Dark-field spectroscopy of plasmon resonance in metal nanoislands: effect of shape and light polarization

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Abstract. We present the experimental dark-field scattering studies and the simulation of plasmonic properties of isolated silver nanoislands. The nanoislands were fabricated on a soda-lime glass substrate using silver-sodium ion exchange, subsequent thermal poling and annealing of the processed glass substrate in hydrogen. The morphology of the nanoislands was characterized with atomic force microscopy and scanning electron microscopy; the dimensions were 100-180 nm in base and 80-160 nm in height. We measured and modeled dark-field scattering spectra of the silver hemiellipsoidal nanoparticles differing in size and shape. The SPR position varied from 450 nm to 730 nm depending on the particle shape and dimensions. Both experiments and simulation showed a red shift of the SPR for bigger nanoislands of the same shape. Losing the axial symmetry in nanoislands resulted in the resonance splitting, while their elongation led to an increase in the scattering of p-polarized light.

1. Introduction

Unique optical property of metal nanostructures that is the excitation of surface plasmon resonance (SPR) by an incident light-wave [1] is nowadays applied in nonlinear optics [2], photovoltaics [3] and surface-enhanced Raman spectroscopy (SERS) [4]. The last one is of a particular interest due to the promising opportunity of the monomolecular sensing in the case of the coincidence of the SPR frequency with an eigenfrequency of molecules under study [5,6]. Thus, governing the SPR position via control over size and shape of metal nanostructures will allow an effective light manipulation and broadening of a SERS spectral range [7,8]. This paper is dedicated to experimental studies and numerical modeling of the SPR properties of differently shaped isolated silver nanoislands. We grew

the nanoislands on an ion-exchanged soda-lime glass by carrying out a thermal poling treatment of silver-enriched glass with the profiled anodic electrode and subsequent annealing of the glass in hydrogen [9].

2. Single silver nanoislands fabrication

The technique to grow an array of isolated silver nanoislands on a glass substrate includes three consequent steps: ion exchange, thermal poling treatment and annealing in a hydrogen atmosphere [9]. According to this technique, we placed a soda-lime glass slide [10] for 20 minutes in $Ag_{0.05}Na_{0.95}NO_3$ melt heated up to 325 °C. This resulted in the enrichment of the subsurface region of the glass with silver ions. The ion-exchanged glass was subjected to thermal poling at 300 °C under applied DC voltage of 500 V. At this stage, the silver ions were buried into the bulk of the glass in the regions where the anodic surface of the glass contacted with used profiled electrode (square net of 300x300 nm^2 deepenings with the periodicity of 5 μm). After the poling for 4 minutes 30 seconds, we treated the sample in a hydrogen atmosphere at the temperature of 250 °C for 30 minutes to reduce Ag^+ ions remained subsurface after the previous step. The out-diffusion of the reduced silver resulted in the growth of silver nanoislands at the positions corresponding to the anodic electrode deepenings in the poling. To avoid a contamination/degradation of the nanoislands in the air, the surface with grown nanoislands was coated with 5 nm thick titania layer using the atomic layer deposition (ALD) technique [11,12].

3. Experiments and modeling

We used an atomic force microscope (AFM) and a scanning electron microscope (SEM) to characterize the shape and the size of the fabricated nanoislands. The scattering spectra characterizing resonant properties of individual nanoislands were measured using a confocal dark-field setup (Figure 1a). In the experiments, each nanoisland was illuminated at oblique incidence by the s- and p-polarized light from a halogen lamp focused at the sample surface with M Plan Apo 10x/0.26 objective lens. The beam waist was approximately 1 μm. Light scattered by the nanoisland was collected with an 100x/0.7 objective lens and then directed to the 1800 gr/mm grating of Horiba LabRAM™ HR UV-VIS-NIR spectrometer.

