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Laser generation and fragmentation of selenium nanoparticles in water and their testing as an additive to fertilisers

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Abstract. **The generation of selenium nanoparticles in water and their fragmentation by a neodymium laser with a pulse repetition rate of 10 kHz and an average power of 20 W is experimentally investigated. The size distribution of selenium nanoparticles is determined using a measuring disk centrifuge. The particle morphology is analysed by transmission electron microscopy. It is found that laser ablation of a selenium target in water provides mainly submicron particles, which must be subjected to laser fragmentation in a solution to obtain selenium nanoparticles about 100 nm in size. These selenium nanoparticles are used as an additive to soil in which some crops are grown. The optimal selenium content in soil is determined.**

Keywords: *laser ablation, liquid, nanoparticles, selenium, fertilisers.*

1. Introduction

Selenium is a trace element that is necessary for functioning of most living organisms and all mammals; it is present in soil, water, crops, and animal origin products [1]. Since food is the main source of selenium, its consumption is determined by the amount of food [2] and the Se content in it. The selenium concentration in cultivated plants can be increased by adding selenium or its compounds to the fertilisers introduced into soil. To date, there have been attempts to apply both organic (selenium-containing amino acids, chelates, etc.) and inorganic (oxides, salts, and minerals) selenium compounds as fertilisers. However, inorganic selenium compounds are washed away by rains into the infertile soil horizon. Organic selenium compounds are not washed away actively but undergo fast destruction. Nanosized selenium in the zero-valence state is of great interest as a potential additive to fertilisers. First, nanoparticles are not washed away to infertile horizons for a long time. Second, zero-valence selenium is not dissolved in water and aqueous solutions, due to which its penetration into plants occurs as a result of gradual oxidation of nanoparticle surface and selenium release in the form of oxides.

The selenium content in soil and, correspondingly, in the plants grown on this soil may differ significantly in different countries [3]. The urgency of this study is substantiated by the recent results obtained by an international group of researchers, who reported a found correlation between the selenium content in soil and the mortality rate from COVID-19 in different regions of China [4]. The difference in the mortality rates for regions with different selenium contents in soil reached a factor of 5.

Selenium nanoparticles were obtained previously by laser ablation of a selenium target in water [5]. The radiation source was a copper vapour laser with an average power of 8 W at both generation lines (510.6 and 578.2 nm) and a pulse duration of 15 ns. The thus prepared selenium nanoparticles were less than 100 nm in size. Subsequent tests on laboratory animals showed biocompatibility of selenium nanoparticles and made it possible to determine the necessary dose of Se in organism [6]. We used a pulsed near-IR laser with an average power of 20 W to form selenium nanoparticles. The transition to a larger radiation wavelength allowed us to weaken the influence of laser radiation scattering on the selenium nanoparticles already formed in water and increase their generation rate. When the mass of obtained selenium particles became sufficiently large, they were subjected to subsequent fragmentation using the same laser source. The laser fragmentation was described in detail in [7–13]. It implies laser irradiation of a colloidal solution of micro- or nanoparticles, with the laser beam waist located in the solution. When the laser beam interacts with individual particles, the latter undergo melting and division into smaller parts. Then the fabricated selenium nanoparticles were added to soil (in which seedlings of some crops were grown) in order to determine the optimal selenium concentration in the latter.

2. Experimental

Selenium nanoparticles were fabricated by laser ablation of a selenium target in water. The radiation source was a neodymium laser with a pulse energy of 2 mJ, a wavelength of 1064 nm, and a pulse repetition rate of 10 kHz. The pulse duration was 10 ns. The irradiation was performed in two stages. In the first stage a selenium target located in a continuous-flow reactor filled with water was irradiated (Fig. 1).

