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Synthesis of Al-Al_2O_3 nanostructures by laser ablation

The results of synthesis of aluminum nanoparticles (NPs) by laser ablation are presented. Water, ethanol, chlorobenzene were used for the synthesis of NPs as solvents. Measurements of sizes and shapes of NPs are carried out. Particle's sizes was determined using the dynamic light scattering method. Sizes of nanoparticles depends on the boiling point of solvents. Electron microscopic images show that the formation of spherical nanoparticles. Absorption spectra of solutions of aluminum NPs and aluminum oxide (Al_2O_3) NPs are measured. A computer simulation of extinction spectra of aluminum NPs and Al_2O_3 NPs in an aqueous solution was also carried out. Extinction spectra of Al and Al_2O_3 nanoparticles of different sizes in the water were calculated by using Mie theory. The comparison of results of measurements and the simulation showed a significant difference. Luminescence spectra of aqueous solutions of aluminum NPs and aluminum oxide NPs were measured with the ultraviolet excitation. Results of measuring of the luminescence spectrum of the water of aluminum NPs indicate the presence of Al_2O_3.

Keywords: Al nanoparticles, Al_2O_3 nanoparticles, Al-Al_2O_3 nanoparticles, absorption spectrum, luminescence.

Introduction

Recently, there are an increase in the attention of various research groups to the development of methods for the synthesis and the practical use of metal nanoparticles (NPs). This interest is related to the observation of a surface plasmon resonance in NPs, which leads to a fundamental change in optical and electrical properties of materials with metal nanoparticles [1, 2]. Optical and electrical properties of NPs depend on a number of factors such as the size of the nanoparticles, their shape and their material. The most popular materials with plasmon properties are silver, gold and copper. However, the number of plasmon materials is much larger and includes most metals [3], as well as some semiconductor materials [4, 5].

However, as is known [6], the specific surface of NPs increases with decreasing particle sizes. The growth of the specific surface area of nanoparticles leads to an increase in a chemical activity of metal particles [7]. One of the main way to protect nanoparticles from destruction is the synthesis of a protective shell. The shell can be organic or inorganic materials. The most commonly used substances are oxide materials, such as TiO_2 or SiO_2.These oxide materials lead to form stable NPs [8]. Methods for the synthesis of shells with an accuracy of one nanometer have been developed.

One of the direction of using metal NPs is photovoltaic. A review of scientific publications on the using of the plasmon effect in photovoltaics shows to increase the efficiency of both inorganic [9-10] and organic solar cells [11, 12]. In most cases, silver and gold NP are used, which have the maximum plasmon effect in the visible spectral range [9, 10, 13]. It is also proposed to use aluminum NPs in solar cells [14].

In this paper, results of the synthesis of Al nanoparticles by the laser ablation and the study of their optical properties are presented. The influence of solvents on the size and optical properties of synthesized NPs was studied.

Experiment

The method of the laser ablation in a liquid was used for the synthesis of Al NPs. The installation scheme for obtaining nanoparticles is shown in Figure 1. The solid-state Nd: YAG laser (1) (SOLAR LQ 215) was used for the ablation. The second harmonic of the laser is used (λ_{gen} = 532 nm, E_{imp} = 90 mJ, τ = 7 ns, ν = 20 Hz). The laser radiation was directed with a mirror (2) and focused by a lens (3) onto a horizontally placed target - an aluminum plate (5) in a cell with a liquid (4).

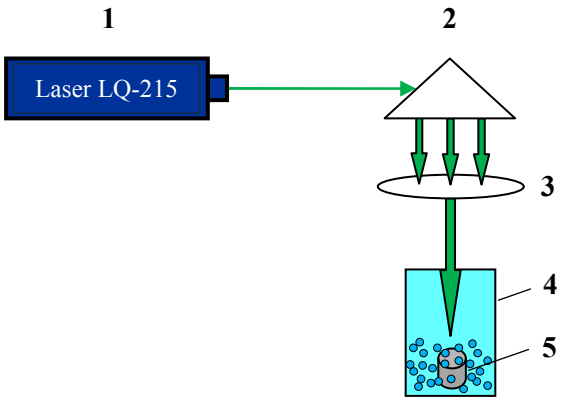


Figure 1. Scheme of the plant for obtaining aluminum nanoparticles by the laser ablation in a liquid

Various solvents were used for the ablation. The ablation time was determined qualitatively, by changing the color of the solvent. The data on the ablation time are given in Table 1.

