

LASER SYNTHESIS OF Pt NANOPARTICLES AT AIR

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Experiment

At the present work for the formation of colloidal solutions of Pt nanoparticles the Nd: YAG ($\lambda = 1064$ nm) laser was used which provides a pulse duration of 20 ns and an average pulse energy of 200 mJ, which when focused into a spot with $d = 1$ mm may help obtain the power density of ~ 1 GW/cm². The pulse repetition rate was 5 Hz. The typical exposure time for optically dense samples of metal colloids has been chosen to be 15 min for one sample ($v=120$ ml).

The process of synthesis occurred in the air, followed by penetration of the formed Pt metals nanoparticles into the water medium. Experimental scheme of the laser synthesis method is deposited at the Fig. 1.

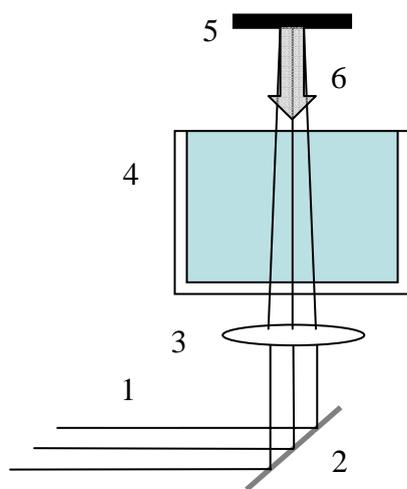


Fig. 1. Experimental setup

The intense laser irradiation I is turned by the angle 90° with interference mirror 2. Then the laser beam is focused with the help of lens 3 and comes through the pan with a medium of penetration to metal target 5. The correction of additional focusing caused by parallel-sided lay of liquid was done by experimental way. The condensed phase of target material (formed within the erosion laser jet) directly permeates through opened liquid surface. Target 5 represents massive plate of platinum, chemical homogeneity of which has been confirmed by the government certification.

For the investigation of metal nanoparticles properties in optical media it's appropriate to apply the complex of direct and indirect methods, in order to obtain the most complete information about the condition and properties of metal nanophase [1]. For direct methods of diagnostics of ultrafine metallic phase parameters the following techniques were used in this study: scanning electron microscopy (SEM NEON 40 Carl Zeiss) and registration of the characteristic spectrum of microscopic objects excited by a narrowly focused electron beam (electron probe). The indirect methods are presented by

absorption spectroscopy of surface plasmon resonance (SPR) and by a comparison of the actual shape of the SPR band with model spectral dependences of efficient factor of extinction, computed according to the Mie theory /2/.

Modelling the efficient factor of extinction of metallic colloidal systems in order to compare it with the real spectra of SPR is a well-known method of approximate estimation of the parameters of the ultrafine metal phase in optically transparent media /3/. In order to determine the spectral shape efficient factor of extinction the approach was used based on the theory of interaction of electromagnetic field with small spherical particles, proposed by Mie /4, 5/. This theory is widely used for modeling of the optical characteristics of low-dimensional objects /2/, it is based on the decomposition of electromagnetic fields interacting with a small particle on vector spherical harmonics, with subsequent calculation of the coefficients of this distribution. The main positions of the approach are presented in /6/. For numerical calculations MiePlot 4207 software was used. The program allows the dependences of extinction effectiveness factors, absorption and scatter on the wavelength of incident planar radiation front to be calculated taking into account the spectral dependences of imaginary and real parts of the refractive index of particle material and aqueous environment. A normal spherical particle-size distribution with different values of the scatter is taking as a model.

Then the experimental sample was subjected to an investigation using the SEM techniques, for which small amount (~ 1 ml) of colloid was deposited on a carbon film, the water slowly evaporated, the nanoparticles of metal gradually deposited on the substrate. After this, the formed sample of metal colloid was evacuated and subjected to SEM. SEM image of Pt colloid is placed in figure 2a.

