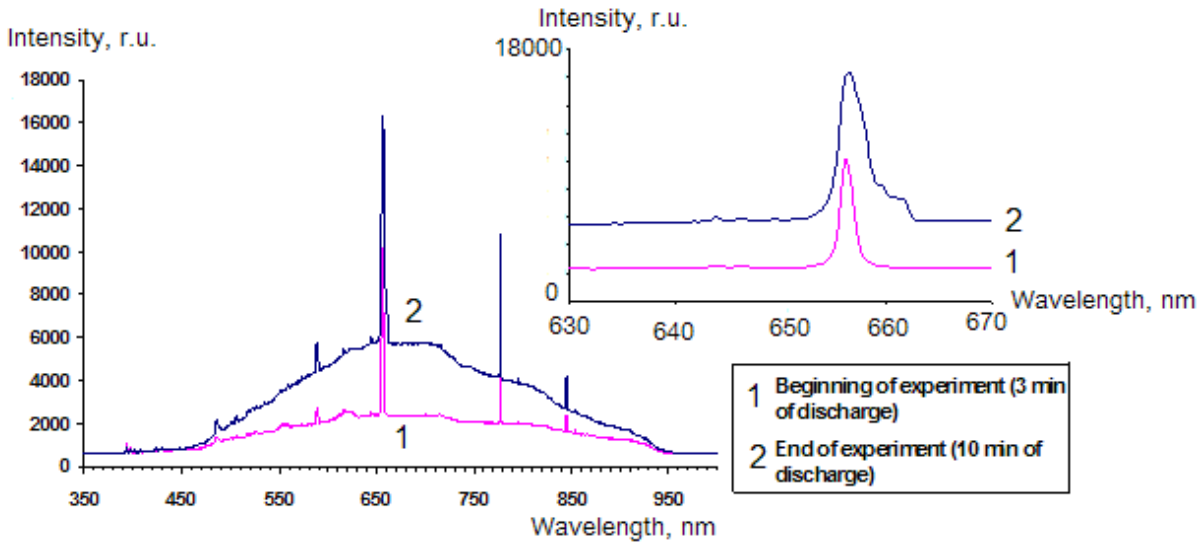

Figure 2. Optical spectra of plasma discharge at tungsten electrodes in water

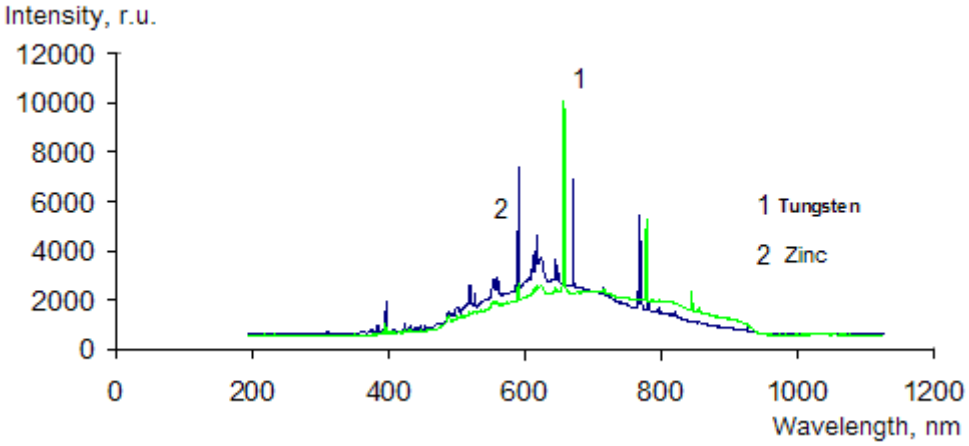

Figure 3. Optical spectra of plasma discharge at tungsten and zinc electrodes in water.

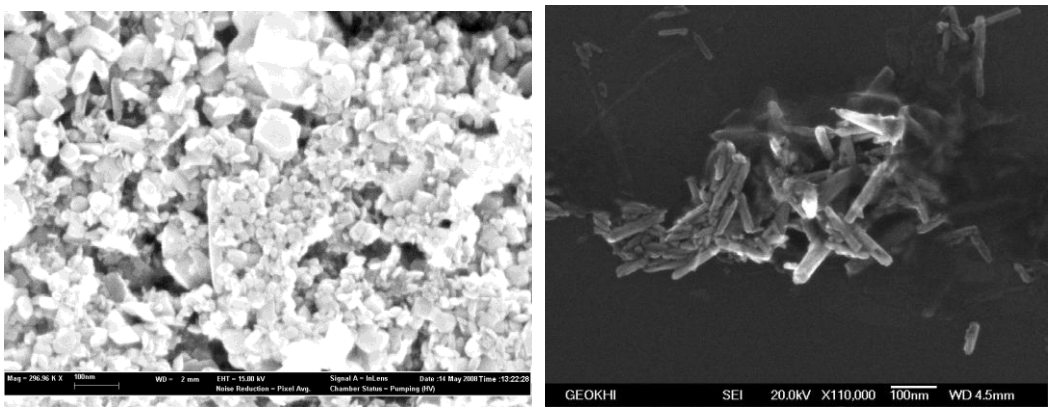

Figure 4. Various kinds of agglomerations of tungsten oxide and zinc oxide particles

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.

