Synthesis of prolate gold nanoparticles for use in plasmon-enhanced overtone near-infrared spectroscopy

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Abstract. Gold nanoparticles were obtained by the method of three-stage growth from a seed solution. Scanning electron microscopy images as well as comparison of extinction spectra to the results of numerical simulations prove the formation of prolate nanoparticles. Such particles with localized plasmon resonance in the NIR region are much-needed for the plasmon-enhanced overtone spectroscopy.

1. Introduction

Near-infrared (NIR) spectroscopy is a type of vibrational spectroscopy that studies the interaction of light with matter in the wavelength range from 750 nm to 2500 nm. As a practical application of NIR spectroscopy, it is possible to conduct quantitative and qualitative analyses of organic molecules in a non-invasive and non-destructive way. This method can successfully detect substances containing functional groups such as CH, NH, SH or OH. Moreover, the spectra in the NIR region can be used to distinguish compounds from each other, since the overtones of the valence vibrations of the hydrogen atom that is part of these groups depend on which atom the hydrogen atom is bound to. NIR spectroscopy has received a new impetus due to the emergence of intensive sources and reliable radiation receivers, which have been intensively developed in recent years for applications in telecommunications based on optical fiber.

A significant limitation in the use of NIR spectroscopy is the relatively low intensity of the absorption bands of dipole vibrational transitions in this spectral region compared to those in the mid-infrared region. One of the promising ways to increase the probabilities of vibrational transitions is associated with their enhancement in the near field of metal nanoparticles with plasmon resonances. To do this, it is necessary to fulfill the resonant condition of the spectral overlap between the absorption band of the plasmon resonance and the absorption band of the overtone vibrational transitions [1,2]. Since the plasmon resonance in gold nanospheres is located in the visible range of the spectrum, to create chemical sensors that work on the basis of registering optical transitions characteristic of organic substances in the near infrared region gold nanoparticles of a different shape, such as gold nanorods, are needed.

Currently, insufficient attention is paid to the synthesis of nanoparticles with plasmon resonances in the near-infrared region of the spectrum. Most of the papers is devoted to the synthesis and study of nanoparticles with plasmon resonances at wavelengths smaller than 1000 nm. Therefore, the creation of...
such nanoparticles, whose plasmon resonance is located at wavelengths of about 1500 nm, which are characteristic of the first overtone of the valence vibrations of the hydrogen atom, is an urgent task.

The position of the plasmon resonance of a nanorod depends on the ratio of its length to its diameter, which is called the aspect ratio. Depending on the magnitude of the aspect ratio, the position of the plasmon resonance in the gold nanorods can vary from the visible wavelength range to the infrared. Therefore, the aim of this work is to select a method for the synthesis of gold nanorods, in which the peak of their absorption will fall in the near infrared range.

2. Experimental section

The method we used for the synthesis of gold nanorods was that small spherical nanoparticles were first grown, which served as a seed in the subsequent stages of synthesis, in which the length of the nanorods increased without changing their diameter [3,4]. Growth control was achieved by using HAuCl$_4$•3H$_2$O (hydrogen tetrachloroaurate (III)) and CTAB (cetyltrimethylammonium bromide).

To synthesize the gold nanorods a gold seed solution from hydrogen tetrachloroaurate, trisodium citrate, and sodium borohydride were prepared. To achieve the nanoparticles with an aspect ratio greater than 10, a three-stage method of nanoparticle growth was employed. In this case, solutions of HAuCl$_4$, CTAB, and ascorbic acid were added to three test-tubes. Further, these test-tubes were designated as "A", "B" and "C", respectively. Next, a seed solution was added to each test-tube. From the resulting solutions, 1 ml of solution A was added to solution B, and then 1 ml of solution B was added to solution C.

The purification of nanoparticles from the synthesis by-products was carried out in several stages. To begin with, 1 ml of the solution was taken from the test-tube C and centrifuged to deposit the nanoparticles on the bottom of the test-tube. The supernatant was selected and added to the sediment 500 ml of polyethylene glycol (PEG). The procedure was repeated 2-3 times.

3. Results

Figure 1 shows scanning electron microscopy (SEM) images of nanoparticles with the desired aspect ratio of 13, produced by the three-stage seeding method. Figure 1(a) clearly shows that nanoparticles of different geometries were prepared from simple spheres to nanowires of several hundred nm in length. The nanorods of interest are also present.

![Figure 1. SEM-images of purified gold nanoparticles taken from solution C after the synthesis and deposited on the silicon substrate, where (a) and (b) are the SEM images from different spots. The scale bar is 100 nm.](image)

The size and shape distribution of the prepared gold nanoparticles were determined from SEM-images using ImageJ software. Particularly, 100 nanowires, 100 nanorods, and 100 spheres were chosen to plot the histogram. The analysis of the histograms shows that the average length of the nanowires is 589 nm, the have the average length of the nanorods is 128 nm, and the average diameter of the nanospheres is 38 nm. Using these geometrical parameters, the absorption (ACS), scattering (SCS), and extinction (ECS) cross-sections of nanowires, nanorods, and nanospheres in water were numerically
calculated in the COMSOL Multiphysics software. The resulting spectra are shown in Figures 2, 3 and 4.

**Figure 2.** Absorption, scattering, and extinction cross-sections of the gold nanowire (590 × 18 nm) in the homogenous medium ($n_{\text{water}} = 1.33$).

**Figure 3.** Absorption, scattering, and extinction cross-sections of a gold nanorod (128 × 28 nm) in the homogenous medium ($n_{\text{water}} = 1.33$).

**Figure 4.** Absorption, scattering, and extinction cross-sections of the gold nanosphere (diameter of a 38 nm) in the homogenous medium ($n_{\text{water}} = 1.33$).

After the first synthesis, the nanoparticles were selected and purified from solutions B and C, and then the absorption spectra were measured using a Shimadzu UV Probe-3600 spectrophotometer. The measuring of the absorption spectra of the gold nanoparticles were done in deuterium water (D$_2$O) (Figure 5).
Figure 5. Absorption spectra of gold nanoparticles from solutions B and C.

The spectra have the pronounced plasmon resonance absorption band around 530 nm, which indicates the presence of spherical nanoparticles in solutions. It is worthy to notice, the appeared absorption band about 1700 nm, indicating the presence of the prolonged nanoparticles in the shape of nanorods, are located within the vibrational frequencies of CH and NH functional groups of many organic molecules.

4. Conclusion
The synthesized gold nanoparticles were examined using scanning electron microscopy. It turned out that the morphology of the nanoparticles is different, as there are both the desired nanorods and nanowires, as well as nanoparticles of other shapes, in particular, triangles and spheres. The average size of the obtained nanoparticles was determined. The obtained absorption spectra indicate that prolate gold nanoparticles with the plasmon absorption band in the near-infrared region have been synthesised. Thus, the results obtained make it possible to tune the plasmon resonance band, by tailoring the size and shape of the nanoparticles, for the development of label-free sensor based on surface-enhanced near-infrared absorption effect.

5. Acknowledgements
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6. References
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