Investigation of photoinduced nucleation and growth of silver nanoparticles

M Churo and L Matyushkin
Department of micro- and nanoelectronics, St. Petersburg Electrotechnical University LETI, Prof. Popov str. 5, St. Petersburg 197376, Russia
E-mail: mashachuro@yandex.ru, leva.matyushkin@gmail.com

Abstract. The influence of electromagnetic radiation with maxima wavelengths of 455, 520 and 630 nm on silver nanoparticles growth was investigated. The corresponding possibility of the plasmon resonance spectrum reconstruction in the visible range is shown. Investigations of the radiation frequency influence on the shape and size of the particles both at the stages of growth and at post-synthetic processing have been carried out. The possibility of transformation of spherical particles with a diameter of 20 nm into triangular shaped objects with a triangle edge length of 60–90 nm is shown. To study the optical characteristics of silver particles transmission spectroscopy was used as the primary diagnostic technique. The results of photometric measurements are in agreement with the data of scanning electron microscopy, which shows the transformation of the particles shape as a result of electromagnetic radiation.

1. Introduction
Nanoparticles of noble metals are of broad practical interest due to their unique optical properties [1, 2, 3, 4]. A lot of the applications are due to the plasmon resonance effect, which is the collective oscillation of the electron density relative to the crystal lattice at the resonant excitation frequency. Being excited in a nanoparticle, the oscillation is spatially limited and therefore called localized plasmon resonance. In this paper, the investigation of the plasmon resonance effect is carried out for the example of silver nanoparticles characterized by the highest intensity of plasmon resonance and high extinction coefficient [5]. Since silver in a nanostructured form efficiently interacts with external radiation of the visible range, these properties can be used to synthesize the nanoparticles themselves efficiently.

The study of electromagnetic radiation effect on the nucleation and growth of metal particles is of particular interest. With the close arrangement of ions and charged clusters relative to the surface of nanoparticles, electron density oscillations that occur under the action of external radiation can lead to the reduction of small charged particles and their adsorption on the surface of the metal nanoparticle. As a result, the new electromagnetic field distribution is obtained leading to a gradual increase in the number of particles. The particles shape can be controlled using different radiation frequencies and corresponding various geometry of electron density oscillations, which in turn leads to a rearrangement of the plasmon resonance spectrum of the ensemble of metal nanoparticles.
2. Experiment
The synthesis procedure used is based on the well-known citrate method of silver particles synthesis, but the thermal influence is replaced by photoinduced influence [6]. As sources of radiation, we used an RGB-LED strip with 14.4 W total power. The radiation from the group of light-emitting diodes corresponding to the blue light had a wavelength of the maximum of the spectrum $\lambda_{ex} = 455$ nm, green — $\lambda_{ex} = 520$ nm and red — $\lambda_{ex} = 630$ nm. Optical density spectra of colloidal solutions formed as a result of exposure to radiation were measured with PE-5400UV spectrophotometer (Ecohim LTD, Russia).

![Graph](image)

**Figure 1.** Evolution of the optical density spectrum of silver nanoparticles under exposure to radiation with $\lambda_{ex} = 455$ nm (numbers in the legend are hours of exposure). The inset shows the dependence of optical density of main maximum on the exposure time.

The mixed solution of silver nitrate and sodium citrate was irradiated with radiation at wavelength $\lambda_{ex} = 455$ nm (Fig. 1); in the legend time is given in hours. Inset in Fig. 1 represents the dependence of the optical density maxima on the time of exposure. The 430 nm peak (Fig. 1) of plasmon resonance is associated with spherical nanoparticles of small size. The appearance of the longwave tail can be a result of the formation of larger nanoparticles or non-spherical particles [7]. When the solution was exposed to radiation with $\lambda_{ex} = 370$ nm, nanoparticles also form. However, when the solution was exposed to a radiation with $\lambda_{ex} = 520$ nm and 630 nm, nanoparticle nucleation was not observed. Thus, we can assume that there is a certain threshold value of the photon energy at which the nucleation of silver nanoparticles begins to occur.

