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## Effect of the thickness of plasmonic gold nanostructures on the surface enhanced Raman scattering

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**Abstract.** In this work, we studied the influence of the thickness of plasmonic nanostructures composed of gold nanoparticles on the intensity of lines in SERS spectra of methylene blue (MB), 1,2 bis(4 pyridyl)ethylene (BPE), and malachite green (MG) used as analytes. Plasmonic nanostructures were patterned on alumina substrates by dry aerosol printing with spark discharge synthesized gold nanoparticles (mean size 9.5 nm) and represented layers 3 mm × 3 mm in size with the thickness of about 0.3, 0.4, and 0.5 μm. The enhancement factor was estimated at  $5.5 \times 10^6$  for MB,  $8.0 \times 10^6$  for BPE, and  $2.1 \times 10^7$  for MG by using SERS spectra measured on nanostructures with the optimal thickness of 0.4 μm.

**Keywords:** nanoparticles, gold, spark gas-discharge, focused deposition, plasmonic nanostructures (PN), SERS

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Материалы конференции

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## Влияние толщины плазмонных наноструктур золота на поверхностно-усиленное комбинационное рассеяние света

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**Аннотация.** В данной работе исследовано влияние толщины плазмонных наноструктур, состоящих из наночастиц золота, на интенсивность линий в SERS спектрах метиленового синего (МВ), 1,2-бис(4-пиридил)этилена (ВРЕ) и малахитового зеленого (МЗ), использованных в качестве анализируемых соединений. Плазмонные наноструктуры были сформированы на подложках из оксида алюминия сухой аэрозольной печатью наночастицами золота (средний размер 9,5 нм), синтезируемыми методом искрового разряда, и представляли собой слои размером 3 мм × 3 мм, толщина которых составляла



приблизительно 0,3, 0,4 и 0,5 мкм. По результатам анализа SERS спектров, измеренных на наноструктурах с оптимальной толщиной 0,4 мкм, сделана оценка коэффициента усиления:  $5,5 \times 10^6$  для MB,  $8,0 \times 10^6$  для BPE и  $2,1 \times 10^7$  для MG.

**Ключевые слова:** наночастицы, золото, искровой газовый разряд, сфокусированное осаждение, плазмонные наноструктуры, SERS

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## Introduction

Surface Enhanced Raman Scattering (SERS) is a method for increasing the sensitivity of Raman spectroscopy, allowing the recording of spectra of low concentrations of a substance, down to individual molecules [1, 2]. SERS can be used in areas such as biochemistry and biosensors, catalysts, materials science, food additives, and pesticides [3, 4]. The method is based on the use of plasmonic nanostructures (usually silver or gold nanoparticles). Finding the analyte close to such structures makes it possible to enhance the Raman signal by orders of magnitude.

Two mechanisms are responsible for signal enhancement: electromagnetic (EM) and chemical (CE). The enhancement factor (EF) of SERS due to CE is 10–100 [5], while EM makes it possible to achieve signal enhancement with an EF of about  $10^6 - 10^8$  [5]. Noble metal nanoparticles exhibit a strong local surface plasmon resonance in the visible and near-IR ranges, which makes them applicable as plasmonic nanostructures for Raman spectroscopy.

Dry aerosol printing is one of the promising methods for the formation of plasmonic nanostructures. In this method, the synthesis of nanoparticles is performed by ablation of metal electrodes in an inert gas, allowing the use of various metals and their mixtures for the synthesis of nanoparticles, while being a relatively simple method with high chemical purity and small size of the synthesized nanoparticles. This synthesis is widely used to obtain aerosol nanoparticles, with further application in printed electronics, functional coatings, and spectroscopy [6].

In this work, we evaluated the effect of the thickness of plasmonic nanostructures (PN) formed by gold nanoparticles using “dry” aerosol printing on the surface enhancement of Raman scattering and the SERS signal enhancement factor using organic substances: methylene blue (MB), 1,2 bis(4 pyridyl)ethylene (BPE) and malachite green (MG).

