Optical properties of Al nanoparticles prepared by laser ablation method

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Abstract. The results of the synthesis and study of the optical properties of aluminum nanoparticles (NPs) processed by the laser ablation method are presented. Water, ethanol and chlorobenzene are used as solvents for the synthesis of nanoparticles. Measurements of the size and shape of the obtained NPs are carried out. The absorption and luminescence spectra of NPs are measured. The extinction spectra of aqueous solutions of Al nanoparticles and Al-Al_2O_3 nanostructures were simulated. Studies demonstrate the formation of Al-Al_2O_3 nanostructures during laser ablation of aluminum in water and ethanol liquids.

1. Introduction

The development of methods for the synthesis of metal nanoparticles is one of important directions of the modern materials science. The main attention is given to the synthesis of such nanoparticles (NPs) as silver and gold [1, 2]. Less attention is paid to the development of methods for the synthesis of other types of metal NPs. Aluminum NPs are promising materials for the use in various optoelectronic devices [3, 4]. The search for methods for the synthesis of aluminum NPs with known characteristics is an important task.

The method of laser ablation in a liquid is one of simple methods for the preparation of NPs. However, both the aluminum NPs and complex nanostructures (NSs) containing Al and aluminum oxide are formed during this process depending on the solvents used. For example, the laser ablation of Al in water [5] results in a formation of aluminum oxide (Al_2O_3) along with Al NPs. The Al-Al_2O_3 NSs formed can have a core/shell structure, where the core is an Al nanoparticle and the shell is an oxide layer Al_2O_3. It is necessary to use various methods of studies including optical methods to obtain more complete information about the synthesized nanostructures.

The results of the synthesis of Al nanoparticles by laser ablation and studies of their optical properties are presented in this paper.

2. Experiment

Laser ablation was used as a method for the synthesis of Al NPs in a liquid. The second harmonic of a Nd:YAG laser SOLAR LQ 215 is used (wave length λ_{gen} = 532 nm, pulse energy E_{imp} = 90 mJ, pulse duration τ = 7 ns, pulse frequency ν = 20 Hz). The laser radiation was directed by a mirror and focused by a lens onto a horizontally placed target - an aluminum plate in a cell with liquid.

Various solvents were used for ablation. Data on the ablation time are given in table 1. The average size of the obtained Al nanoparticles was determined by dynamic light scattering using a Zetasizer Nano ZS particle size analyzer. The morphology and energy dispersive spectra of Al NPs were obtained using a Tescan Mira 3 scanning electron microscope. The absorption spectra were recorded on a Cary 300 (Agilent) spectrophotometer. The luminescence spectra were measured by Cary Eclipse (Agilent).

The program Mie plot V.4.4.11 was used for simulating the extinction, absorption and scattering spectra of Al NPs and nanostructures of Al-Al_2O_3 in water. The numerical calculation algorithm used is described in detail in [6, 7]. The dielectric constants of Al and Al_2O_3 solid materials are given in [8, 9].

3. Results and discussion

The sizes of NPs formed in various solvents are shown in table 1. As shown in [10], the size of NPs depends on the boiling point of the solvent. Indeed, NPs with the smallest size are formed for the liquid with the highest boiling point (chlorobenzene). On the contrary, NPs with the largest size are obtained for the solution with the lowest boiling point (ethanol). The concentration of NPs in water was determined. The mass of the target was weighed before and after the ablation process. The concentration of Al NPs in water was equal to 1.38×10^{-9} mol/L.

Table 1. Characteristics of the laser ablation process and optical properties of aluminum NPs

Medium	Ablation time (min)	Boiling point, ^{0}C	Average particle size r (nm)	λ_{abs}^{max} (nm)	$\lambda_{1/2}$ (nm)
Ethanol	10	78	2.5	199	114
Water	4	100	19	1) 196; 2) 209; 3) 263	1) 34; 2) 17; 3) 40
Chlorobenzene	2	131	7.5	1) 229; 2) 265	1) 13; 2) 41

Main characteristics of the absorption spectra are given in table 1. A three-fold dilution was used to measure the absorption spectrum of Al NPs in water. The absorption spectra for NPs in water and ethanol have a main maximum in the range 195-200 nm (figure 1, curves 1 and 2). These spectra are in a good agreement with the spectral data obtained in other works [5, 11]. In water, the absorption spectrum contains additional bands with maxima at 209 and 263 nm. The absorption spectrum has peaks at 229, 264 nm for Al NPs in chlorobenzene. The solution becomes yellow during ablation of the aluminum target in chlorobenzene. The spectrum of Al_2O_3 NPs with a size of 125 nm in water also is shown in figure 1, curve 4.