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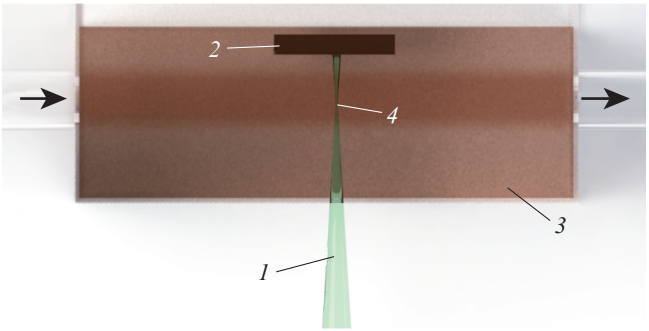

Figure 1. Schematic of the experiment on laser generation of selenium nanoparticles in a continuous-flow cell:
(*1*) laser beam; (*2*) selenium target; (*3*) colloidal solution of selenium particles; (*4*) laser beam waist. The arrows indicate the direction of colloidal solution circulation.

The laser beam waist was located in a flow of colloidal solution of nanoparticles. Since the selenium ablation threshold is about 1 J cm^{-2}, the laser beam defocused on the target provides supply of new nanoparticles to the circulating solution. When passing through the region of the laser beam waist, the already fabricated selenium nanoparticles can be subjected to further fragmentation. Since selenium is a brittle material, the primary nanoparticles formed as a result of target ablation have submicron sizes. Therefore, the nanoparticles obtained in this scheme were subjected to laser fragmentation: subsequent irradiation of the colloidal solution of nanoparticles in the absence of target.

The size distribution of selenium nanoparticles was investigated using a measuring centrifuge DC24000 (CPS Instruments) according to the following technique: a colloidal solution in a volume of 100 mL was sprayed onto a disk rotating with a speed of 20000 rpm. The morphology of selenium nanoparticles was studied in a transmission electron microscope (TEM) JEM 2100 (Jeol) with an accelerating voltage of 200 keV and in the regime of scattered electrons (STEM).

Addition of selenium nanoparticles to the soil was performed at solution concentrations of 1, 5, 10, and 25 μg kg^{-1}. To this end, the initial colloidal solution of nanoparticles was diluted with water so as to provide a ratio of 100 g selenium-containing solution per 1 kg soil. Then the soil was mechanically mixed to make the nanoparticle distribution uniform. The growth of radish and arugula in soils with different selenium contents under standard conditions (illumination 16 h per day, temperature 22 °C) was performed in a climatic chamber. The leaf area was measured as a function of growth time and the amount of selenium nanoparticles added to the soil.

3. Results and discussion

The generation rate of selenium particles in a continuous-flow cell is 2.4 mg min^{-1} [14]; however, not all particles have small sizes. Figure 2 shows their TEM image. Most particles have a spherical shape, a fact indicating that they were in the molten state when contacting water in the cell. Since the selenium melting temperature is only 250 °C, the surface tension of the melt makes particles spherical.

The size distribution peak for the selenium particles obtained after the target ablation is near 400 nm [14]. The suspension of selenium micro- and nanoparticles in water was

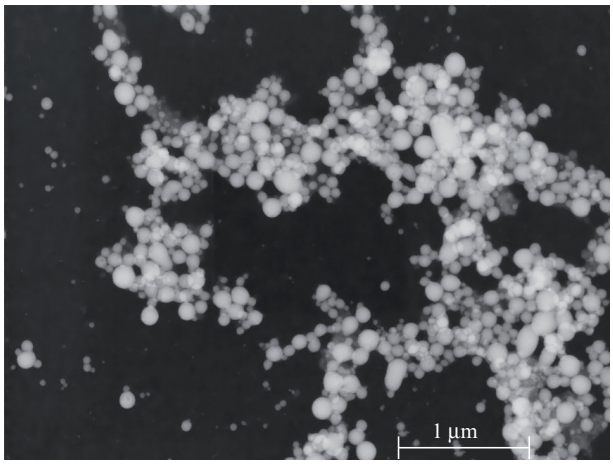

Figure 2. TEM image of selenium particles obtained by laser ablation of a target (STEM regime).

subjected to laser fragmentation using the same laser source. The size distributions of nanoparticles after the fragmentation are shown in Fig. 3.