Average dimensions of obtained Al nanoparticles were determined by a dynamic light scattering using Zetasizer Nano ZS particle size analyzer. The NPs morphology was studied with Tescan Mira 3 scanning electron microscope. Absorption spectra were recorded on Cary 300 (Agilent) spectrophotometer, and the luminescence was measured by Cary Eclipse (Agilent).

Results and discussion

The distribution of NP sizes (d) in various solvents is shown in Figure 2 and Table 1. As shown in [15], the size of NPs depends on the boiling point of a solvent. Indeed, NPs with the smallest size are formed for a liquid with a high boiling point (chlorobenzene). NPs with the largest size are obtained for a solution with a low boiling point (ethanol).

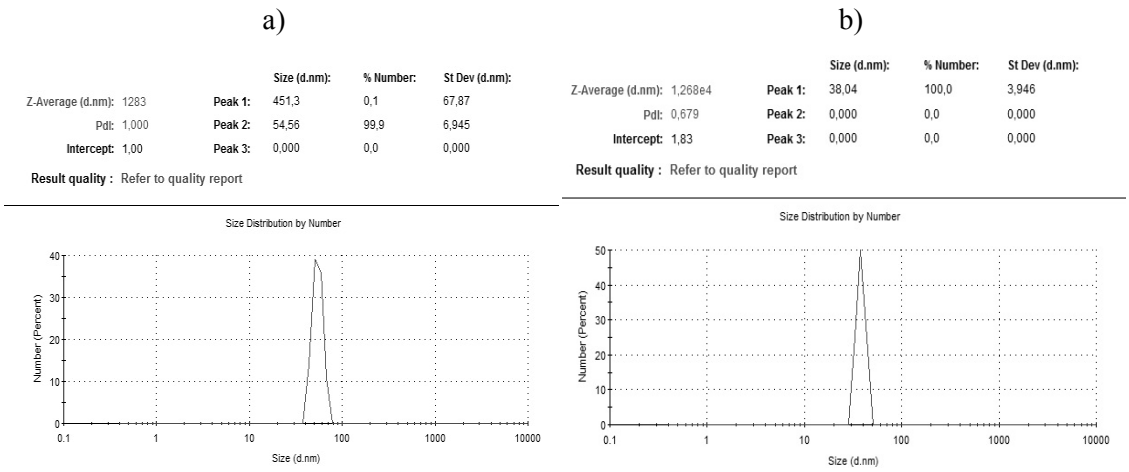


Figure 2. The distribution of sizes of aluminum NPs in the ethanol (a) and in the water (b)

Table 1

The dependence of dimensions of Al NPs from the solvent

Medium	Ablation time (min)	Boiling point, ^{0}C	Average particle size d (nm)
Ethanol	10	78	55
Water	4	100	38
Chlorobenzene	2	131	15

Electron microscopic images of NPs are shown in Figure 3. NPs have a predominantly spherical shape. Nanoparticle sizes (d) differ from sizes obtained by the laser light scattering method (Fig. 2, Table 1). This may be due to an aggregation process of NPs after transferring particles to a solid surface.

a) b)