## Materials and Methods

The experimental setup used for the synthesis of gold nanoparticles and their focused deposition on a substrate, is schematically shown in Figure 1 and includes the following key elements: nanoparticle generator, a coaxial nozzle for focused deposition, and a coordinate table to which the substrate is attached, with the ability of moving in a horizontal plane at given speeds relative to the coaxial nozzle.

Nanoparticles are synthesized by spark ablation (Fig. 1, *a*) of gold electrodes with a material purity of 99.99% in a flow of nitrogen  $N_2$  with a purity of 99.9999% and transported to a coaxial nozzle (Fig. 1, *b*) with a  $Q_a$  flow of 1 L/min for further deposition on the substrate. A focusing gas  $Q_{sh}$  is also fed into the coaxial nozzle at a flow rate of 0.1 L/min in order to focus the deposition of nanoparticles and prevent clogging of the nozzle.

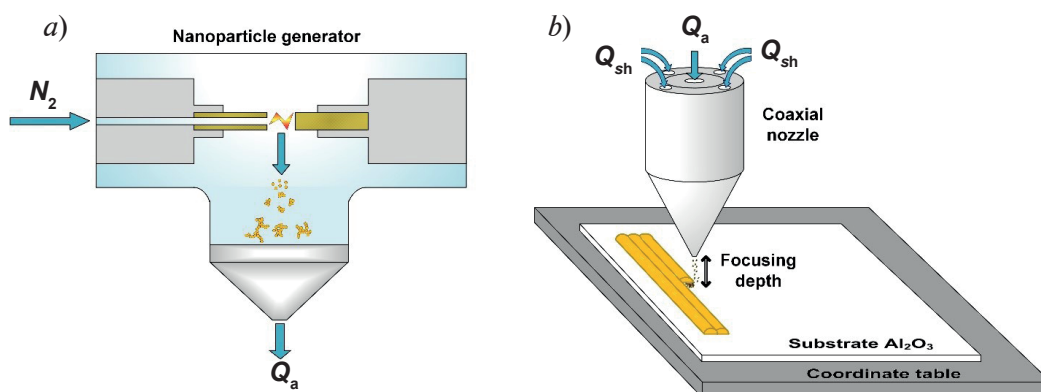


Fig. 1. The scheme of the experimental setup: nanoparticles generator (a) and focused deposition of nanoparticles through a coaxial nozzle on a moving substrate attached to a coordinate (b)

The size and elemental composition of nanoparticles are studied using a transmission electron microscope (TEM). Using a Sensofar S-neox optical 3D profilometer, the geometric characteristics of the formed PN, which are formed in the form of square areas  $3\text{ mm} \times 3\text{ mm}$  in size and  $0.3$  to  $0.5\text{ }\mu\text{m}$  thick using “dry” aerosol printing [7, 8]. The thickness of nanostructures is controlled by the time of their formation on the substrate.

Raman spectra are obtained using a Thermo Scientific™ DXR. The device employed a laser with a wavelength of  $780\text{ nm}$  and a circular aperture with a diameter of  $50\text{ }\mu\text{m}$ . The laser power was set to  $5\text{ mW}$ , a signal accumulation time of  $1\text{ s}$  and each spectrum was averaged over 5 signals. To evaluate the signal enhancement, we chose substances widely used as test analytes in Raman spectroscopy: MB, BPE and MG [9, 10]. To prepare the test solutions, substances were dissolved in a 1:1 mixture of water and isopropyl alcohol. We varied the concentrations of the solutions from  $10^{-6}$  to  $10^{-3}\text{ mol/L}$ .

