



## Full Length Article

## Raman enhancement by individual silver hemispheroids



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## ABSTRACT

A study of Raman scattering enhancement by single hemispheroidal silver nanoislands grown on a glass surface via out-diffusion technique combined with thermal poling of the glass is presented. It was demonstrated in the experiments and confirmed by numerical modeling that maximal enhancement of Raman signal occurs when the diameter of a silver nanoisland fell between 90 and 115 nm, and the thickness of the Rhodamine 6G dye analyte layer was  $\sim 3$  nm. In this case the surface plasmon resonance (SPR) in the silver hemispheroid corresponded to the wavelength of the laser used to excite Raman scattering, 532 nm, and maximal enhancement by an single hemispheroidal nanoisland,  $\sim 5 \times 10^7$ , was close to one provided by a typical silver nanoisland film. Varying lateral diameter of the silver hemispheroid allowed us shifting the SPR wavelength and enhancing particular lines in R6G Raman spectra.

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## 1. Introduction

About two decades ago the advance in the study of plasmonic properties of single gold and silver nanoparticles had opened a way of developing nanoscale chemical and biological sensors [1,2] and probing of single molecules [3–6]. These applications became possible due to the giant enhancement of Raman scattering signal conditioned by the appearance of high local electric field in the vicinity of the nanoparticles under the excitation of localized surface plasmon resonance (SPR). The efforts aimed at establishing relations between the size/shape of nanoparticles, the spectral position of the SPR and Raman enhancement allowed finding these for single Au nanospheres, nanoshells, and nanosphere and nanoshell dimers [7], for rectangular nanoparticles of different size [8]. It is worth to note that the majority of the results was obtained for colloidal [9,10] and formed by lithographic techniques [11,12] nanoparticles. However, in many cases metal nanoparticles are formed on solid substrates using other techniques, like ones based on their formation from deposited metallic films [13–15] and out-diffusion of metallic particles from the glass substrate [16,17]. Both techniques can result in hemispheroidically shaped nanoparticles. In our recent paper we have presented the relations of shape

and size with resonant properties of hemispheroidal nanoparticles grown on the surface of a silver-sodium ion exchanged soda-lime glass slides using out-diffusion combined with thermal poling [18]. Below we discuss Raman signal enhancement by individual hemispheroidal silver nanoparticles grown with the latter technique.

## 2. Experimental

## 2.1. Sample preparation

The 2D square array of single silver nanoislands and a nanoisland film were fabricated using technique based on the silver out-diffusion described in details elsewhere [19]. Firstly, 1 mm thick microscope glass slides [20] were immersed at 325 °C for 20 min in a salt melt containing 5 wt.% of silver nitrate and 95 wt.% of sodium nitrate. The silver-sodium ion exchange resulted in the enrichment of the glass subsurface layer with silver ions [21]. Then the prepared samples were washed with water and acetone. Secondly, a patterned carbon anodic electrode was pressed to the ion-exchanged glass surface, the cathodic electrode being a nickel foil. The pattern of the anodic electrode presented a square net of 400 nm deep square holes with 200, 300 and 400 nm sides, the net being 5  $\mu$ m in period. Placing the slide with the electrodes in a furnace and applying of 500 V DC to the anode at the temperature of 300 °C (thermal poling of the glass) resulted in a shift of silver ions from the glass surface deeper into the glass bulk in the poled regions. After the

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poling for 1 min, only  $\text{Ag}^+$  ions located at the positions corresponding to the electrode holes (unpoled regions) remained just under the glass surface. Reduction of the  $\text{Ag}^+$  ions via annealing of the poled slides in hydrogen at the temperature of  $300^\circ\text{C}$  for 10 min and the out-diffusion of silver atoms resulted in the self-arrangement of single silver nanoislands on the anodic surface of the slide [22]. Single nanoislands grew at the positions corresponding to the anodic electrode holes. In parallel, the formation of a nanoisland film in the unpoled slide area took place [23].

In Raman experiments, we used Rhodamine 6G (R6G) dye in 1 mM and 0.1 mM water solution. A  $10\ \mu\text{l}$  drop of 1 mM R6G solution was placed on the surface of the glass slides with formed single nanoislands and the nanoisland film and dried in the ambient condition, with the diameter of the spot remaining on the slide surface being equal to 3–4 mm. In this case, the estimated R6G thickness was about 260 nm. The estimation was carried out under the assumption of the dense packing and uniform distribution of the dye molecules, wherein a single R6G molecule occupied volume of  $\sim 0.4\ \text{nm}^3$  as reported in literature [24]. Possible coating thickness variations due to the solute redistribution within the drop during evaporation [25] are small as compared to the scale of typical nanoisland size ( $\sim 100\ \text{nm}$ ) and corresponding localization area of the SPR electric field. However, in the experiments with 0.1 mM R6G solution, which drop should dry with remaining layer of R6G  $\sim 10$  times thinner, the uniformity of R6G thickness is an important issue. In these experiments, we used  $5\ \mu\text{l}$  drop and then either dried it or incubated the dye molecules during 5 min with following blowing out of the remaining drop. The latter technique allows providing the homogeneous distribution of R6G without the appearance of a solid ring corresponding to the perimeter of the initial drop [26]. In case of the dried 0.1 mM R6G solution drop, estimated thickness of the remaining film should be about 10 nm. Thickness of the R6G layer determined with the atomic force microscope (AFM) Veeco Dimension 3100 proved to coincide with this estimation, however the blowing out of the 0.1 mM drop resulted in only 3 nm thick remained R6G layer. This indicates that only about 30% of R6G molecules were incubated during 5 min while other 70% were removed together with the remaining water.

