Near-field mapping of three-particle plasmonic structures

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Abstract. We probe the resonance properties of complex plasmonic structures by Scanning Near-field Optical Microscopy (SNOM). Groups of three differently arranged silver nanoparticles covered with Surface-Enhanced Raman Scattering (SERS) analyte Rhodamine 6G were chosen to visualize electric field distribution nearby the nanostructures. The particles were grown on the surface of a silver-ion-exchanged glass using thermal poling and annealing of the processed glass substrate in hydrogen atmosphere. The morphology of the nanoparticles and their arrangement in the groups were characterized with Atomic Force Microscopy (AFM). The near-field SERS maps superimposed on the AFM scans of the studied groups of nanoparticles visualize the Raman hotspots with 100 nm resolution.

1. Introduction
In recent years, silver and gold nanoparticles (NPs) are of great interest for engineers and scientists because of physicochemical and plasmonic properties of such NPs [1, 2]. These Ag and Au NPs are especially promising for biological and chemical sensing [3], photochemistry [4] and nanomedicine [5]. A widely used sensing strategy relies on the Surface-Enhanced Raman Scattering (SERS) mechanism [6]. The phenomenon occurs because of high local electric field (E-field) enhancement provided for both incident and scattered lightwaves by plasmons excited in the NPs. Because of good confinements of the plasmons, the regions of the highest enhancement (so called hotspots) are placed nearby the NPs. Thus, SERS signal from a molecule depends on its positioning relatively to a hotspot [7]. In this regard, spatial distribution of hotspots in ensembles of metal NPs, which strongly depends on shapes and arrangement of the NPs, is critical. In a simple case of one- or two-particle system E-field distribution nearby the nanoparticles of a known shape can be easily computed [8, 9], while a complex plasmonic structures could become an issue. In this case, visualizing hotspots using a near-field (NF) mapping is of interest. Here, we present results of NF characterization of silver nanoisland triplets grown on a glass substrate.

2. Experimental
2.1. Fabrication of plasmonic structures
To fabricate the plasmonic structures we used the electric-field induced patterning technique [10], which allows growing 2D array of groups consisted of two or more silver nanoislands. According to this technique, we immersed a soda-lime glass slides [11] in AgNO₃/NaNO₃ melt containing 5 wt.% of silver nitrate and heated up to 325 °C. After 20 minutes of the processing silver ions were supposed to replace sodium ions in the subsurface region of the glass [12], and one of the ion-exchanged slides was subjected to 1 min thermal poling at 300 °C under DC voltage of 500 V. In the poling, we used a profiled anodic electrode patterned with the square net of 300x300 nm² hollows with the periodicity of 0.5 μm. We did not pole another slide, which was aimed at the formation of silver nanoisland film.
Then both prepared samples passed the last step that was annealing in hydrogen (300 °C, 10 min). In the annealing, silver ions deepened under the poled regions of the glass surface could not reach the surface of the glass contrary to the unpoled regions (correspond to the hollows in the electrode) of this slide and the unpoled glass sample. Thus, the poling prevented silver reduction by hydrogen. This resulted in the formation of a random silver nanoisland film on the surface of the unpoled glass and groups of silver nanoislands only in the unpoled regions of the glass slide, which was poled with the patterned electrode. In this way, we fabricated 0.5 μm in period square array of silver nanoisland triplets.

2.2. Near-field mapping. Micro-Raman measurements

The nanoislands were covered with a dye Rhodamine 6G (R6G) to use SERS for E-field distribution visualization. The drop of 10 μl aqueous solution of R6G in the concentration of 10⁻³ M was dried on the sample surface in the ambient condition with ~ 5 mm diameter of the spot remaining on the substrate.

The SERS near-field mapping was performed via the cantilever-based SNOM setup NTEGRA Spectra (NT-MDT) equipped with linear polarized 532 nm Nd:YAG laser. The aperture of the hollow-pyramid cantilever (SNOM_NC) was equal to 100 nm. The tapping mode of the measurements was used to keep the distance between the cantilever and the sample surface (~10 nm) and to collect SERS spectra from each point of 500 nm x 500 nm scan area with 100 nm step (see figure 1). The incident and the scattered light beams passed through the cantilever aperture were focused/collected by 100x/0.5 Mitutoyo objective. Acquisition time varied from 20 to 60 s/point depending on the laser intensity which was kept in the range 2–4 kW/cm² to avoid R6G degradation. Data analysis was performed using the image analysis Nova software (NT-MDT).

![Figure 1](image_url)

**Figure 1.** (a) Schematic of cantilever-based SNOM setup NTEGRA Spectra (NT-MDT) and (b) methodology of near-field SERS mapping, from left to right: deposition of 10 μl aqueous solution of R6G in the concentration of 10⁻³ M on the substrate; excitation of silver nanoislands with 532 nm laser and collection of Raman signal through 100 nm aperture SNOM cantilever; moving the cantilever with 100 nm step over the 500 nm x 500 nm scan area.