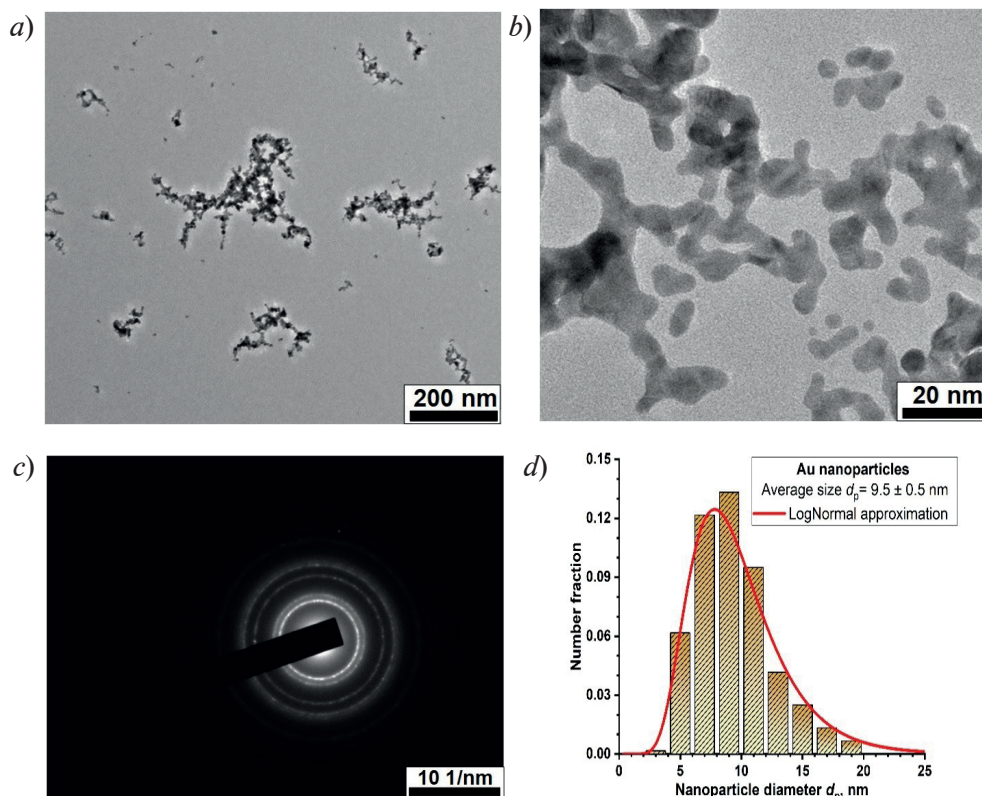


Fig. 2. TEM images of nanoparticles synthesized in a spark gas-discharge by ablation of gold electrodes in an nitrogen atmosphere ( $N_2$  purity 99.9999%) (a, b) and the corresponding electron diffraction pattern (c) and particle size distribution (d)

## Results and Discussion

Synthesis of nanoparticles in a pulsed gas-discharge nanoparticle generator [11] was carried out at an energy of a single discharge pulse between gold electrodes of 6.8 mJ with a frequency of discharge pulses of 10 Hz. As a result, primary nanoparticles with an average size  $d_p = 9.5$  nm were synthesized, which formed agglomerates with an average size  $d_a = 102$  nm. Fig. 2, *a*, *b* shows TEM images of nanoparticles at different magnifications, an electron diffraction pattern (Fig. 2, *c*) that corresponds to crystalline gold without any impurities, and the size distribution of primary nanoparticles (Fig. 2, *d*), obtained from the results of a study of a sample of 300 particles.

The synthesized gold nanoparticles were deposited on  $\text{Al}_2\text{O}_3$  alumina-ceramic substrates. Focused deposition was performed with a coaxial nozzle with an outlet diameter of 300  $\mu\text{m}$  at a distance of 4 mm from the substrate. The coordinate table with the fixed substrate moved relative to the coaxial nozzle at a speed of 7 mm/s, which was chosen as optimal for the formation of PN. The thickness of the PN-s was varied by the printing time at a constant speed. To vary the thickness of the plasmonic nanostructures, a certain number of repetitions of the coordinate table movement route was set.

