Laser ablation method for the generation of chromium, iron, manganese, nickel, scandium, titanium and vanadium, nanoparticles: control of size and properties

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Abstract. Using method of laser ablation of massive targets in liquids, nanoparticles (NP) of chromium, iron, manganese, nickel, scandium, titanium and vanadium with controlled characteristics were generated. To generate NP with the desired characteristics, both ablation of macro-sized butt and fragmentation are consumed. Laser fragmentation is the process of melting large NP into small ones using laser radiation. The influence on the distribution of NP by diameter (size) of such key parameters of laser irradiation as the density of energy of beam and power of the laser is determined. To obtain NP devoid of surface oxide films, organic solvents or water saturated with molecular hydrogen were used as a working fluid. The proposed approaches allow one to obtain NP that meet the following criteria: 1). the type of NP tends to be spherical; 2). 95% of NP have a certain radius; 3). NP consist of a single chemical element, the quantity of impurities is minimal; 4). the crystal lattice of NP is metallic. If necessary, it is possible to generate NP with a surface layer consisting from oxides, as well as fully oxidized NP.

Keywords: nanoparticles, laser fragmentation, laser ablation, transition metals

1. Introduction

Currently, the processes accompanying laser breakdown in colloidal solutions of various nanoparticles, processes associated with the generation of nanoparticles and their characterization are being actively studied [1-3]. It is known that during optical breakdown of aqueous solutions containing nanoparticles, fragmentation and oxidation of these nanoparticles and their surfaces occurs. During optical breakdown, generation of molecular hydrogen [4], molecular oxygen [5], ozone, hydrogen peroxide and other active molecules and atoms is observed [6]. When ablating pieces of minerals, metals or polymers, the above products are also formed. These products are formed by laser plasma. The formation of plasma on macroscopic pieces or nanoparticles proceeds as follows. Laser radiation is absorbed. Rapid heating of the material occurs. The material is melting. A vapor-gas shell forms on the surface of the material. When the shell collapses, molten particles fall into the medium.
Acoustic and shock waves accompany the process, plus optical and ultraviolet radiation is observed. Physicochemical processes occurring during optical or ablation are affected by the material with which laser radiation interacts [7]. It is fundamentally difficult to obtain nanoparticles of the same size. If we are talking about obtaining nanoparticles with a similar surface topology, oxide-free, with the same properties, then the task is complicated many times [8-11]. Of course, there are exceptions to this rule [12]. The aim of this work is to obtain nanoparticles of the same size, topology, deprived of oxide layers or, conversely, coated layers of the desired size, up to complete oxidation.

2. Methods

2.1. Generation of nanoparticles

Metallic nanoparticles were obtained by laser ablation in a liquid. The experimental setup for nanoparticle generation by laser ablation is shown in Fig. 1. We used a ytterbium-doped fiber laser with a variable pulse duration of 4-200 ns, a pulsed wave of 1064 nm, an energy of 1 mJ per pulse, a pulse repetition rate of 20 kHz, and an average power of about 20 W. As a working medium, deionized Milli-K water was used in an amount of 10-15 ml. Polished metal pieces were used as a primary target for laser ablation. The target of the corresponding material was immersed in the medium so that the liquid layer above the target surface was about 1-2 mm. The exposure times of the target were from 5 to 20 minutes. For laser fragmentation of nanoparticles in a medium, an Nd: YAG laser with a fixed pulse duration of 10 ns, $\lambda = 1064$ nm, pulse energy of 2 mJ, pulse repetition rate of 10 kHz, and an average power of about 20 W was used. Laser radiation was introduced into the experimental cuvette from below, to prevent defocusing of the laser radiation on the resulting air bubbles. The times of radiation exposure on nanoparticles during their fragmentation ranged from 15 to 30 minutes.

