

SENSITIVE SERS PLATFORM OF BIMETALLIC NANOPARTICLES IMMOBILIZED ON THE GOLD GRATING SURFACE

Yevgeniya KALACHYOVA, Vaclav SVORCIK, Oleksiy LYUTAKOV

*Department of Solid State Engineering, University of Chemistry and Technology Prague,
Czech Republic, EU, kalachyy@vscht.cz*

Abstract

Surface-enhanced Raman spectroscopy (SERS), stemming from the gigantic light energy focusing near the plasmon-active surface, provides the possibility to reveal the presence of targeted analytes under extremely dilute conditions. At present, SERS sensors have been making significant progress regarding practical applications in the analytical and bioanalytical fields. The main delaying factors in SERS development are related to the poor signal reproducibility. Proposed work is aimed at the achievement of highly-reproducible SERS results. The high sensitivity of SERS has been achieved through the immobilization of sharp-edges bimetallic specific nanoparticles - gold/platinum nanourchins (Au@PtNPs), on the gold grating surface, through the 1,4-benzendithiol (BDT) or 4-sulfobenzenediazonium tosylate (ADT-SH). Gold grating, able to support the surface plasmon polariton (SPP) excitation and propagation, was created on the polymer substrate using the excimer laser modification with further metal deposition. Bimetallic nanoparticles, able to efficiently excite the localized surface plasmons (LSPs), were synthesized using the wet chemical approach. Immobilization of Au@PtNPs on the gold grating allows to achieve SPP-LSP coupling and significantly SERS enhancement, with the maintaining of signal reproducibility, provided by the periodical surface. More detailed experiments show that in the case of ADT-SH, the better Au@PtNPs grafting density and SERS enhancement factor were achieved. Moreover, the produced structure allows SERS measurements with a portable Raman spectrophotometer.

Keywords: Multibranching nanoparticles, gold gratings, coupling, plasmonics, SERS

1. INTRODUCTION

Surface-enhanced Raman spectroscopy (SERS) is a way to significantly increase the weak naturally weak Raman signal. Recently significant advancements in the field of SERS substrate design and preparation were reported [1-4]. However, despite the many methods, proposed to realize the uniform SERS response the construction and realization of large area, homogenous substrate is complicated. Among the common techniques, aimed to solve this challenge through achieving of the uniform distribution of plasmon hot spots, the self-assembling can be mentioned [5]. Alternatively, the significant SERS enhancement can be realized through the utilization of nanostructures with the high number of so-called hot-spots [6-8], for example nanoparticles with urchin-like symmetry [9]. The immobilization or growth of gold nanoparticles with sharp edges on the different substrates was proposed to combine both mentioned above approaches: creation of hot spots homogenous distribution and high SERS enhancement factor [10].

In this work the immobilization of gold urchin-like particles on the patterned gold grating surface was proposed and studied. The immobilization of gold nanourchins was performed on the metal surface, using the thiol chemistry for monolayer formation [11-12]. The high SERS response has been achieved through the immobilization of specific nanoparticles Au@PtNPs on the gold grating surface, through BDT or ADT-SH [13]. Prepared structures were checked using the UV-Vis, AFM, and Raman spectroscopy techniques.

2. EXPERIMENTAL SECTION

2.1. Materials

Chloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 99.9 %), silver nitrate (AgNO_3 , 99.0 %), chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, 99.0 %), ascorbic acid (AA, 99.0 %) and 1,4-benzendithiol (BDT, 99.0 %) were purchased from Sigma-Aldrich. 4-sulfobenzendiazonium tosylate (ADT-SH) were prepared according to the described procedure [4].

All chemical reagents were used as received without further purification. Deionized water was used throughout the experiments.

2.2. Preparation of Au@Pt Multibranching NPs

Au@Pt Multibranching NPs (Au@PtNPs) were synthesized by known procedure [11]. 100 μL of 10 mM aqueous HAuCl_4 solution was mixed with 3 mL of deionized water, and then 6 μL of 10 mM aqueous AgNO_3 solution was added under magnetic stirring for 30 s. After the solutions had been thoroughly mixed, 2 μL of 100 mM ascorbic acid was “quickly” added, and the solution was stirred vigorously for 10 s at room temperature (RT). When reducing agent was added the color of the mixture changed immediately from yellow to dark blue, indicating the formation of gold multibranching NPs (AuMs). Then the AuMs were dispersed in 3 mL of water and were purified by centrifugation at 5000 rpm for 10 min.

For further use the resultant precipitates were re-dissolved in 3 mL of deionized water. Then the 15 μL of 10 mM aqueous H_2PtCl_6 solution was mixed with 3 mL of prepared AuMs. After the solutions had been thoroughly mixed, 10 μL of 100 mM AA was “quickly” added and stirred for 30 s at room temperature (RT). The color of the prepared mixture changed from dark blue to grey, indicating the formation of Au@PtNPs. Then the Au@PtNPs were dispersed in 3 mL of water and were purified by centrifugation at 5000 rpm for 20 min. For further use the resultant precipitates were re-dissolved in 3 mL of deionized water.