Figures 3, *a* and 3, *b* show a photograph of an alumina-ceramic substrate with formed PN of various thicknesses and characteristic cross-sectional profiles of nanostructures in their extreme right part, obtained on an optical 3D profilometer, respectively.

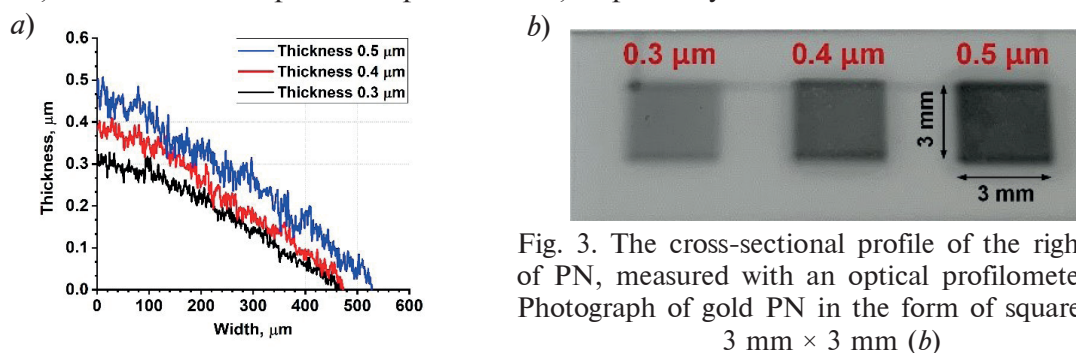
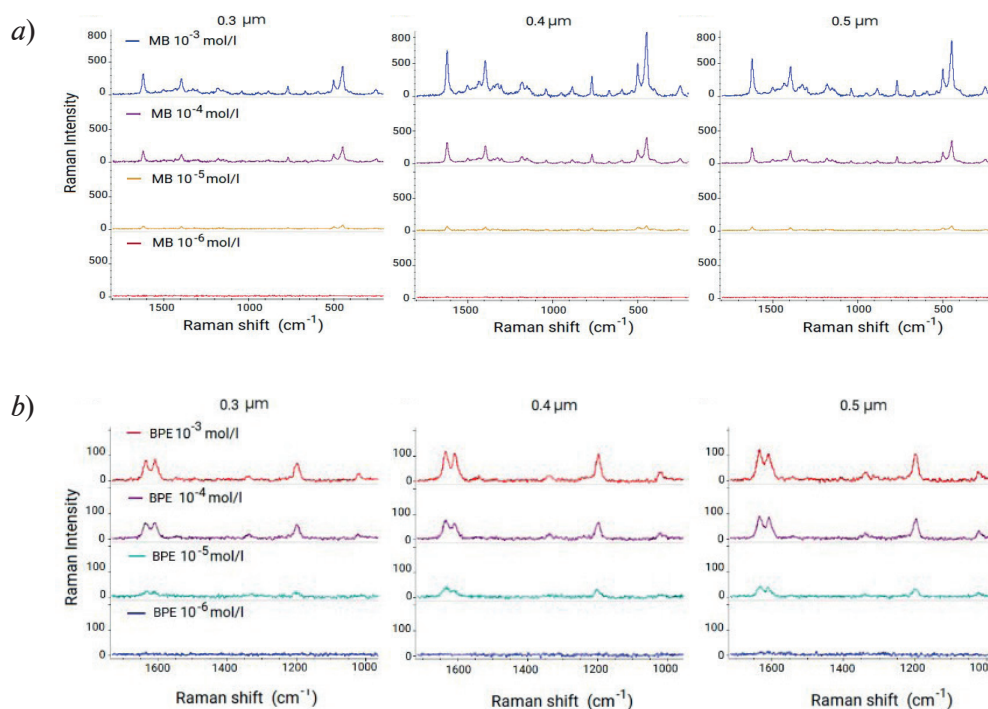


Fig. 3. The cross-sectional profile of the right side of PN, measured with an optical profilometer (*a*); Photograph of gold PN in the form of square pads 3 mm  $\times$  3 mm (*b*)

Figure 4, *a*-*c* shows the Raman spectra for MB, BPE and MG obtained on gold PN with thickness 0.3–0.5  $\mu\text{m}$  after deposition of organic substances with concentrations from  $10^{-6}$  to  $10^{-3}$  mol/L.