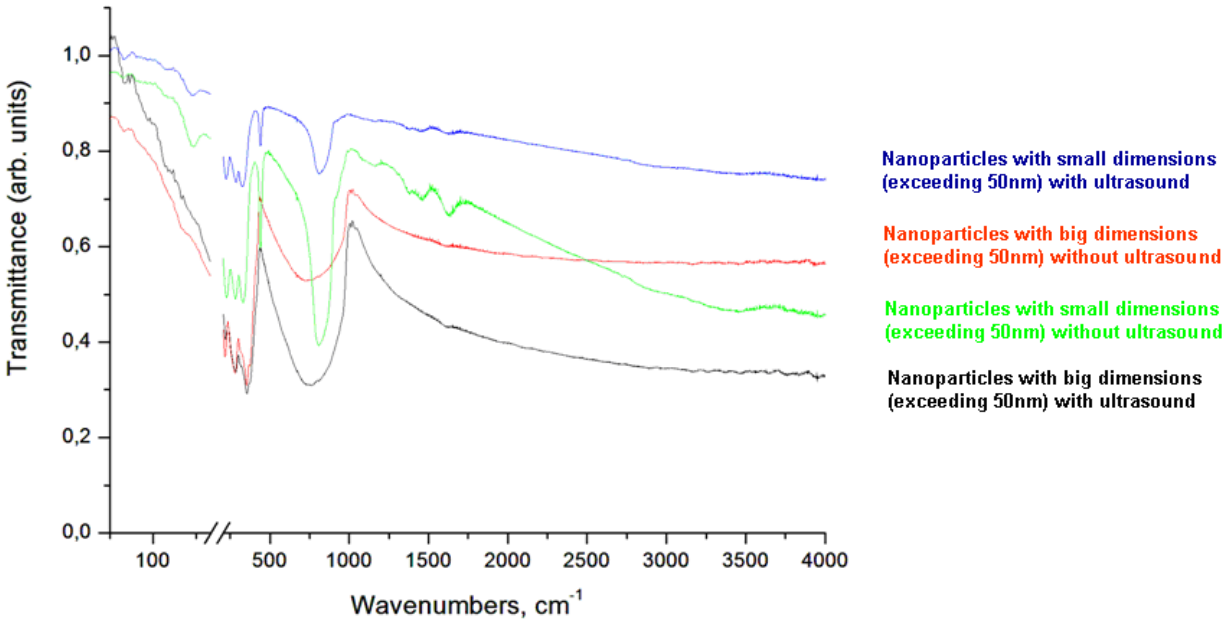

Figure 5. Infrared transmission spectra of nanoparticles of tungsten oxide created in the plasma discharge

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.

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. So, we can assume that ultrasonic cavitation treatment promotes entrainment of hydrogen into tungsten oxide particles.

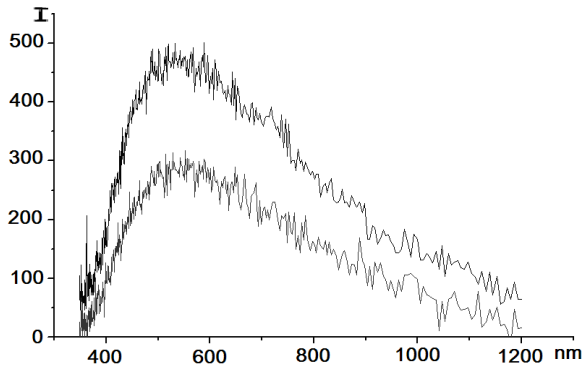

Figure 6. Photoluminescence spectra excited by 308 nm xenon – chlorine pulsed laser of tungsten oxide nanoparticles obtained by acoustoplasma technique with the intensity of ultrasonification below the cavitation threshold (lower curve) and above the cavitation threshold (upper curve).

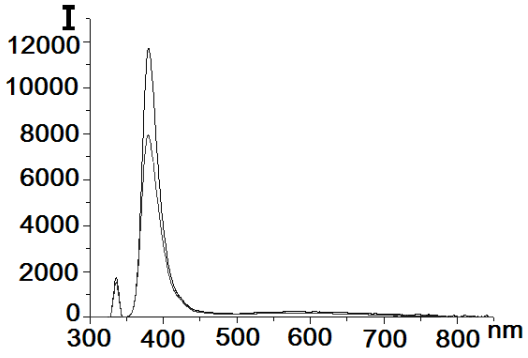

Figure 7. Photoluminescence spectra excited by 337 nm nitrogen pulsed laser on zinc oxide nanoparticles obtained by acoustoplasma technique with the intensity of ultrasonification below the cavitation threshold (lower curve) and above the cavitation threshold (upper curve).

Photoluminescence spectra of tungsten oxide nanoparticles excited by xenon – chlorine laser (308 nm emission) differ significantly from the emission spectra of the same particles in plasma (figure 1 and 2). The emission maxima are observed at about 550 nm (instead of 650 nm for plasma discharge). Narrow emission lines corresponding to hydrogen and other gases (clearly seen in the plasma discharge) are not observed at all. These spectra are observed for small particles which correspond to WO_3 composition.

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

Important observation is that the intensity of ultrasonic power during synthesis substantially affects the optical properties of synthesized nanoparticles. It was also demonstrated on ZnO particles (Fig. 7).

Important feature 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 advantageous in view of possible applications for creation of optically active materials.

As a result of these experiments, acoustoplasma technique has been demonstrated to be new interesting approach to get nanomaterials in two ways in the same reaction – solid powders precipitating in the reaction vessel and gaseous aerosol containing oxide nanoparticles exhibiting the density comparable with that of air. Two perspective avenues of the utilization of these nanopowders can be performed: nanoparticles could first be deposited on a flat substrate and so create a surface modifying coating and the second option is an entrainment of the nanoparticles into the monomer matrix which can be polymerized afterwards yielding a polymer with immobilized nanoparticles.

4. 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. Nanoparticles, synthesized by acoustoplasma technique demonstrate interesting physical properties and can be effectively applied for different applications, such as chemical catalyst, radiation detectors, solar cells, lasers, medical therapy etc.

Acknowledgments

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