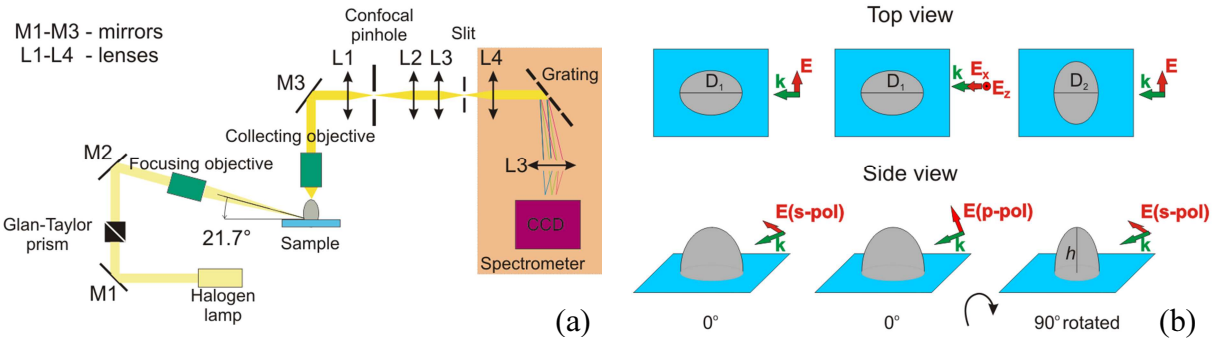

Figure 1. (a) Schematic of the dark-field spectroscopy setup. (b) Three dark-field measurement configurations: the sample in the initial position was lightened by s- (left) and p-polarized (middle) light, and after rotation on 90° it was illuminated by s-polarized light (right), the angle of incidence is 68.3°. **k** and **E** arrows denote the directions of exciting light propagation and polarization, respectively.

To analyze the influence of the incident light-wave polarization and the nanoislands' orientation (relatively to the polarization plane of the wave) on its optical response we used three configurations of the dark-field experiments. As shown in the Figure 1b, firstly the sample was lightened by 1) s- and 2) p-polarized wave, and after 90° rotation around the axis perpendicular to the glass surface, it was also illuminated by 3) s-polarized light.

The results of AFM and SEM measurements and measured scattering spectrum of a typical single silver nanoisland excited by s-polarized light-wave are shown in Figure 2. One can see that the nanoisland is shaped as a prolate hemiellipsoid with a slightly elliptical base.

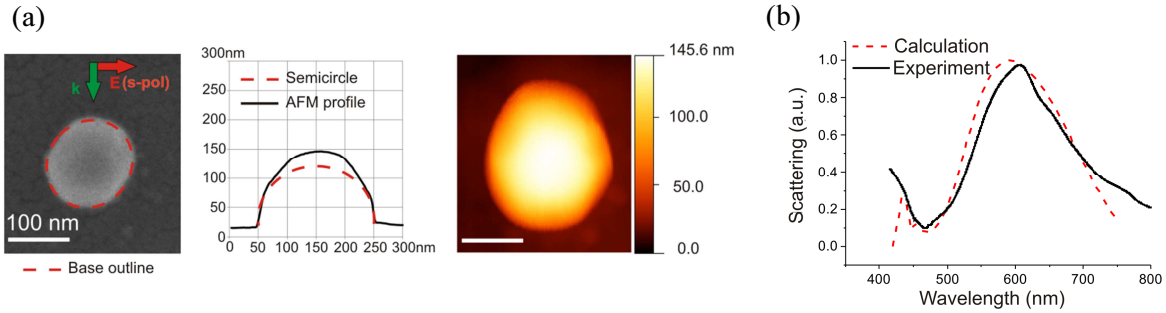

Figure 2. (a) SEM image (left), AFM profile (middle) and height map (right) of a single silver nanoisland. **k** and **E** arrows denote the directions of exciting light propagation and polarization, respectively; (b) experimental and calculated scattering spectra of this nanoisland.

The numerical model reproduced morphological features of each nanoisland; the calculations of the scattering spectra were performed in COMSOL Multiphysics environment (Radio frequency module: electromagnetic waves, frequency domain). In the simulation, the samples were excited by s- and p-polarized plane waves as shown in Figure 1b; the waves' glancing angle 21.7° corresponded to the dark-field measurements configuration (Figure 1a). The scatterer was a hemiellipsoid with silver dielectric permittivity taken from Johnson and Christy data [13], and the substrate had the typical for ion-exchanged glasses dielectric permittivity of 2.5. Figure 2b demonstrates a good agreement between numerical and experimental spectra of the chosen nanoisland.

4. Results and discussion

The SPR position in studied single nanoislands varied from 450 nm to 730 nm depending on the particle shape and dimensions which were from 100 to 180 nm in base diameter and from 80 to 160 nm in height.