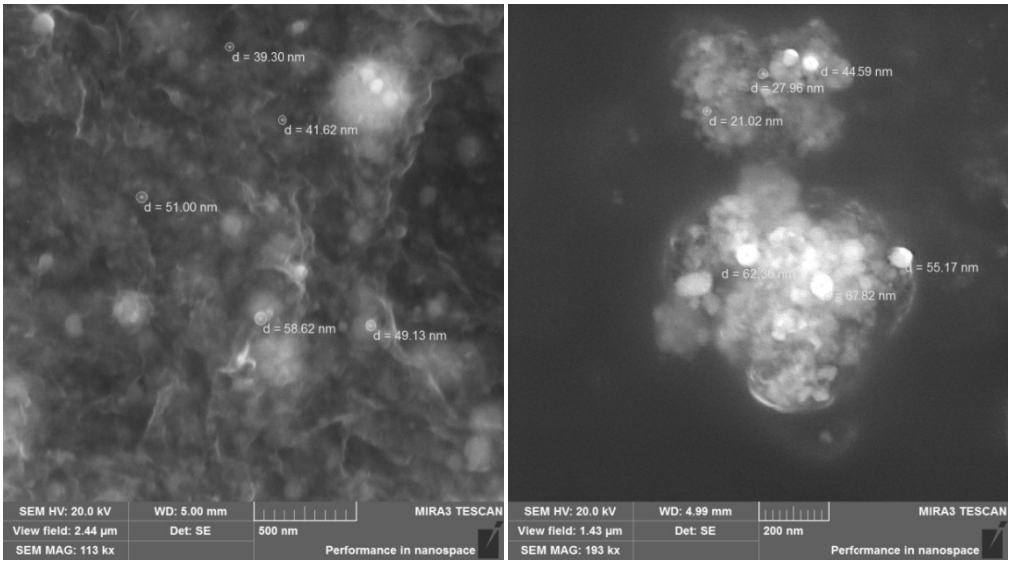
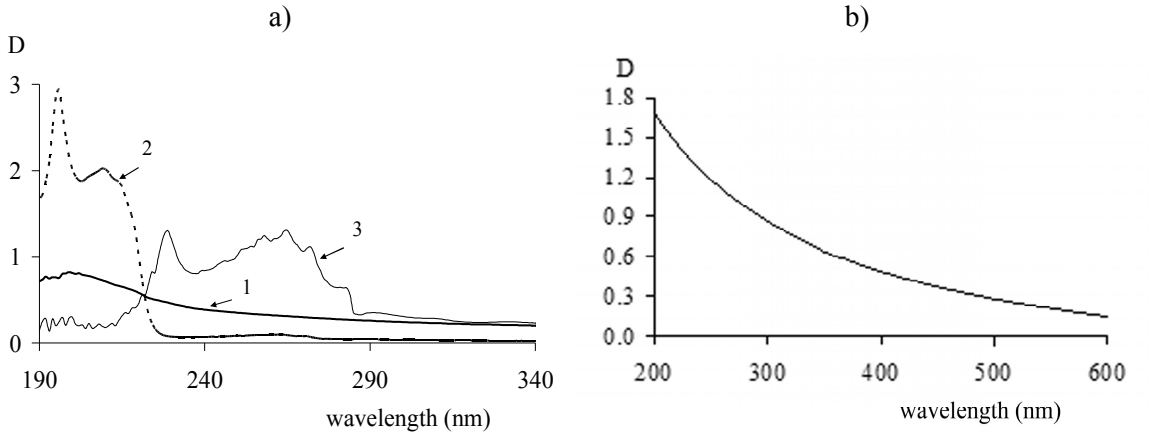


Figure 3. Microscopic images of aluminum nanoparticles in the water (a) and in the chlorobenzene (b)

Absorption spectra of NPs solutions were measured. Absorption spectra of aluminum NPs obtained in various solvents was shown in Figure 4. The spectrum of Al_2O_3 NPs with the average size of 125 nm in the water was also shown in Figure 4b. Main characteristics of absorption spectra are given in Table 2. In the case of Al NPs in the water, it was used 3-fold dilution for the measurement of the absorption spectrum.

Absorption spectra for NPs in the water and the ethanol have a main maximum in the range 195-200 nm. These data are good agreement with spectral data obtained in other works [16, 17]. In the water, the absorption spectrum contains additional bands with maxima at 209, 263 nm. The absorption spectrum has peaks at 229, 264 nm for Al NPs in the chlorobenzene and doesn't have the maximum at 195-200 nm. The solution becomes yellow during the ablation of the aluminum target in the chlorobenzene. The ablation doesn't result in a color change of the solution for the water or the ethanol. Metal NPs are formed with a carbon shell at the ablation of metals in organic solvents [18]. Therefore, the formation of Al particles with a carbon shell is possible in the chlorobenzene.



1 — ethanol; 2 — water; 3 — chlorobenzene

Figure 4. Absorption spectra of Al NPs in various solvents (a) and Al_2O_3 nanoparticles in the water (b)

T a b l e 2

The influence of solvents on characteristics of absorption spectra of Al nanoparticles obtained by the laser ablation

Sample	Medium	λ_{abs}^{max}, nm	$\lambda_{1/2}$, nm
1	Ethanol	199	114
2	Water	196, 209, 263	34 17 40
3	Chlorobenzene	229 265	13 41

A computer simulation of extinction, absorption and scattering spectra was carried out for solutions of Al NPs. The program Mie plot V.4.4.11 was used. Mie theory [1] were used for the simulation. The algorithm of numerical calculations is described in detail in [19, 20]. The frequency dependence of the dielectric constant (ε) of Al and Al_2O_3 solid materials were used for the calculations given in [21, 22]. Extinction spectra for Al nanoparticles in the water are shown in Figure 5. Simulation results show that experimental absorption spectra of an aqueous solution of aluminum NPs (Fig. 2, curve 2) can correspond to solution NPs with a size (r) from 9 to 11 nm. However, the measurement of the size of NPs by the dynamic light scattering method shows of d=38 nm for diameter NPs in the water. Also, the distribution of NPs is the monodisperse (Fig. 2, b). Thus, results of the direct measurement of the NPs size in the water by the dynamic light scattering do not correspond to results of the analysis of absorption spectra and the simulation of extinction spectra of NPs in the water.