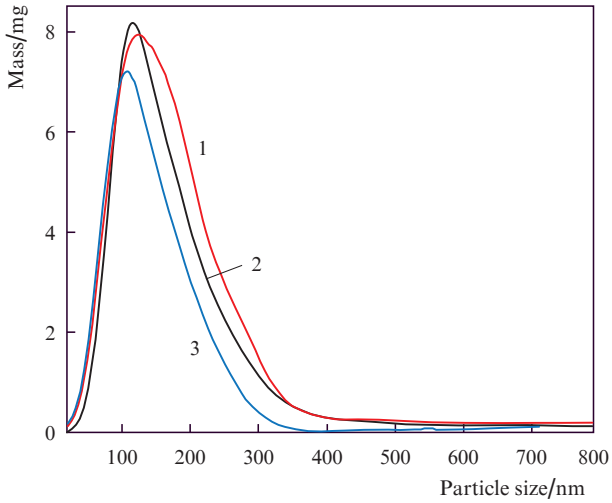

Figure 3. Size distribution for a nanoparticle mass in a 100-μL colloidal solution sample for fragmentation times of (*1*) 90, (*2*) 180, and (*3*) 210 min.

It can be seen that, as a result of fairly long-term fragmentation, most nanoparticles have sizes in the range of 100–150 nm. The majority of particles have small (less than 100 nm) sizes, because the number of particles N and their mass m are related by the evident equality: $N = 3m/4\pi\rho R^3$, where ρ is the selenium density and R is the particle radius.

Figure 4b shows that small selenium nanoparticles (about 10 nm in size) have a pronounced crystalline structure. It was stated previously that small selenium nanoparticles obtained by laser ablation are amorphous, as confirmed by the X-ray diffraction pattern [14]. Indeed, the width of the selenium diffraction peak suggests that the Se nanoparticles are in the amorphous state. However, based on the data of this study, this conclusion can be considered as only partially valid.

Small particles are crystalline, and the broadening of selenium diffraction peak could be related to the small particle size.

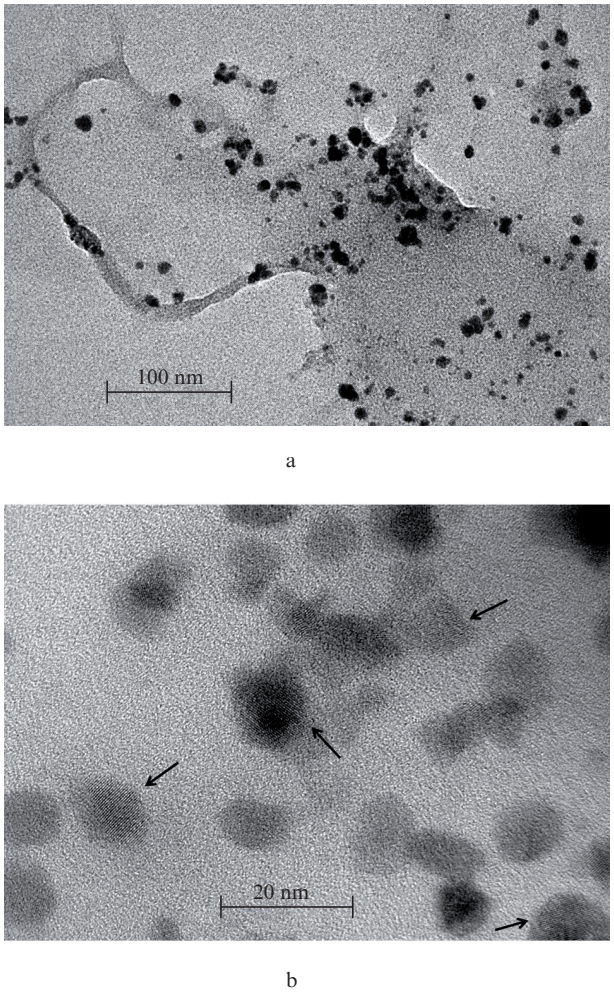

Figure 4. (a) General and (b) enlarged high-resolution TEM images of selenium nanoparticles. The arrows indicate the directions corresponding to distinguishable crystallographic planes of individual particles.