In the case of SPR excitation by s-polarized wave we chose axially symmetric nanoislands with height, h, to diameter, D, ratio h/D~0.9 to estimate the influence of the nanoislands' size on the resonance position. Figure 3 shows that the increase in nanoislands' size resulted in red-shift of the SPR from 600 to 700 nm. At the same time, variations in height measured for a set of nanoislands with base diameter of ~140 nm had no significant influence on the resonant wavelength (Figure 3b). These results are in agreement with the calculated dependences presented in Figure 3. It is worth to note that the account for dielectric coating in the model should move the resonance towards longer wavelengths [14]; this explains the constant shift between the experimental and the calculated SPR positions. The lack of experimental data in Figure 3b is because of the shortage in nanoislands of the same lateral size in the grown array.

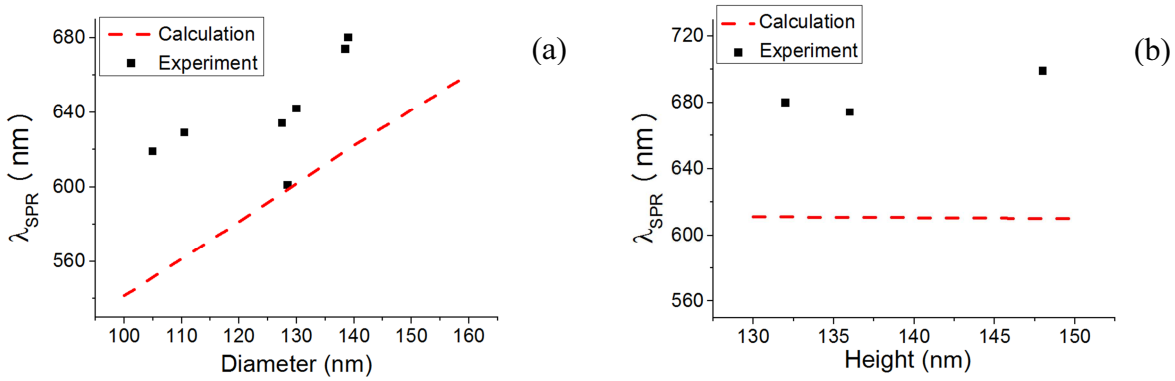

Figure 3. The SPR position versus nanoislands' (a) lateral size (the height to diameter ratio is constant ~ 0.9) and (b) height (the base diameter of the nanoislands is ~140 nm). The dielectric coating is not accounted in the calculations.

In the case of a nanoisland illumination by p-polarized wave, the external electric field has both components: along the substrate surface and normal one. Therefore, the effective dipole excited in the nanoisland should have the both components as well. Since in the geometry of the experiment the dipole excited by normal E-field component substantially does not scatter in the direction of signal collection, mostly the lateral dipole radiation is registered. Thereby, the scattering spectra of the nanoislands illuminated by p-polarized light were expected to be similar to ones in the case of s-polarization. Indeed, the overall shape of scattering spectra and SPR positions measured using s- and p-polarization of the exciting light are similar (Figure 4), and the main difference between these spectra is in intensity.

