Synthesis of gold nanoparticles by the spark discharge method for visible plasmonics

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Abstract. This work demonstrates synthesis of metal Au nanoparticles with a plasmon resonance in the visible optical region by the spark discharge method in atmosphere of argon of purity 6.0. With raising of sintering temperature from 25 to 950 ºC, the morphology of synthesized Au nanoparticles changed from agglomerates to individual particles with decreasing the median size from 270 to 90 nm according to aerosol spectrometer. While by transmission electron microscopy primary nanoparticles with a gold crystalline structure with sizes in range from 5 to 120 nm were observed. Synthesized nanoparticles ensembles had broad absorption peaks with maximum in the visible optical region with peak positions approximately at 490 nm. High temperature sintered particles had a spherical shape and an additional absorption peak at approximately 640 nm.

1. Introduction
The plasmon enhancement effect is interest for purposes such as sunlight energy conversion, catalysis, chemical sensors, cell imaging and Raman spectroscopy. In the last two decades Au nanoparticles characterized by plasmon resonance in a visible range became a subject of intense research, due to variety of optical properties related to surface plasmons, high chemical and physical stability and biocompatibility and ease process of surface functionalization with organic and biological molecules [1].

It is known that the size, shape, presence of pores, the distance between the Au particles in the array and their agglomeration play a crucial role to the position of Surface Plasmon Resonance (SPR) peak. The absorption spectra of particles depend on the thickness and chemical composition of the shell around the particle and also the refractive index of the medium. For spherical Au particles with diameter of 20 nm SPR band position changes from 510 to 590 nm with an increase in the refractive index of surrounding media from 1 to 2 [2]. Whereas for nanorods the maximum of absorption peak is located at yellow-red region with wavelength more than 600 nm and can shift to the near-IR region up to 1000 nm with an increase in aspect ratio (length to diameter) from 2 to 6 [3]. Likewise the redshift of the absorption peak during agglomeration are applied in colorimetric sensing based on plasmon coupling [4].

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Au nanoparticles are successfully applied in Surface-Enhanced Raman Scattering imaging techniques because it simultaneously ensures fingerprint recognition of chemical species and high detection sensitivity, down to single-molecule level. These facts have tend to application of SERS in many fields as electronics, analytical and bio-chemistry, nanomedicine and cultural heritage [5,6]. The important factors that significantly affect the optical properties of plasmonic structures and the Raman enhancement factor are the aggregation degree and particle shape [6]. In the research [7] the SERS effect of rhodamine was observed at excitation at a wavelength of 785 nm near Au nanoparticles about 150 nm and was found that the enhancement factor systematically increases in order: spherical particles, aggregates of spherical particles, triangular nanoparticles and particles in the form of stars. All of this makes the investigation of new methods of the Au nanoparticles with different size, shape and morphology synthesis urgent.

Different chemical and physical methods are used to produce Au nanoparticles, the main synthetic routes based on reduction of chlorauric acid using sodium citrate or sodium borohydrate with various additional ligand exchange modifications [8]. The physical methods include laser ablation in liquid [9], ionizing and microwave radiation and spark discharge synthesis [10,11]. The spark discharge synthesis allows to synthesize spherical nanoparticles [12] with variable morphology and optical parameters [13], which can be used for the production of microstructures by aerosol jet printing [14]. Aggregates of Au nanoparticles and their reshaped under thermal treatment in tube furnace were obtained by different groups, but optical properties of produced nanoparticles were not discussed [15].

Hence the goal of this research is to produce Au particles in the spark discharge and investigate the influence of temperature treatment on the shape, morphology, size and optical properties of obtained aerosol nanoparticles.

2. Methods and Materials

Custom-built spark discharge generator (SDG), the similar scheme of the setup was presented in [16], was used with the following conditions: capacitor 107 nF, discharge voltage 0.6 kV and pulse repetition rate 0.5 kHz. Nanoparticles synthesis was carried out in the discharge chamber that was made from glass (Duran glass, KF50, Millab) in which two hollow Au electrodes (mass fraction of gold is 0.9999) were opposite mounted. Gas path that was made of stainless steel vacuum fittings KF was pumped to a pressure of 0.4 torr before gas supplying. Further argon of purity 6.0 (oxygen volume fraction lesser than 3·10⁻⁶) at a pressure of 1.5 bar and a flow rate of 1 L/min was fed to the discharge chamber through the hollow electrode, that ensured effective nanoparticles removing from the discharge gap. Synthesized nanoparticles has been passed for 2 seconds through a custom-built tube furnace at temperatures from 25 to 950 °C [17] and were collected on TEM copper grid with a carbon film and a cellulose filter.