The formation of aluminum oxide NPs (Al_2O_3) instead of aluminum NPs is possible at the laser ablation of the aluminum target in the water. But the laser ablation of aluminum in the water [16] shows the formation of aluminum oxide (Al_2O_3) together with Al NPs. However, the measured spectrum of Al_2O_3 NPs with a size of 125 nm didn't show the presence of absorption maxima in the 200 -600 nm range (Fig. 4, b). A comparison of the obtained spectral data for Al NPs with the data on the absorption of Al_2O_3 (Fig. 4, b) and the simulation of the spectra of Al_2O_3 NPs (Fig. 5, b) showed that 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.

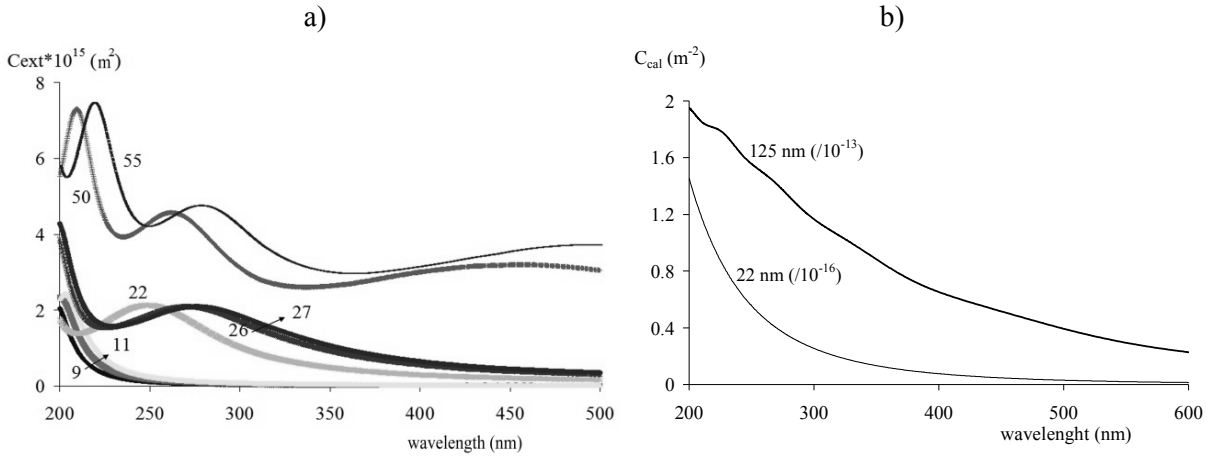


Figure 5. Extinction spectra of Al NPs with various sizes (r) in the water (a) and Al_2O_3 NPs in the water (b)

Luminescence spectra observed for synthesized NPs can be an additional factor that indicates the formation of aluminum oxide as a result of the laser ablation. Absorption spectra of the aluminum are located in the ultraviolet region. The solvent glows observed after the ultraviolet irradiation of the chlorobenzene and the ethanol. Therefore, only aqueous solutions were used to study the luminescence of nanostructures based on the aluminum. The luminescence spectrum of Al_2O_3 and Al NPs in the water is shown in Figure 6.

The comparison of spectra in figure 6 shows presence of Al_2O_3 in the solution. There are luminescence bands with peaks at 380, 403, 426, and 486 nm in the luminescence spectrum of the Al NPs solution. Luminescence bands with maxima at 425 and 486 nm are observed for the luminescence spectrum of Al_2O_3 NPs. Similar results were obtained in [16, 23]. These bands can be attributed to the luminescence of various F centers of a crystalline Al_2O_3. The correspondence between the maximum of the luminescence bands and centers or defects responsible for the appearance of these luminescence bands is given in Table 3 [23].