The formation of aluminum oxide (Al_2O_3) instead of aluminum is possible during laser ablation of an aluminum target in water. However, the measured spectrum of Al_2O_3 NPs with a radius of r = 62.5 nm did not show the presence of the absorption maxima in the range of 200 -600 nm (figure 1, curve 4). The absorption spectrum of Al_2O_3 NPs differs significantly from the absorption spectrum of an aqueous solution of Al NPs obtained by laser ablation. The presence of Al_2O_3 luminescence may be an additional factor indicating the formation of aluminum oxide as a result of laser ablation of an Al target. The absorption spectra of Al are located in the ultraviolet region. The glow of solvents is observed after ultraviolet irradiation of chlorobenzene and ethanol. Therefore, only aqueous solutions were used to study the luminescence of NSs based on aluminum. The luminescence spectra of Al_2O_3 and Al NPs in water are shown in figure 2.

A comparison of spectra in figure 2 shows the presence of Al_2O_3 particles in solutions. There are luminescence bands with peaks at 380, 403, 426, and 486 nm in the luminescence spectrum of Al NPs solutions.

Luminescence bands with maxima at 425 and 486 nm are observed for the luminescence spectrum of Al_2O_3 NPs (figure 3, curve 2). Similar results were obtained in [5, 12]. These bands can be attributed to the luminescence of various F centers of the crystalline Al_2O_3 [12].

Electron microscopic investigation indicates the spherical shape of Al NPs. Energy dispersive analysis (EDX) shows the presence of Al_2O_3 oxide in the composition of NSs. The results of the analysis are shown in figure 3. The oxygen constitutes 60 mass % and the aluminum the remaining 40 mass % in NSs prepared in water. The concentration of oxygen in NSs prepared in ethanol is lower than in NSs prepared in water. This indicates a lower thickness of the oxide layer for Al processed in ethanol.

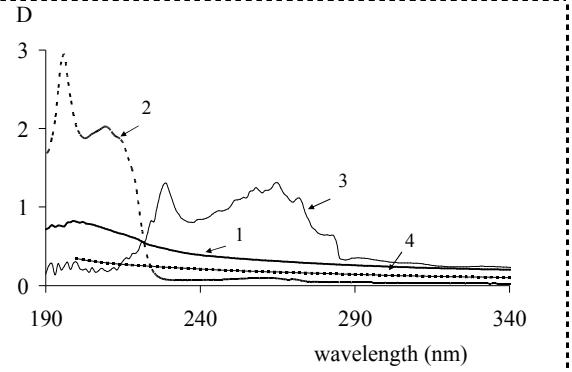

Figure 1. Absorption spectra of Al NPs (1-3) and Al_2O_3 NPs (4) in different solutions: 1 – ethanol; 2,4 – water; 3 – chlorobenzene.

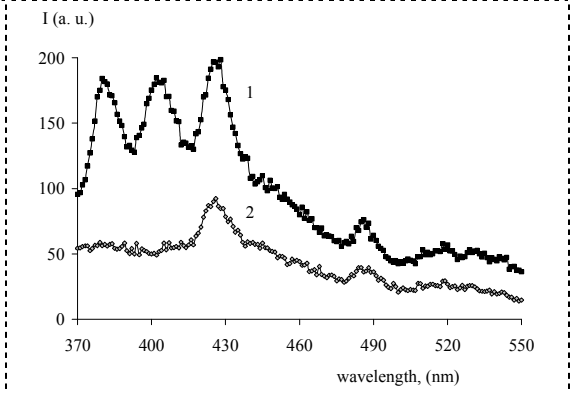

Figure 2. . Luminescence spectra of Al NPs (1) and Al_2O_3 NPs (2) in water.

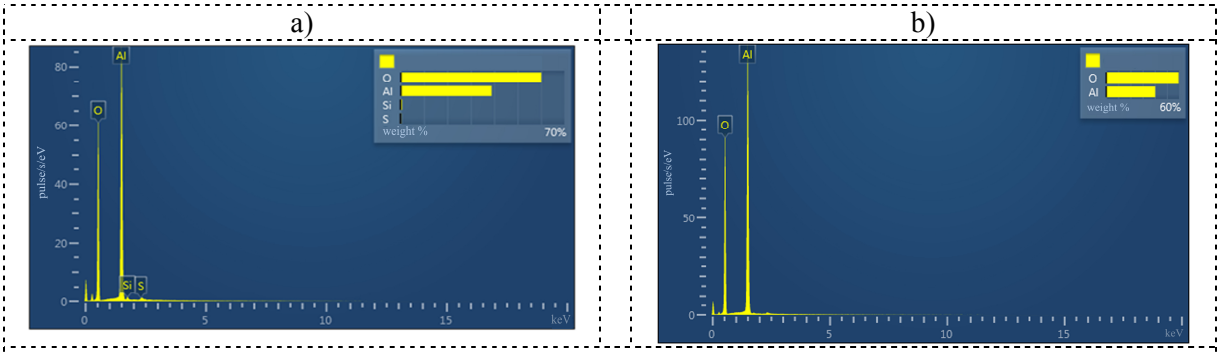

Figure 3. EDX–spectra of Al NPs obtained in the water (a) and in the ethanol (b).

