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Bioavailable nanoparticles obtained in laser ablation of a selenium target in water

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Abstract. **The process of producing colloidal solutions of selenium nanoparticles in water using the laser ablation method is described. The prospects of using nanoparticles of elementary selenium as a nutrition source of this microelement are discussed**

Keywords: *laser ablation, nanoparticles, bioavailability, selenium.*

1. Introduction

The selenium microelement is a biological oxidant of indirect action [1]. Usually, Se is supplied to the organism with food in the form of amino acids or inorganic salts, sodium selenate and selenide [2]. The zero-valent selenium is considered to be bioavailable for humans only in a minor degree [3, 4]. However, the reaction ability increases if a chemical element has the form of nanoparticles [5]. Thus, in recent papers [6, 7] it was shown that the selenium nanoparticles with the size smaller than 100 nm may be assimilated in murine organism.

A separate problem is to produce selenium nanoparticles free of impurities. For this goal the chemical methods of synthesising nanoparticles cannot be used, since the colloidal solutions in this case contain reaction products as well as surface-active substances. An alternative method to synthesise 'pure' nanoparticles is the laser ablation in a liquid, which makes it possible to control the parameters of the process in a way that provides colloidal solutions of nanoparticles with given properties [8].

The aim of this work was to obtain pure selenium nanoparticles using the laser ablation method in a liquid and to investigate their bioavailability.

2. Experiment

Experimental production of nanoparticles by laser ablation of solid targets in a liquid has been thoroughly described earlier [9 – 18]. We used polycrystalline selenium as a target. To obtain Se nanoparticles, we used a pulsed copper vapour laser with the radiation wavelengths 510.6 and 578.2 nm, pulse duration 15 ns, and pulse repetition rate 15 kHz. The mean radiation power amounted to 7 W. The nanoparticles were produced in a glass test tube. The working liquid was water, purified by means of reverse osmosis. Since the selenium density is greater than that of water, the target was located at the bottom of the test tube in the course of irradiation, and the radiation was incident from below. The colloidal solution of selenium nanoparticles in water has red colour and, therefore, strongly absorbs the radiation from a copper vapour laser. Because of high mean power of the radiation, the colloidal solution was heated up to boiling, thus making it necessary to interrupt the process of nanoparticle production for cooling.

Later it was decided to produce the nanoparticles in a flow cuvette. This allows continuous irradiation, since the colloidal solution can pass through the heat exchanger in the course of circulation from the pump to the cuvette. This approach also allows for production of large volumes of colloidal solutions of nanoparticles that may be then partially evaporated to increase the concentration.

Surface-active substances were used neither in the ablation process, nor after it. The colloidal solutions of selenium nanoparticles in water, obtained using the method of laser ablation, possess high stability. Sedimentation of the colloid during a month did not reveal the sediment, characteristic for agglomerated nanoparticles.

The absorption spectra of the colloidal solutions of nanoparticles, obtained by ablation, were recorded in the range 200 – 85 nm by means of the OceanOptics fibre spectrometer. The morphology of the selemium nanoparticles was investigated using the transmission electron microscope (TEM) CX-100 (JEOL) with the electron beam energy 100 keV .[*] For this purpose the colloidal solution was evaporated on a copper grid coated with a carbon membrane. The size distribution of nanoparticles was determined by means of the CPS measuring centrifuge. The X-ray diffraction studies were carried out using the DRON-4 setup with the radiation line CuKα.

3. Experimental results

A representative electron microphotograph of nanoparticles obtained using the method of laser ablation of selenium target in water is presented in Fig. 1. The morphology analysis of the image brought us to the conclusion that the mean size of nanoparticles having a near-spherical shape amounts to 65.3 ± 1.6 nm.

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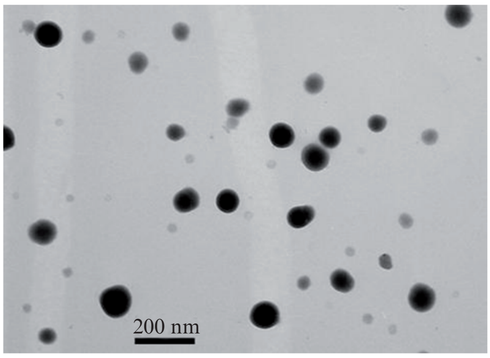

Figure 1. TEM image of selenium nanoparticles.

The absorption spectrum (Fig. 2) of the colloidal solution of selenium nanoparticles demonstrates a decrease in absorption when changing the wavelength from 200 to 600 nm, which explains the red colour of the solution.

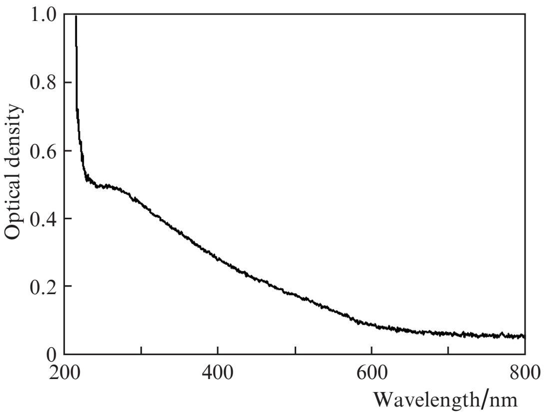

Figure 2. Absorption spectrum of the colloidal solution of nanoparticles.

The size of nanoparticles, obtained as a result of ablation process, lies within 20 – 100 nm. The size distribution, determined using the measuring CPS centrifuge, has a pronounced maximum at 60 nm (Fig. 3), which agrees well with the data of electron microscopic studies (65.3 ± 1.6 nm).