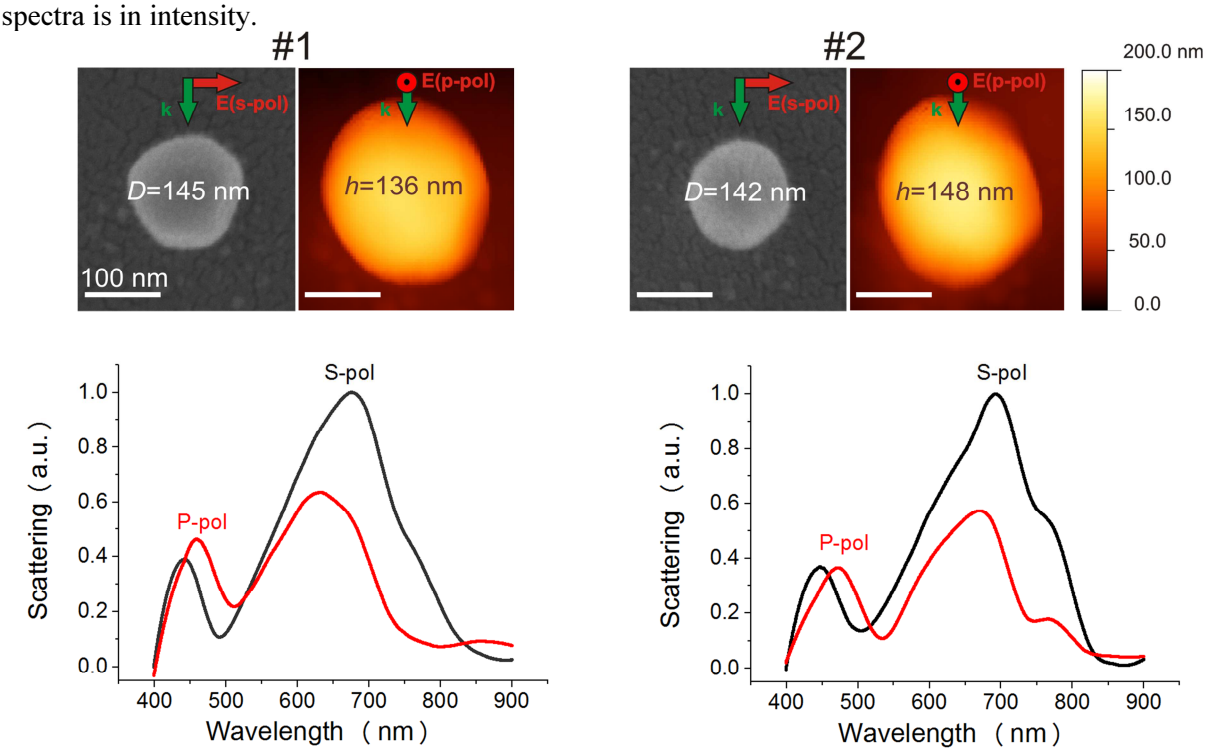

Figure 4. 1st row: SEM (left) and AFM (right) images of single silver nanoislands. **k** and **E** arrows denote the directions of the exciting light propagation and the polarization, respectively. 2nd row: experimental scattering spectra of these nanoislands excited by s- and p-polarized light.

We chose several nanoislands with different eccentricity (Figure 5) to study the influence of the shape in the case of elliptic-base (non-axisymmetric) nanoislands on their spectral characteristics. Even a minor ellipticity of a nanoisland base (nanoisland #1) results in a shift of the SPR position. Pronounced ellipticity affects the shape of scattering spectra, which also depends on the polarization of the incident light-wave (nanoislands #2,3). Figure 5 shows that the spectra corresponding to the excitation by s-polarized wave have a side peak. The 90 degrees rotation of the nanoisland in the lateral plane leads to a redistribution of intensity between this and the main peak. We suppose that two dipoles are excited along minor and major axis of the elliptic cross-section base; that results in appearance of two plasmon oscillation modes with different resonant wavelengths.

Notably, measured resonance positions in scattering spectra of nanoislands lightened by p-polarized wave (Figure 5, 2nd row) almost coincide with ones for 90 degrees rotated nanoislands excited by s-polarized light (Figure 1b). Calculated field distributions (Figure 5, 3rd row) evidence that the effective dipole is excited mainly in the lateral plane of a nanoisland by both polarizations of incident light. This explains previously mentioned coincidence of the spectra measured using s- and p-polarized light-wave. We believe that the appearance of an abnormally large lateral dipole component along the wave propagation direction in the case of p-polarized incident wave is caused by two factors: the wave phase retardation and the high vertical asymmetry of the system substrate-nanoisland. Performed simulation predicts that an elongation of a nanoisland in vertical direction, $h \geq D$, rotates the dipole around the axis lying in the plane of the glass surface. This also predicts an increase in the intensity of the dipolar radiation by elongated nanoislands. We observed this increase in the scattering of p-polarized light by a prolate (strongly elongated) nanoisland (Figure 5, nanoisland #3).