## 2.2. Morphology of the nanoislands

For Raman study of the single nanostructures we fabricated several slides with differently formed nanoislands and the random nanoisland film. The shape and size of the grown structures were characterized with the AFM using fine ( $R < 10\ \text{nm}$ ) tip and the scanning electron microscope (SEM) LEO 1550 Gemini. Diameter and height of the nanoislands were within 70–150 nm and 50–200 nm range, respectively. Thus, the general shape of studied nanoislands was a prolate hemispheroid with the ratio of its height to its base diameter equal to  $\sim 0.7$ . The lateral size of randomly distributed nanoislands in the nanoisland film grown on the unpoled region of the glass slide fell in the range of tens of nanometers while their height was 50–80 nm.

## 2.3. Simulation of plasmonic properties

We simulated plasmonic features of silver hemispheroids covered with R6G layer of different thickness and excited by the light wave directed normally to the substrate surface (*s*-polarization). In the optical extinction of relatively big (larger than  $\sim 50\ \text{nm}$ ) noble-metal nanoparticles the light scattering prevails over absorption [27], and the amount of conduction electrons involved in collective oscillations defines the peculiarities of the scattering spectra corresponding to the modes of surface plasmon resonance (SPR). We reproduced morphological features of all characterized nanoislands in a numerical model and calculated the corresponding scattering

spectra in COMSOL Multiphysics® environment (Radio frequency module: electromagnetic waves, frequency domain). In the simulation, the hemispheroidal scatterer with dielectric permittivity of silver [28] was placed on a semi-infinite substrate with dielectric permittivity  $\epsilon_s = 2.5$  (the ion-exchanged glass [29]). The position of the SPR in nanoparticles strongly depends on the refractive index and thickness of the cover, and we considered the both bare scatterers and ones covered with the R6G analyte layer of different thickness. In the simulation, we calculated the SPR wavelengths of the characterized nanostructures and corresponding electric field distributions. We also accounted for the dimerization of R6G appearing at concentration  $\geq 1\ \text{mM}$  [30] and refractive indices of formed R6G monomer, H- and J-type dimers [31]. Since the mole fraction of R6G molecules in the both dimer states in 1 mM water solution is  $\sim 60\%$  [32] we estimated effective refractive index of the cover as 1.32 [31]. However, 0.1 mM water solution of R6G contains only  $\sim 20\%$  of dimers [32] and refractive index of the cover in this case is close to the index of the R6G monomer that is 1.23.

## 2.4. Raman spectra

For the measurements of Raman spectra we used confocal Raman imaging microscope WITec ALPHA 300 R equipped with a frequency-doubled continuous-wave Nd:YAG laser (532 nm) with output power up to 45 mW. R6G was excited by linear *s*-polarized laser light focused on the sample surface with 100x/0.9 microscope objective. The beam waist was  $\sim 250\ \text{nm}$ , which allowed mapping surface enhanced Raman scattering (SERS) and collecting SERS R6G signal from 5- $\mu\text{m}$ -spaced single nanoislands. Integration time for each point on the Raman maps was 0.1 s. The Raman spectra were collected from the layers of R6G molecules remained after drying the drop of 1 mM R6G water solution and after blowing out the drop of 0.1 mM R6G water solution.

## 3. Results and discussion

AFM and Raman signal intensity at  $1354\ \text{cm}^{-1}$  maps of the same region of the sample surface and typical SEM and AFM images of prepared metal nanostructures are shown in Fig. 1. Comparison of the AFM and Raman maps shows that the Raman signal is visible only in the areas of the nanoisland film and single nanoislands.

Fig. 2 illustrates R6G Raman signal enhanced by a single nanoisland (left) and the nanoisland film (right). The Raman spectrum obtained from the nanoislands for both concentrations of the R6G water solution comprises peaks with wavenumbers corresponding to characteristic Raman lines of the dye [33]. The absence of measurable Raman signal from R6G deposited on the surface of the virgin glass between the nanoislands did not allow the evaluation of the signal enhancement using standard procedure [34]. To evaluate the enhancement, we compared signal acquired at  $1360\ \text{cm}^{-1}$  from single nanoislands,  $I_{\text{island}}$ , with the signal from the random nanoisland film,  $I_{\text{film}}$ , the enhancement of which is comparable with one reported [35,36] for similar plasmonic structures and conditions of the measurements, the reported enhancement being is as high as  $10^8$ .

The comparison resulted in  $\frac{I_{\text{film}}}{I_{\text{island}}} = 11.8$  for 0.1 mM R6G concentration. It should be noted that the contribution of the signal collected from the nanoisland film and an single nanoisland is proportional to the ratio of the enhanced signal generation area and the area of the signal collection  $S$  (as follows from the beam waist diameter shown in Fig. 1,  $S \sim 0.05\ \mu\text{m}^2$ ). For uniformly distributed signal from the nanoisland film this ratio equals to 1, while in the case of single nanoisland it is  $\sim 0.2$  only. Thus, the estimated enhancement factor for an single nanoisland is  $\sim 5 \times 10^7$ .

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