Additionally to the NF cantilever, the setup supported conventional atomic force microscopy (AFM) probe. This allowed us characterizing morphology and arrangement of the prepared nanostructures using AFM with a fine tip (R < 10 nm).

The cantilever could also be excluded from the optical path. In this case, the scattered light was directly collected by the objective and the confocal micro-Raman setup was realized. Corresponding
far-field (FF) SERS spectra were obtained at the same acquisition time and laser power density as NF ones. In calculating the laser power density, we accounted for the laser output intensity and the excitation area that was the beam waist in FF geometry (~0.8 µm²) and aperture size (~0.008 µm²) in NF geometry.

3. Results and discussion
The analysis of AFM images reveals that the lateral size and height of the nanoislands in triplets were within 60–200 nm and 20–80 nm range, respectively. The interparticle gap varied from 10 to 100 nm. The diameter of grainy silver islands of the nanoisland film falls in the range of tens of nanometers while their height was 10–40 nm.

We probed the nanoisland film and the array of silver nanoisland triplets by micro-Raman spectroscopy to verify their capability to enhance Raman scattering. In FF geometry, we were able to register SERS spectrum of R6G dye from the nanoisland film only. The reason is averaging of signal from an individual group over the large signal collection area. In micro-Raman geometry the excitation/collection area was about 1.0 µm in diameter while the enhanced signal was generated nearby individual triplets (~300 nm in size) separated by 0.5 µm. Thus, at best only 4 groups from the whole array would fall into the collection area whereas hundreds of nanoislands at the nanoisland film. However, we obtained NF SERS spectrum from the three-particle system by positioning the SNOM cantilever in the proper region. Figure 2 shows measured FF and NF SERS spectra of R6G molecules.

In figure 2(left) one can see that the NF SERS spectrum shows a lower signal-to-noise ratio compared to the FF one. We smoothed both spectra by Savitzky–Golay filter (15 point smoothing window radius and the second polynomial order [13]) and superimposed FF and NF spectra for the comparison. Overall the NF R6G spectrum is similar to the FF R6G spectrum with respect to band positions, however, the doublets asterisked in figure 2(right) are better pronounced in the NF spectrum.

![Figure 2. Far-field SERS spectrum from R6G deposited on the silver nanoisland film (upper left) acquired at laser power density of 4 kW/cm², 20 s exposition, 1.0 µm beam waist diameter. Near-field SERS spectrum from R6G deposited on the silver nanoisland triplets (lower left) acquired at laser power density of 4 kW/cm², 20 s exposition, 0.1 µm aperture. Superimposed FF and NF SERS spectra (right), differences in the spectra are asterisked. Inset: AFM images of the nanoisland film (up) and the three-particle system (right) with tagged signal excitation/collection region.](image-url)
The relation of the Raman enhancement with the nanoislands morphology and arrangement in the nanoisland triplets is illustrated in figure 3a-d. The NF SERS maps were superimposed on the AFM images of the studied nanostructures. The color indicates detected intensity of the R6G Raman scattering intensity at 1360 cm\(^{-1}\): dark blue is the minimal intensity and bright red is a maximal one. In figure 3a one can see that the maximum enhancement of R6G Raman scattering corresponds to the gap between two bigger nanoparticles. Slight rotation of the group relative to the direction of external E-field corresponds to the rotation of the SERS intensity map (maximal signal area). The absence of a hotspot in the gap between the nanoparticles in the map of similarly arranged group (black arrow in figure 3b), is, most probably, because of the cantilever resolution and the scan step. In the cases of far-separated particles (figure 3c) and particles aligned across the incident lightwave polarization vector (figure 3d) the NF SERS maps are, as expected, mainly uniform and do not show hotspots.

**Figure 3(a-d).** The near-field SERS maps superimposed onto AFM images (ringed with dashed lines) of the nanoisland triplets with differently arranged particles. E arrow denotes the polarization of the incident light. SERS spectra from R6G deposited on the nanoisland triplets acquired at (a) laser power of 4 kW/cm\(^2\), 20 s exposition; (b) 2.5 kW/cm\(^2\), 60 s; (c) 2.5 kW/cm\(^2\), 60 s; (d) 2 kW/cm\(^2\), 60 s. Color bars indicate Raman scattering intensity at 1360 cm\(^{-1}\).

4. Conclusions
We applied near-field optical microscopy to study resonance properties of the triplets with differently arranged silver nanoparticles. The nanoislands were grown via self-assembly of out-diffused silver atoms on a glass substrate patterned with thermal poling, and covered with SERS analyte R6G to visualize electric field distribution nearby the nanostructures. The near-field SERS spectrum included the main R6G bands at 620 cm\(^{-1}\), 1360 cm\(^{-1}\) and 1650 cm\(^{-1}\), and was similar to the far-field one.
collected from the silver nanoisland film. We have obtained near-field SERS maps with 100 nm resolution and demonstrated that spatial variations of Raman signal are in a strong dependence on nanoparticles morphology and arrangement.

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