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Obtaining of nanoparticles of Sc, Ti, V, Cr, Mn, Fe, Co, Ni with controlled sizes and properties using laser ablation

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Abstract. Using laser ablation, nanoparticles of Sc, Ti, V, Cr, Mn, Fe, Co, Ni with controlled sizes and properties were obtained. To obtain nanoparticles of a given size, not only ablation of massive targets was used, but fragmentation (exposure to a mixture of micro- and nanoparticles by laser radiation). The evolution of the particle size distribution function in the process of their laser fragmentation is investigated and its key parameters determining it are established, such as the energy density of a laser beam in a medium and the peak power of laser radiation. Different schemes for introducing laser radiation into colloidal systems have been used. To obtain nanoparticles that do not contain oxide films, organic alcohols (ethanol and propanol-2) were used as the working fluid. The obtained nanoparticles met the following criteria: 1). At least 95% of the particles in the preparation have the specified diameter; 2). The shape of the nanoparticles is close to spherical; 3). The composition of the nanoparticles does not include a significant amount of impurities and oxides; 4). In most of the nanoparticles, a metal crystal lattice is observed, although under certain conditions it is possible to obtain nanoparticles, both with the outer oxide layer and entirely consisting of oxides. The stability of the obtained colloidal nanoparticles was investigated. It is assumed that the solvent is saturated with molecular hydrogen to prevent oxidation of nanoparticles during storage.

1 Introduction

The tendency to miniaturization and the need to improve technological processes have led in the last twenty years to a significant increase in the number of research works devoted to obtaining and studying the properties of nanoparticles [1-3]. Methods of synthesis of
nanomaterials are currently one of the most rapidly developing areas of modern science. At the same time, there is a demand for obtaining nanoparticles of a certain composition, size and shape [4]. It is known that the physical characteristics of nanoparticles substantially depend on these three quantities. Unfortunately, most of the currently known synthesis methods make it possible to obtain nanoparticles with a rather wide distribution in size and shape. If we consider chemical methods, even careful control of reaction parameters such as time, temperature, mixing speed, concentration of reagents and stabilizing additives, does not always allow to obtain nanoparticles of the same shape and with the required size distribution [5]. Often, the obtained nanoparticle preparations consist of a number of fractions; in this connection, along with the development of methods for synthesizing nanoparticles with a narrow size distribution, the techniques for separating the obtained nanoparticles into fairly monodisperse fractions are improved [6].

To date, the generation of nanoparticles in the process of laser ablation of solids in liquids is being investigated in a number of leading laboratories around the world. Laser ablation in liquids has become an alternative to chemical methods for the synthesis of nanoparticles [7]. A characteristic feature of the laser method is the potential to generate: 1). "Pure" nanoparticles that do not contain unwanted ions and surfactants; 2). Monodisperse nanoparticle size distribution; 3). nanoparticles whose shape is close to spherical. In this paper, laboratory protocols for the production of transition metal nanoparticles were created. Metallic nanoparticles Cr, Sc, V were obtained using laser ablation for the first time. In addition, the work created synthesis protocols to avoid oxidation and aggregation of transition metal nanoparticles during storage in a colloidal form.

2 Methods

1.1 Production of metal nanoparticles

Production of metal nanoparticles was performed using laser ablation in a liquid. A solid target was located at the bottom of a glass cell under a thin layer of working fluid (usually several millimeters), and the laser radiation was focused on the target surface. Working fluids are chosen transparent at the laser wavelength, thus, the laser radiation is absorbed in the target material [8]. Schematic diagram of the installation for the production of nanoparticles is shown in Figure 1 [9]. In some cases, the obtained nanoparticles were subjected to further laser fragmentation, with the most successful optical scheme in which laser radiation is introduced into the cell through the bottom. This scheme allows avoiding defocusing of laser radiation on gas bubbles formed in a liquid and, by heating the bottom, leads to more uniform mixing of fragmented colloidal solutions. Nd:YAG laser with a fixed pulse duration (λ = 1064 nm, τ = 10 ns, repetition frequency 10 kHz, average power up to 20 W, pulse energy 2 mJ), as well as a fiber Yb laser with variable pulse duration (λ = 1064 nm, τ = 4–200 ns, repetition frequency 20 kHz, average power up to 20 W, pulse energy 1 mJ) and scan heads (Ateko-TM galvanic scan heads) for control laser radiation are used.
1.2 Characterization of nanoparticles