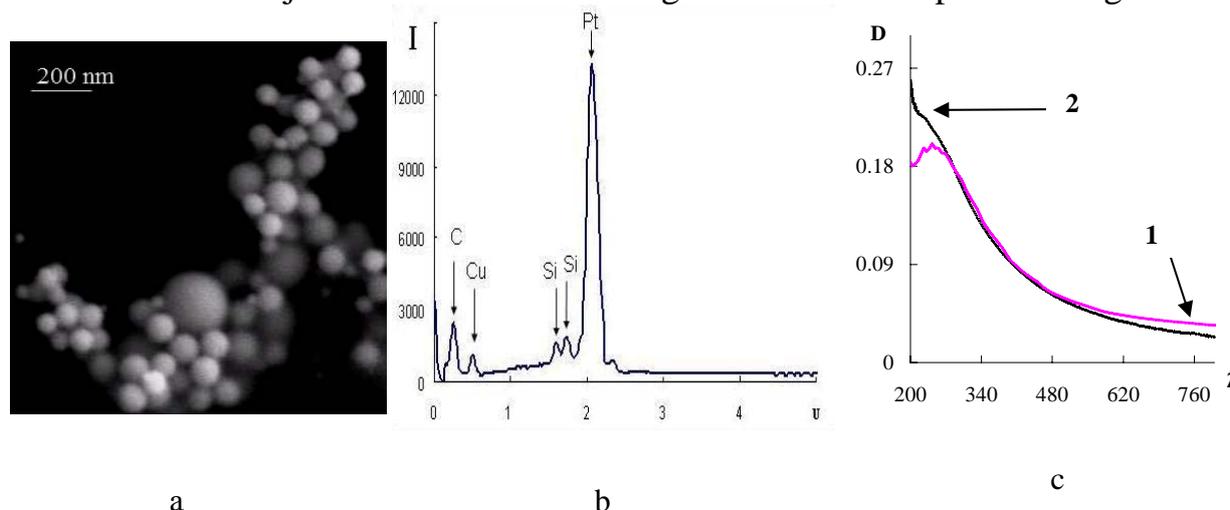


Figure 2. The results of the studies of experimental Pt colloid: a) SEM image of particles deposited on the substrate; b) range of the characteristic radiation of particles in electron-beam; c) SPR band spectrum (1 - a real, 2 - model)

At this picture we can see spherical nanoobjects, which differ considerably in size. A common feature of the image under consideration is a grouping of the smaller objects around the large ones, which might suggest the mechanism of aggregation of particles visualized conglomerates.

At the same time during the processing of a large array of such images it becomes apparent that in the case of local absence of large objects smaller particles are reluctant to form an array, trying to evenly distribute the area of the substrate. Thus the visualized combining of particles often cannot be representative for the determination of an average particle size of a real colloid and of the characteristics of their size distribution, in fact, only giving the information about the predominant form of produced nanoobjects.

During the next stage of the study the revealed conglomerates of nano-sized objects were subjected to excitation by a narrowly focused electron beam (electron probe) in order to initiate and to further register the spectrum of characteristic radiation (X-rays). The result of this procedure is shown at Figure 2b. On the base of this spectrum one can conclude that the visualized nanoparticles are chemically homogeneous and consist entirely of the target material. The detection of minor traces of foreign elements is due to the way of making preparations and to the type of substrate used.

The result of absorption spectroscopy of the sample of Pt colloidal solutions is placed in Figure 2c (curve 2). Pt colloid is characterized by wide "spectral wing" ascending in the short-wavelength area which is in good agreement with the parameters of platinum colloid formed by chemical methods /7/.

Modelling spectral dependence of the efficient factor of extinction, which was approximated according to the Mie theory, is shown at Figure 2c (curve 1). The modelling parameters (mean diameter and variance of the distribution on the diameter values of the solid metal spheres) are chosen in such way as to ensure the maximum compliance with the actual contours of extinction (curve 2 in Figure 2c).

According to the results of modelling the efficient factor of extinction we can state that the evaluation of average particle diameter in real Pt colloid is 25nm, with the dispersion of particle size distribution of 25%. The values of the optical characteristics of this metal are taken from /8/. This value is typical for the dispersion of ultrafine metallic systems formed by condensation processes /1/.

Conclusion.

Based on the technique of laser synthesis in an air atmosphere an industrial technology of formation of the Pt nanoparticles flow can be developed. The

main advantages of this technological approach are the simplicity of technical realization of the process, low cost production and high rate of synthesis of metal nanoparticles. When used as a medium for the introduction of water the formation of water colloidal solutions of the processed metals with high optical density is possible. For the diagnosis of the spectral and morphological parameters of the formed colloids it is expedient to use set of direct (SEM and registration of the characteristic spectrum upon excitation by an electron beam) and indirect (SPR spectroscopy and modeling of the extinction of the colloid based on the Mie theory) methods.

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