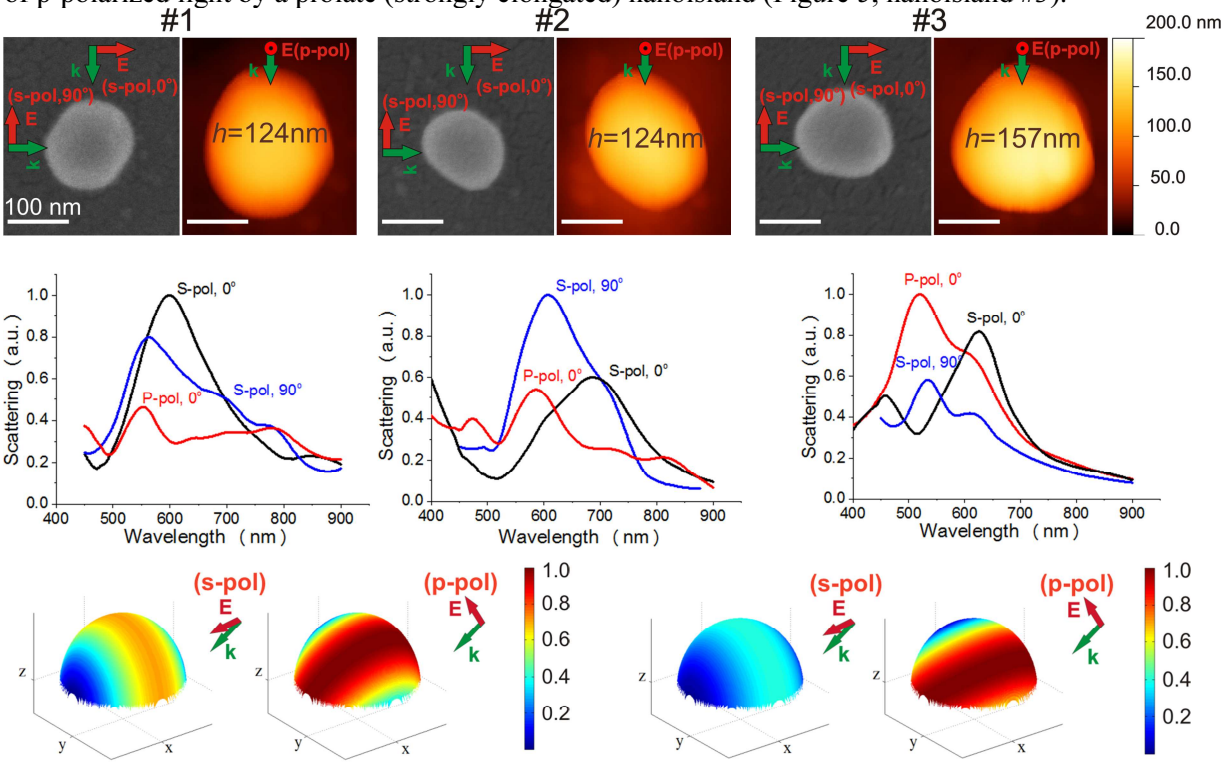

Figure 5. 1st row: SEM (left) and AFM (right) images of three nanoislands with different ratio, l, of major to minor axis of base diameter (#1: l = 1.1, #2: l =1.2, #3: l =1.2) and height, h (#1: h=124 nm, #2: h = 124 nm, #3: h = 157 nm); 2nd row: dark-field scattering spectra of the nanoislands; 3rd row: calculated radiation pattern of two different nanoislands. Modeled nanoislands are axisymmetric with the diameter D = 150 nm and the height h = 120 nm (left) and h = 170 nm (right).

Thus in the standard geometry of scattering measurements, including Raman scattering, regardless to the polarization of the exciting light the main parameter influencing the spectral position of a nanoisland plasmon resonance is its lateral dimension.

5. Conclusions

We applied dark-field scattering spectroscopy to study plasmonic properties of isolated single silver nanoislands. An array of the nanoislands was fabricated using thermal poling of ion-exchanged glass with the profiled electrode followed by the annealing of the glass in hydrogen. The dark-field experiments have demonstrated that an increase in the size of the similarly shaped nanoislands results in linear red shift of the SPR wavelength. At the same time the SPR position did not depend on the height of the nanoislands. In the case of non-axisymmetric nanoislands the appearance of two resonances was registered. These resonances corresponded to the excitation of plasmon oscillations along two axes of the elliptic base of the nanoislands. The increase in the scattering of p-polarized light-wave by strongly prolate nanoislands was predicted in the performed modeling and demonstrated in our experiments.

Acknowledgements

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