The extinction spectra for Al nanoparticles in water obtained by simulations are shown in figure 4. The simulation results show that the experimental absorption spectrum of aluminium NPs in water (figure 1, curve 2) may be due to the NPs with radius r in the range from 9 to 11 nm. However, the measurement of sizes of NPs by the dynamic light scattering method shows the presence of NPs with a radius of r = 19.5 nm in water. Also, the distribution of the NPs is monodisperse. Thus, the results of direct measurements of the NPs size in water by dynamic light scattering do not correspond to the results of analysis of the absorption spectra and the simulation of extinction spectra of NPs in water. The appearance of the absorption band with a maximum at 263 nm can be explained by the presence of NPs with a size of 26-27 nm.

The extinction spectra of core/shell NSs were simulated with Al as the core and Al_2O_3 as the shell. Sizes of the core and shell were varied to obtain the extinction spectrum of Al NPs in water. The extinction spectra were simulated starting from λ = 200 nm due to the capabilities of the code and availability of dielectric constants of Al and Al_2O_3. Therefore, the spectra were compared to the

maximum at 209 nm. Two bands (figure 6, curve 2) are present in the extinction spectrum of NPs with a large core radius r_{core} = 24 nm and Al_2O_3 shell thickness h_{shell}=3 nm. A shift to the shortwave region of the absorption maxima occurs with a decrease in the particle size.

The short-wave maximum of extinction spectra becomes inaccessible for size of NSs r_{NSs} = 20 nm (r_{NSs}= r_{core}+ h_{shell}). The extinction band with a maximum at 210 nm is observed for a NS with r_{core} = 12.5 nm and h_{shell} = 0.5 nm (figure 5, curve 2). This size exceeds the size of NPs obtained by dynamic light scattering. However, the size of the simulated NSs is closer to the data of table 1 than the size from simulations of Al NPs.

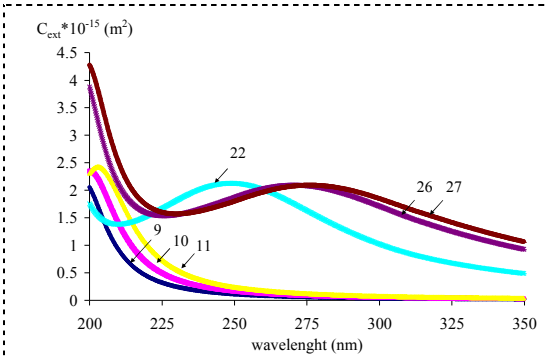

Figure 4. Extinction spectra of Al NPs with various sizes (r) in the water.

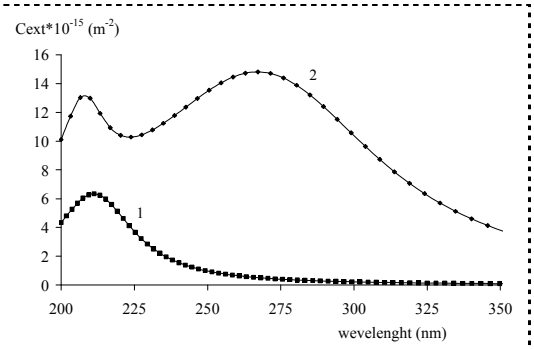

Figure 5. Extinction spectra Al–Al_2O_3 NSs in the water 1 - r_{core} = 12.5 nm, h_{shell} = 0.5 nm; 2 - r_{core} = 24 nm, h_{shell} = 3 nm.

Thus, the results of direct measurements of the size of Al NPs in water do not correspond to the results of the analysis of the absorption spectra and the simulation of the extinction spectra of Al NPs in water. The results of the measuring of the luminescence spectra and EDX-analysis of aluminum NPs indicate the presence of Al_2O_3 in the solution. A comparison of the obtained spectral data for Al NPs with the data on the absorption of Al_2O_3 and simulation of spectra of Al_2O_3 NPs shows that the spectra of synthesized NPs can't be explained by the formation of only the Al_2O_3 NPs. The obtained data indicate the formation of nanostructures based on Al and Al_2O_3.

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