The addition of selenium nanoparticles to soil changes the growth rate of some plants. Figure 5 shows the dependence of the area of radish and arugula leaves on the selenium concentration. It can be seen that the optimal selenium concentration in soil is 5–10 μg kg^{-1}.

Along with the leaf area, we measured also the weight of radish roots. It was shown that, when growing radish for 30 days in soil with selenium nanoparticles added in concentrations of 5 and 10 μg kg^{-1}, the biomass accumulation rate was almost 20% higher as compared with the test sample, and the radish roots ripened almost completely for 30 days. Obviously, selenium entered the biomass of grown plants.

4. Conclusions

Generation of selenium particles and their subsequent fragmentation into nanoparticles was experimentally implemented using a pulsed neodymium laser with a high average power. The fragmentation stage was found to be necessary, because the initial particles have submicron sizes. High-resolution TEM images of selenium nanoparticles show that even small selenium nanoparticles (about 10 nm in size) have a crystalline structure. It was demonstrated that the zero-valence selenium nanoparticles obtained by laser ablation and fragmentation of selenium in water can be used as an efficient additive to agricultural fertilisers. The optimal selenium concentration in soil is 7–12 μg kg^{-1}.

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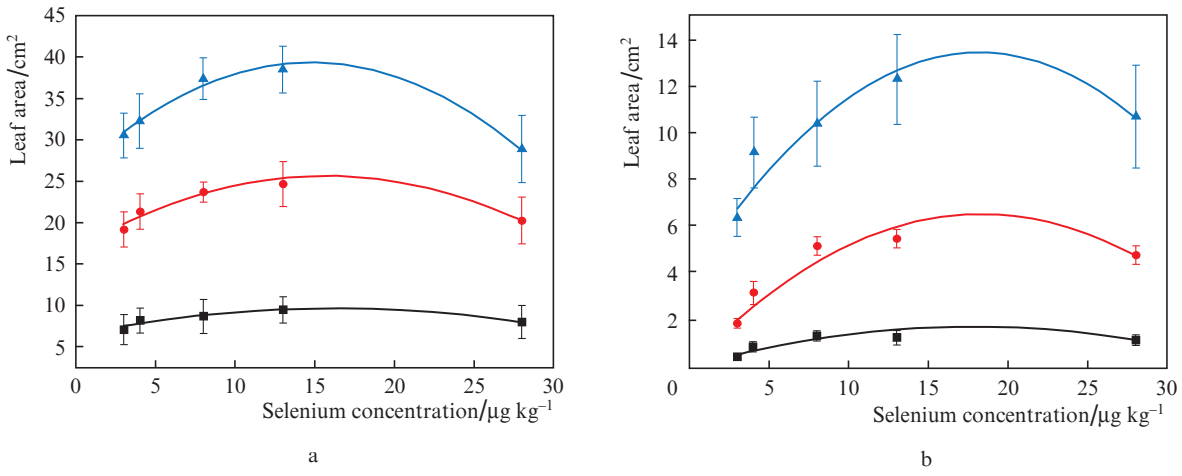

Figure 5. Dependences of the area of (a) radish and (b) arugula leaves on the selenium concentration in soil for growth times of (■) 5, (●) 10, and (▲) 30 days. The initial selenium concentration in soil is 2–4 μg kg^{-1}.

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