The particle size distribution in the flow was measured by using a TSI SMPS 3936 Aerosol spectrometer. These measurements give an equivalent size of the primary nanoparticles agglomerates. The images of primary nanoparticles, their size and crystal structure was received by microscopy studies on transmission electron microscope (TEM) Jeol JEM 2100 (200 kV) with energy dispersive X-ray spectrometer X-MAXN OXFORD Instruments. The UV-vis-NIR spectra of nanoparticles on a cellulose filter were obtained using JASCO V–770 spectrophotometer.

3. Results and Discussion

TEM and electron diffraction images show that the particles have crystalline structure, the average primary particle size in ten samples synthesized at 25, 100, 150, 180, 210, 350, 500, 650, 800 and 950 °C varies from 5 to 120 nm. With an increase in sintering temperature (from 210 °C) the median agglomerates diameter decreases more than twice, that means the sintering of nanoparticles occurs (Figure 1a). However, according to TEM images complete sintering with the formation of spherical particles occurs at temperatures above 950 °C. All obtained nanoparticles nevertheless of its morphology have only face-centered gold cubic crystal structure (Figure 1c). The average diameter of primary nanoparticles is estimated to be 8.9 ± 4.6 nm (Figure 1d), while after sintering at 950 °C the
agglomerates reshaped into individual near-spherical nanoparticles with mean size of 56 ± 23 nm and a broad size distribution (Figure 1e).

Figure 1. (a) Dependence of median agglomerates diameter of the Au nanoparticles on the sintering temperature; Insets: TEM image of typical Au particles at 25, 650 and 950 °C. (b) High-resolution TEM image of nanoparticles in aggregate, sintered at 25 °C, (c) Selected Area Diffraction Pattern from Au nanoparticles aggregate, produced in spark discharge without thermal treatment and histograms of the particle size distribution of primary Au nanoparticles sintered at (d) 25 and (e) 950 °C.

The measurements of the Au nanoparticles absorption spectra showed the presence of broad extinction peaks in the visible optical region with peak positions approximately at 490 nm for all sintering temperatures. There are two samples for particles sintered at 950 °C with collection time 30 and 45 minutes. The second sample has an additional extinction peak at 640 nm (Figure 2a), which can be associated with agglomeration of nanoparticles deposited on the filter due to the long collection time [1].

Figure 2. (a) Extinction spectra of synthesized Au nanoparticles sintered at 25, 650 and 950 °C, (b) simulated extinction curves according to the Mie theory for individual monodispersed Au nanoparticles in argon media with the sizes of 9 and 56 nm.
According to the Mie theory (Figure 2b) with an increase in the primary nanoparticles diameter from 9 to 56 nm there is a slight shift of the extinction peak from 503 to 510 nm, which is absent in the experimental extinction spectra. The mismatch is caused by the broad size distribution of sintered nanoparticles. In future experiments the size distribution of primary nanoparticles can be narrowed by extraction of monodisperse aerosol flow using a differential mobility column, which separates nanoparticles by their electrical mobility.

Thus, a simple synthesis of metal Au nanoparticles with plasmon resonance in the visible optical region by the spark discharge method has been shown. By changing sintering temperature from 25 to 950 °C one can vary the average size of primary nanoparticles and their agglomerates from 9 to 56 nm and from 270 to 90 nm, respectively. However, regardless of the sintering temperature, nanoparticles have a broad extinction peak of 490 nm, which caused by a broad size distribution of sintered primary nanoparticles. To vary the extinction peak, in addition to thermal treatment it is necessary to obtain nanoparticles with a narrow size distribution by separating sintered nanoparticles by size. It is possible to focus nanoparticles on substrate or collect them for production nano-inks [17], that give capacity to use this method as a nanoparticles source in the aerosol jet printing [16].

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