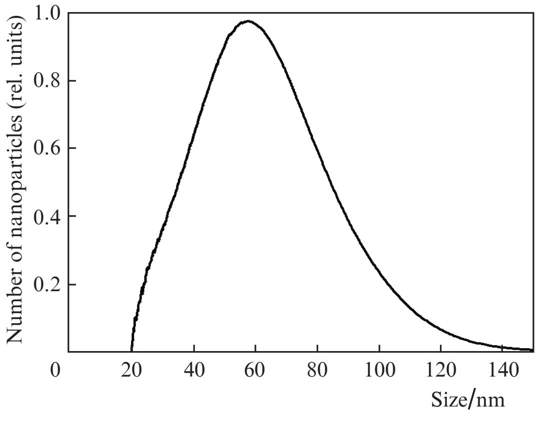

Figure 3. Size distribution of nanoparticles.

Figure 4 represents diffraction patterns from three samples of selenium, the ingot that served as a target for ablation, the powder obtained by sedimentation of the solution followed by drying at room temperature, as well as the powder obtained by sedimentation from the solution with subsequent drying at the temperature of 120 – 150 °C in atmospheric air.

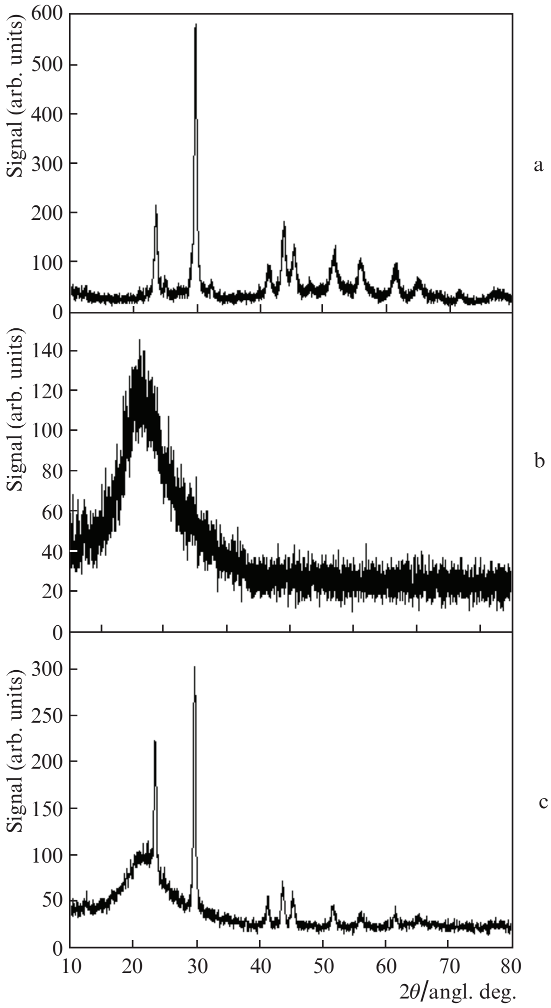

Figure 4. X-ray diffraction patterns of the initial polycrystalline sample of selenium (a), powder of red selenium nanoparticles (b), and powder of selenium nanoparticles heated in air (c)

In the diffraction patterns of the ingot (Fig. 4a) and the heated powder (Fig. 4c) the peaks are observed that correspond to two phases of selenium, the hexagonal one (No. 06-0362 according to the PCPDFWIN database) and the monocline one (No. 24-1202). From the ratio of peak intensities one can estimate the quantity of monocline phase in the ingot and heated powder. This quantity does not exceed 5% of that in hexagonal phase.

In the diffraction pattern of the deposited red-colour powder (Fig. 4b) a strong halo is observed that corresponds to the X-ray-amorphous state of selenium, i.e., the state in which the size of selenium crystallites does not exceed a few nanometres. The weak peaks that can be distinguished against the halo background could not be associated with any selenium phase. However, they are not fluctuations, since they are reproduced in repeated measurements.

4. Discussion

The obtained results show that the laser ablation of the target made of polycrystalline selenium and merged in water leads to formation of colloidal solution of X-ray-amorphous nanoparticles of red selenium. In other words, in laser ablation the allotropic modification of the target material takes place. The resulting nanoparticles have dimensions from 20 to 100 nm with the maximum at 60 nm. Amorphisation is probably due to the high rate of cooling of nanoparticles, removed from the surface of the melted layer of the target under the pressure of the surrounding water vapour [19]. The subsequent heating of nanoparticles in air causes their crystallisation. The transition of selenium from amorphous state to crystalline one begins at the temperature of 115–125 °C [20], which is in good agreement with the results obtained in the present paper.

Selenium is of great interest as a component of biologically active food additive. Laser-assisted production yields selenium nanoparticles, free of impurities and surface-active substances, which allows immediate use of these particles for testing in laboratory animals without any additional treatment. Detailed studies of bioavailability of the selenium preparation on the basis of a colloidal solution of selenium nanoparticles were carried out in rats [21].

The analysis has shown that the nanoparticles of elementary selenium, introduced into the gastrointestinal tract of rats subjected to selenium-deficient nutrition budget, may be assimilated by the organism in amounts, approximately corresponding to the physiological need for this microelement. Selecting a food source of Se, one should take into account not only the bioavailability, but also its toxicity, which is essentially lower in elementary selenium than in its inorganic compounds (selenides and selenates).

5. Conclusions

Using the method of laser ablation of a massive target by the radiation of copper vapour laser, the colloidal selenium nanoparticles in water were produced. In contrast to the initial target, the obtained nanoparticles are amorphous. The prospects of using the elementary selenium nanoparticles as a food source of this essential microelement may be clarified after their detailed toxicological characteristic.

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