The size of the obtained nanoparticles was characterized using an analytical centrifuge DC24000 (CPS Instruments), a fast and sensitive particle size analyzer of colloidal solutions. To confirm the absence of oxides and/or impurities in nanoparticles, as well as independent confirmation of the morphology of nanoparticles, a Carl Zeiss 200FE transmission electron microscope with electron loss energy spectroscopy was used. All the methods used by us are described in detail earlier [10].

3 Results

Using laser ablation, Sc, Ti, V, Cr, Mn, Fe, Co, Ni nanoparticles were obtained. When using deionized water as the working fluid at the ablation stage, it is possible to obtain large metal nanoparticles consisting mainly of metal, although containing oxidized layers and parts. Figure 2A shows scandium nanoparticles as a representative example. However, after fragmentation in water or aqueous solutions of such particles practically does not remain. Figure 2B shows a representative photograph of the drug scandium after partial fragmentation. During fragmentation, almost all of the smaller nanoparticles formed consist of oxides, in some rare cases they have a metallic core surrounded by an oxide layer.
It was previously shown that the oxidation of nanoparticles during laser ablation is due to the generation of molecular oxygen. The fewer oxygen atoms in the chemical structure of the working fluid, the less intense the formation of molecular oxygen [11]. However, oxidation is less intense. It seems the way out is simple, you need to use working fluids that contain no oxygen atoms, such as hydrocarbons. However, when using this approach, it is extremely difficult to transfer the obtained nanoparticles to aqueous media. The second problem is the formation of organic shell on the nanoparticles. To solve these problems, we compromised and used alcohols as a working fluid. This approach allows one to obtain nanoparticles without an oxide layer (Figure 3), as well as surface oxidized nanoparticles with a metal core (Figure 4). The more oxygen atoms in an alcohol molecule structure, the more soluble and oxidized nanoparticles will be. When storing the obtained nanoparticles in aqueous colloids, their aggregation and oxidation is observed. When aqueous colloids are saturated with molecular hydrogen, the rate of oxidation and aggregation decreases significantly.

Fig. 2. TEM image of Sc nanoparticles. A – HR-TEM image of the surface layers of scandium nanoparticles with a size of 100 nm. B – TEM image of a perparate of scandium nanoparticles after partial fragmentation, the dark particle in the lower left corner has a size of 100 nm and is shown in detail in figure 3A.

Fig. 3. TEM image of nanoparticles. A – Nickel nanoparticles obtained by fragmentation in propanol-2. B – Vanadium nanoparticles obtained by fragmentation in propanol-2.
Fig. 4. TEM image of nanoparticles. A – Iron nanoparticles obtained by fragmentation in ethanol. B – Nickel nanoparticles obtained by fragmentation in ethanol.

It should be noted that using laser fragmentation, we can produce nanoparticles of given sizes. As an example, Figure 5 shows several particle size distribution functions. It is shown that the average size is typical, about 20 nm, although nanoparticles are obtained from various materials.

Fig. 5. Size distribution of nanoparticles.

4 Conclusions

In this paper, it was shown that using laser ablation it is possible to obtain nanoparticles of Sc, Ti, V, Cr, Mn, Fe, Co, Ni with controlled sizes and properties. Laboratory protocols for the production of transition metal nanoparticles were created. The results are in good agreement with the results of studies by other scientists [12-22].

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