2.2. Methods used in the study of nanoparticles

The average size of NP was studied using DC 24000 analytical disk centrifuge (CBC Instruments). Centrifugation on an analytical disk is a fast, reliable and sensitive method for analyzing medium-sized nanoparticles that are contained in a liquid. To determine the morphology, confirm the presence of an oxide layer or impurities on the surface of the nanoparticles, and additionally determine the size of the nanoparticles, we used a 200FE (CarlZeiss) transmission electron microscope with a spectroscopic attachment to measure the energy loss of electrons. The methods we use, the necessary settings, and the subtleties of the experiment are described earlier in our articles [13-15].

Figure 1. Experimental installation for laser ablation of a volumetric target in a liquid medium.
3. Results
Laser ablation yielded scandium, titanium, vanadium, chromium, manganese, iron and nickel nanoparticles. If deionized water is used as working media, then in the ablation, large metal NP can be obtained. Such NP mainly consist of metal, although its may contain oxide surface layers or its parts. As a representative example, Figure 2A shows micrographs of a NP generated from scandium. After the complete fragmentation of such particles in aqueous solutions or pure water, the manifestation of small scandium nanoparticles is observed. It is shown that during fragmentation in aqueous solutions, the formation of fully oxidized NP is observed. In rare cases, the formation of NP with a surface oxide layer and a metal core is observed. A typical microphotography of the scandium preparation after partial fragmentation in water media is shown in figure 2B. It should be noted that when changing aqueous solutions to aliphatic liquids, oxide layers are practically not formed.

![Figure 2](image_url)

**Figure 2.** Micrographs of nanoparticles generated obtained by using transmission electron microscopy.

A - Microphotography of a part of a nanoparticle consisting of scandium about 100 nm in size.

B - Micrograph of scandium preparation obtained after partial fragmentation of large nanoparticles. The non-fragmented black nanoparticle (lower left corner) has a characteristic diameter of 100 nm.

C — Micrograph of nickel nanoparticles made by laser fragmentation in isopropanol.

D - Micrograph of nickel nanoparticles generated by laser fragmentation in isopropanol.

E - Micrograph of an iron nanoparticle made by laser fragmentation in pure alcohol.

F - Micrograph of a nickel nanoparticle made by laser fragmentation in pure alcohol.

It is known that during laser ablation oxidation of NP is observed. This is due to the generation of molecular oxygen and its reactive species during ablation. It is obvious that the fewer oxygen atoms enter the ablation medium, the less molecular oxygen and its active forms are formed. However, there is another part of the problem. When using media that do not contain oxygen atoms, the oxidation of
nanoparticles is not observed. Nanoparticles are generated entirely metal. However, such nanoparticles are difficult to transfer to water environments. Such nanoparticles aggregate, precipitate, and a large amount of aliphatic substances is transferred to the water with them. In addition, under certain boundary conditions, nanoparticles are observed to form a shell from polymerized aliphatic media. To solve the problem, we used amphiphilic liquids, mainly low-atom alcohols. The use of different alcohols as ablation and fragmentation media makes it possible (depending on the boundary conditions) to generate as nanoparticles devoid of a surface oxide layer (completely metallic) (Fig. 2C, 2D), and nanoparticles containing an oxide layer on the surface (a metal core surrounded by an oxide layer) (Fig. 2E, 2F). Alcohols must be saturated with hydrogen before use. This measure allows us to obtain the purest nanoparticles. Thus, employing laser fragmentation, NP of various specified diameters were generated. Figure 3, as an example, shows a series of diameters of nanoparticles. In this case, we obtained nanoparticles from various metals with the same average diameter of about 20 nm.

![Figure 3. Size distribution of nanoparticles.](image)

Nanoparticles of iron (FeNP), chromium (CrNP), scandium (CsNP), manganese (MnNP), nickel (NiNP), titanium (TiNP) and vanadium (VNP).

4. Conclusions
Thus, it has been shown that using laser ablation of metal pieces in liquid media it is possible to generate chromium, iron, manganese, titanium, scandium, nickel and vanadium NP with a clearly defined diameter and characteristics. Laboratory regulations for the generation of metal NP are developed.

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