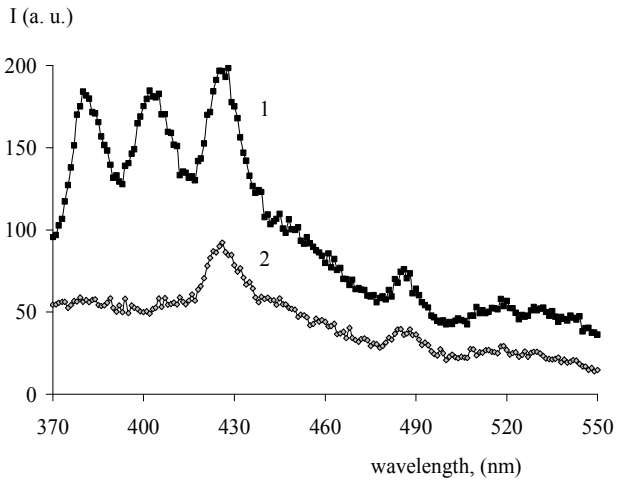


Figure 6. Luminescence spectra of Al NPs (1) and Al_2O_3 NPs (2) in an aqueous solution

Table 3

Spectral characteristics of the defective luminescence of Al-Al_2O_3 nanostructures in the water

Maximum luminescence, nm (eV)	Probable centers and defects in Al2O3
380 (3,26)	F, F_2^+
403 (3,08)	F_s
426 (2,91)	F, Al_i^+(interstitialatom)
486 (2,55)	Al-OH

Thus, the conducted studies showed that laser ablation of the aluminum in various solvents leads to the formation of Al NPs. The size of NPs depends on the properties of the solvent. Absorption and luminescence spectra of synthesized NPs are measured. The analysis of absorption and luminescence spectra of Al NPs in the water showed that laser ablation in water forms Al-Al_2O_3 nanostructures.

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Лазерлік абляция әдісімен Al-Al_2O_3 наноқұрылымдардың синтезі

Мақалада лазерлі абляция әдісімен алюминий нанобөлшектерінің (НБ) синтезі келтірілген. Суды, этил спиртін және хлорбензолды синтездеу үшін әртүрлі еріткіштер қолданылған. Алынған НБ көлемдері мен пішіндерін өлшеу жұмыстары жүргізілді. Сәуленің динамикалық шашырау әдісін қолданып, бөлшектердің көлемі анықталды. Нанобөлшектің көлемі қолданған еріткіштің қайнау температурасына тәуелді екендігі айқындалды. Электронды-микроскопиялық суреттерден лазерлі абляция кезінде сфералы нанобөлшектердің пайда болуын көруге болады. Алюминий НБ және алюминий оксидінің жұтылу спектрі өлшенді. Сонымен қатар алюминий НБ сулы ерітіндісінің экстинкция спектрінің компьютерлік симуляциясы жүргізілді. Өлшеу және симуляция нәтижелерін

салыстыру олардың анағұрлым айырмашылықтарын айқындады. Алюминий НБ люминесценттi спектрлерiн өлшеу нәтижелері ертітіндіде алюминий оксидінің бар болуын көрсетті.

Кілт сөздер: Al нанобөлшектері, Al_2O_3 нанобөлшектері, жұтылу спектрі, люминесценция.

Д.А. Афанасьев, Н.Х. Ибраев, М.Е. Касымов

Синтез наноструктур Al-Al_2O_3 методом лазерной абляции

В работе приведены результаты синтеза наночастиц (НЧ) алюминия методом лазерной абляции. Использованы различные растворители для проведения синтеза: вода, этиловый спирт, хлорбензол. Проведено измерение размеров и формы полученных НЧ. Размер частиц определялся при использовании метода динамического рассеяния света. Установлено, что размер наночастиц зависит от температуры кипения используемого растворителя. Электронно-микроскопические снимки показывают, что в ходе лазерной абляции происходит образование сферических наночастиц. Проведено измерение спектров поглощения растворов НЧ алюминия и оксида алюминия (Al_2O_3). Также проводилась компьютерная симуляция спектров экстинкции НЧ Al и Al_2O_3 в водном растворе. В рамках теории Ми были рассчитаны спектры экстинкции наночастиц Al и Al_2O_3 разного размера в воде. Сравнение результатов измерений и симуляции показало значительное их расхождение. При ультрафиолетовом возбуждении были измерены спектры люминесценции водных растворов НЧ алюминия и оксида алюминия. Результаты измерения спектров люминесценции НЧ алюминия указывают на присутствие в растворе Al_2O_3.

Ключевые слова: наночастицы Al, наночастицы Al_2O_3, спектр поглощения, люминесценция.

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