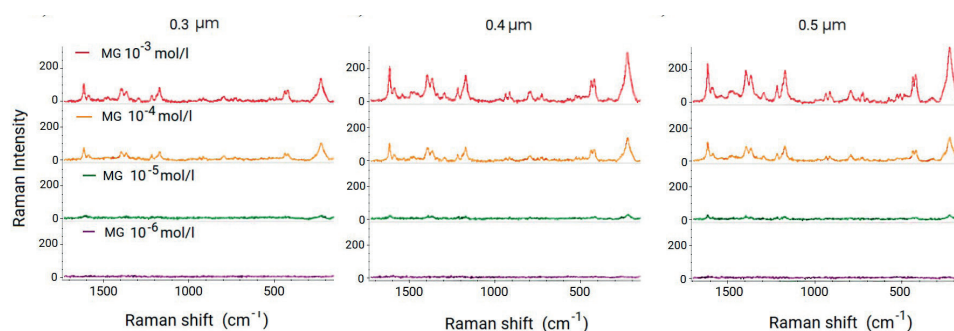


Fig. 4. Raman spectra for MB (a), BPE (b) and MG (c) obtained on gold PN 0.3  $\mu\text{m}$ , 0.4  $\mu\text{m}$  and 0.5  $\mu\text{m}$  thick, after deposition of solutions with concentrations from  $10^{-6}$  to  $10^{-3}$  mol/L.

It was found that the 0.4  $\mu\text{m}$  thick PN produced a significantly higher signal for each substance compared to the 0.3  $\mu\text{m}$  thick PN and, in general, slightly lower than on the 0.5  $\mu\text{m}$  thick PN. In this case, the structures with a thickness of 0.4  $\mu\text{m}$  showed lower variation in the intensity of spectral lines as compared to 0.5  $\mu\text{m}$  thick structures. The threshold concentration (detection limit) for the analyzed substances was found to be as low as  $10^{-6}$  mol/L with the selected measurement parameters. To calculate the enhancement factor, we recorded the spectrum of a 10- $\mu\text{l}$  drop of a solution containing the particular analyte at a concentration of  $10^{-3}$  mol/L. In calculations, the ratio between SERS and Raman signals and the ratio between number of analyte molecules contributed to the signal in each case [12, 13] was used. The height of the drop was estimated using macro photography, while the area of the “working” surface with nanoparticles was estimated from SEM images [13]. We took into account that only 7% of the surface area of gold nanoparticles was involved in SERS [12]. In calculations, we used spectra measured on 0.4  $\mu\text{m}$  thick PN and obtained the following values of enhancement factor:  $5.5 \times 10^6$  for MB,  $8.0 \times 10^6$  for BPE, and  $2.1 \times 10^7$  for MG.

### Conclusion

We have investigated the possibility of using plasmonic nanostructures fabricated by dry aerosol printing with spark discharge synthesized gold nanoparticles for implementing SERS. Plasmonic nanostructures with a thickness of 0.4  $\mu\text{m}$  were found to be optimal from the viewpoint of reaching a compromise between the SERS signal, its reproducibility, and time required to pattern the structure. The SERS enhancement factor characteristic of fabricated nanostructures is estimated at  $5.5 \times 10^6$  for methylene blue,  $8.0 \times 10^6$  for 1,2 bis(4 pyridyl)ethylene, and  $2.1 \times 10^7$  for malachite green.

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