Aluminum nanoparticles synthesis in spark discharge for ultraviolet plasmonics

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Abstract. In this paper, we demonstrate an ability to produce aerosol metal Al nanoparticles with plasmon resonance in the ultraviolet region in a spark discharge generator in pure argon atmosphere. The sizes of the obtained primary particles with metal Al core and natural oxide shell in the range from 4 to 50 nm, which were collected in agglomerates with mean size from 190 to 260 nm, were observed. Simulation extinction spectra according to Mi theory for obtained particle ensembles were calculated. It was experimentally and theoretically found that obtained nanoparticles ensembles demonstrate the broad extinction peaks with maximum below 250 nm depending on the synthesis conditions.

1. Introduction

The feature of metal particles to increase the local intensity of electromagnetic radiation has become an active research field in recent years. A plenty of studies were discussed the properties of plasmon structures of noble metals - Au and Ag nanoparticles characterized by plasmon resonance in the visible range. After theoretical justification [1] of using Al as promising material for creating plasmon structures that enhance luminescence in the ultraviolet region of the spectrum, interest in the synthesis of nanoparticles and nanostructures based on nanoscale aluminum has greatly increased [2]. In addition, Al is perspective material because it has the following advantages: demonstration of surface plasmon resonance in the ultraviolet (UV) region, low cost, abundant in nature and high stability due to the presence of the shell natural oxide. A perspective applications of Al nanoparticle-based plasmon nanostructures in chemical and biological sensors [3], silicon solar cells [4] and organic dyes [5] and plasmon lasers [6] has been shown. Thus, the research of new methods for synthesis of Al nanoparticles and the study of its dimensional and optical properties is an actual task for science and technology.

2. Methods and materials

To obtain nanoparticles, the spark discharge method is used. It is a cheap and an energy efficient method [7, 8]. The method allows to synthesize metal and semiconductor nanoparticles [9] with a core-shell structure and a crystalline structure of the core of nanoparticles. The synthesized particles are collected in agglomerates with a primary nanoparticle size of about 10 nm. The size of the obtained particles can be changed directly in the gas path [10]. To change the particle size, a tube furnace is used, which allows to sinter particles at temperatures below the material melting
temperature [11]. Moreover, this method can be used as a nanoparticles source in aerosol jet printing [12-14] to form plasmon nanostructures for optoelectronic applications.

The spark discharge process [15] was carried out with the following conditions: pulse repetition rate of 500 Hz at a voltage of 1.5 kV in an argon flow 2 L/min. Argon working gas of purity 6.0 at a pressure of 1,3 atm and two D16 grade aluminum alloy electrodes were used. Nanoparticles aerosol passed through a custom-build tube furnace with the temperature from 25 to 700 °C [16] and were collected on a nanofiber filter AFA-RMB-20 and TEM copper grid with carbon film. For the formation of a thin oxide film on the nanoparticles surface, which prevents their oxidation in air, an argon atmosphere of 4.8 was created in the gas path, in which the nanoparticles remained for 1 hour.

The microscopy studies were carried out on transmission electron microscopy (TEM) Jeol JEM 2100 (200 kV) with energy dispersive X-ray spectrometer X-MAXN OXFORD Instruments. The UV-vis-NIR spectra of nanoparticles dispersions in a quartz cuvette were obtained using JASCO V–770 spectrophotometer. The agglomerates size distribution in the flow was measured using a TSI SMPS 3936 Aerosol spectrometer.

3. Results and Discussions
A change in the median diameter of the agglomerates with a sintering temperature, measured in gas flow by the aerosol spectrometer, shows only a small decrease in size below 400 °C from ~ 260 to ~ 190 nm (Figure 1a). According to TEM images primary particles, synthesized in spark discharge, form large agglomerates. The average primary particle size in six samples, synthesized at 25, 260, 400, 500, 600 and 700 °C, varies from 13 to 18 nm with lognormal particle size distribution. Most of the particles in the samples, prepared at low temperatures below 400 °C, are characterized by sizes in the range from 5 to 30 nm. For the samples, synthesized at high temperatures above 500 °C, the grows of width of particle size distribution were observed and the sizes of most primary particles varies from 5 to 60 nm. A few single particles with sizes up to 120 nm were also detected.

![Figure 1](image.png)

**Figure 1.** Particle size analysis: (a) Dependence of median particle diameter of the agglomerates on the sintering temperature; Insets: TEM image of typical particles at 25, 260 and 600 °C, (b) typical SAED pattern from agglomerate, (c) high resolution TEM image of a single nanoparticle.

Typical high resolution TEM image (Figure 1c) shows the core-shell structure of nanoparticles with a metal crystal aluminum core and amorphous shell 3 nm in thickness. Selected area electron
diffraction (SAED) patterns, collected from agglomerates prepared at different sintering temperatures (Figure 1b), includes four rings corresponded to crystal plane spacings 2.3, 2.0, 1.4 and 1.2 Å, which indicates the presence only FCC Al nanocrystals and refer to the (111), (200), (220) and (311) Al lattice planes, respectively. The typical particle size distributions of primary nanoparticles obtained at the low (25 – 400 °C) and high (500 – 700 °C) temperatures of tube furnace are presented on Figure 2.

![Figure 2](image1.png)

**Figure 2.** Particle size distributions at sintering and its approximation by lognormal functions for the samples prepared at temperatures (a) 260 and (b) 600 °C.

Simulated and experimental extinction spectra for obtained ensembles of Al nanoparticles, with denoted at Figure 2 particle size distributions and additionally dispersed in isopropanol, are presented on Figure 3. The spectra of extinction cross sections for spherical Al nanoparticles of the core-shell type with an aluminum core and dielectric Al2O3 shell, located in a dielectric medium, were calculated using the Mi theory with modification of Mi coefficients for nanoparticles with a dielectric shell [17]. The following values of refractive indices n at a wavelength of 300 nm were used in the calculations: n (Al2O3) = 1.81 [18], n (isopropanol) = 1.41 [19]. The dispersion of n (Al2O3) and n (isopropanol) was not taken into account by the calculation program; the dielectric function of Al was set in accordance with [20].

![Figure 3](image2.png)

**Figure 3.** (a) Theoretical calculation and (b) experimental extinction spectra for particles synthesized at 260 and 600 °C.

The extinction spectra calculated for nanoparticles ensembles with a log-normal size distribution obtained by TEM for aerosol Al-nanoparticles shows that the multimode structure characteristic of large nanoparticles is “masked” and, due to the wide size distribution, the extinction spectra of the
nanoparticles ensembles have one maximum at 212 and 214 nm for nanoparticles prepared at 260 and 600 °C, respectively. Whereas, pursuant to the experimental specter for 260 °C sample one broad peak at position 230 nm with long-wave shoulder were observed. For the 600 °C sample a shift of peak maximum to 244 nm and appearance of extra low-intensity peak in the blue region around 400 nm were detected. The mismatch between the peak positions in theoretical and experimental spectra is supposed to be caused by the presence of large agglomerates, which were not taken into account in the simulations.

Thus, we demonstrated that using the spark discharge method metal Al nanoparticles with core-shell structure can be produced. Independently on sintering temperature in tube furnace primary nanoparticles with average size from 13 to 18 nm formed large agglomerates, which size dropped by 25 % with increasing temperature from 25 to 700 °C. Experimental extinction spectra of obtained nanoparticles indicate the presence of plasmon resonance in the UV region below 250 nm. According comparison of simulated and experimental spectra we supposed that agglomeration process influence on the position of extinction peak and lead to its shift to red region.

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