The size and shape of nanoparticles can be influenced by radiation not only during their synthesis but also after the synthesis, since free, unreacted ions and silver clusters remain in the solution. For a long time, under the influence of electromagnetic radiation, nanoparticles grow in solution, while silver ions remain in it. The wavelength of external radiation determines the shape and size of the nanoparticles obtained. Synthesis of initial particles of 20 nm in diameter monodisperse silver nanoparticles was produced by citrate-ascorbic acid procedure [8].
Figure 2. Evolution of the optical density spectrum of silver particles with long-term effects of radiation with $\lambda_{\text{ex}} = 455$ nm. The inset shows the dependence of optical density of maxima on the exposure time.

Figure 3. Evolution of the optical density spectrum of silver particles with long-term effects of radiation with $\lambda_{\text{ex}} = 520$ nm (numbers in the legend are hours of exposure). The inset shows the dependence of optical density of maxima on the exposure time.
When using electromagnetic radiation with a wavelength of 455 nm, the photoinduced synthesis lasted for six days until all the silver ions reacted in the solution. On the optical density spectrum (Fig. 2) during the first day, the first peak (1 in Fig. 2) shifts toward higher frequencies, which may be due to the etching of nanoparticles surface by chlorine ions. At the same time, an additional peak (2 in Fig. 2) of plasmon resonance appears at a lower frequency, probably due to the appearance of larger spherical nanoparticles or with a change in the shape of the particles. And the first peak almost completely disappears. The dependence of the optical density on the time of exposure to radiation has a similar character for both peaks. The tuning of the plasmon resonance spectrum mainly occurs during the first 20 hours and completely stops after three days.

When silver nanoparticles solution was exposed to radiation with $\lambda_{ex} = 520$ nm, the reconstruction of the plasmon resonance spectrum is observed. The result is in Fig. 3. As with exposure to $\lambda_{ex} = 455$ nm radiation, the second peak (2 in Fig. 3) appears, but it corresponds to the longer wavelength. The dependence of the optical density on time also has an exponential character.

![Figure 4](image)

**Figure 4.** Evolution of the optical density spectrum of silver particles with long-term effects of radiation with $\lambda_{ex} = 630$ nm (numbers in the legend are hours of exposure). The inset shows the dependence of optical density of maxima on the exposure time.

The appearance of two additional longwave weak broad peaks (2, 3 in Fig. 4) is noticeable on the optical density spectrum under long-term exposure to radiation from $\lambda_{ex} = 630$ nm as a result of photoinduced synthesis. This effect is due to the appearance of several plasmonic modes, i.e. with the change in the shape of the particles.

### 3. Results and discussion

From the optical density spectra it can be said that photoinduced synthesis in the absence of nuclei leads to the formation of mainly spherical particles, while in post-synthetics, the formation of nonspherical nanoparticles is observed. Let us study in more detail the effect of post-synthesis on the particle size and shape.
It can be concluded that the closer the wavelength to the maximum of the main plasmon resonance, the more clearly the formation of additional optical density maxima shifted to the wavelength of the excitation. On the other hand, the greater the difference in the wavelengths of the plasmon resonance and the exciting radiation, the more extended the extinction spectrum can be obtained.

Figure 5. Changing the shape of a particle under the influence of radiation (scanning electron microscopy of individual particles)

In the image of particles obtained with scanning electron microscopy (image is obtained in secondary electrons), it was determined that the spherical nanoparticles have a diameter of 25–80 nm. The formation of larger spherical particles is due to the fact that in addition to the effect of radiation, the solution also heats up because of the absorption of electromagnetic radiation. There are also non-spherical particles in solution. On the basis of the obtained results, the non-spherical particles have the form of a triangular shape with an average rib length of 70 nm. Figure 5 shows the transformation of a spherical nanoparticle into a triangular shape as a result of exposure.

4. Conclusions

As a result of work silver nanoparticles of various sizes and shapes were synthesized under the influence of electromagnetic radiation of different spectral range. The effect of radiation on the processes of growth and nucleation of silver particles was investigated. To nucleate particles, it is necessary that the radiation energy is above a threshold value that exceeds 2.4 eV.

In the post-synthetic effect of radiation, a change in the optical density spectrum is observed: the appearance of an additional peak at a frequency of a lower frequency of electromagnetic radiation. The plasmon resonance spectrum of the obtained particles varies in the visible range.

With the help of scanning electron microscopy, images of silver particles of various shapes and sizes formed during post-synthetic exposure were obtained. As a result of radiation, triangular shaped objects with a rib length of 70–90 nm are formed.

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