2.3. Preparation of Au grating

Polymer films (Solution of epoxy resin - photoresist, Su-8, purchased from Microchem) were spin-coated (1000 rpm) from a solution onto freshly cleaned glass substrates (supplied by Glassbel Ltd, CR) during 10 min. The prepared samples were dried under 50 °C for 24 h and irradiated by UV-source for 30 min. After UV-irradiating samples were dried under 90 °C for 2 h.

Then the flat polymer surface was patterned by KrF excimer laser by known procedure [11]. As a result, the periodic surface structures were created on the Su-8 surface.

Gold was then deposited onto a patterned surface by vacuum sputtering (gold thickness 50 nm, DC Ar plasma, gas purity of 99.995 %, gas pressure of 4 Pa, discharge power of 7.5 W provided by Safina, Czech Republic).

2.4. Samples grafting with Au@Pt NPs

Freshly prepared samples of Au gratings were inserted into methanol solution of BDT ($10^{-6} \text{ mol} \cdot \text{L}^{-1}$) and water solution of ADT-SH ($10^{-6} \text{ mol} \cdot \text{L}^{-1}$) for 24 h. After incubation modified samples were washed with methanol and distilled water. Then prepared samples immersed into solutions of Au@PtNPs for 24 h.

Finally, the samples were cleaned in the ultrasonic bath (in distilled water) and dried under N_2 flow.

Procedures of sample preparation is illustrated in **Figure 1**.

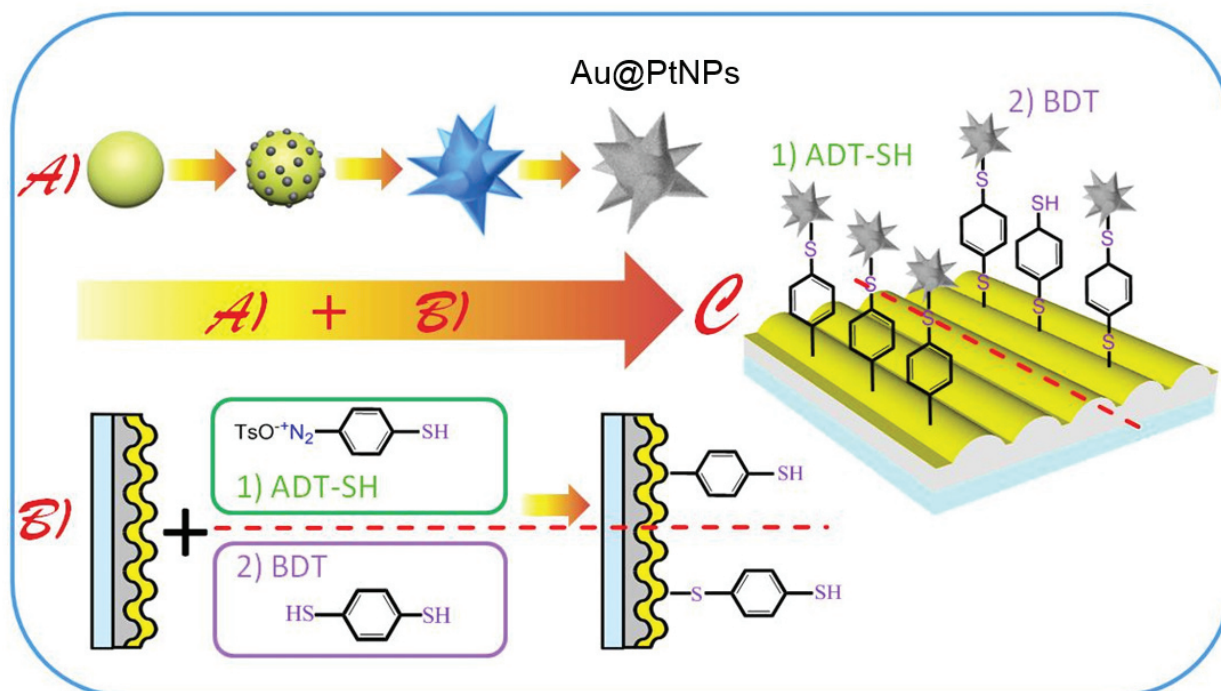


Figure 1 Schematic representation of the LSP-SPP coupled system preparation: (A) - preparation of Au@PtNPs; (B) - preparation of gold grating and grafting of ADT-SH and BDT linkers; (C) - grafting of Au@PtNPs through the ADT-SH and BDT linkers

3. RESULTS AND DISCUSSION

3.1. Characterization of solid films

3.1.1. Transmission electron microscopy (TEM)

TEM images of nanoparticles were obtained on JEOL JEM-1010 instrument operated at 80 kV (JEOL Ltd., Japan). This technique confirms the presence of shape edges in the AuMs structures, which is responsible for efficient photon-plasmon conversion and allows achieving huge SERS enhancement (**Figure 3a**). After deposition of Pt layer the AuMs conserve their shape (**Figure 3b**), providing the possibility for efficient SERS detection [14].

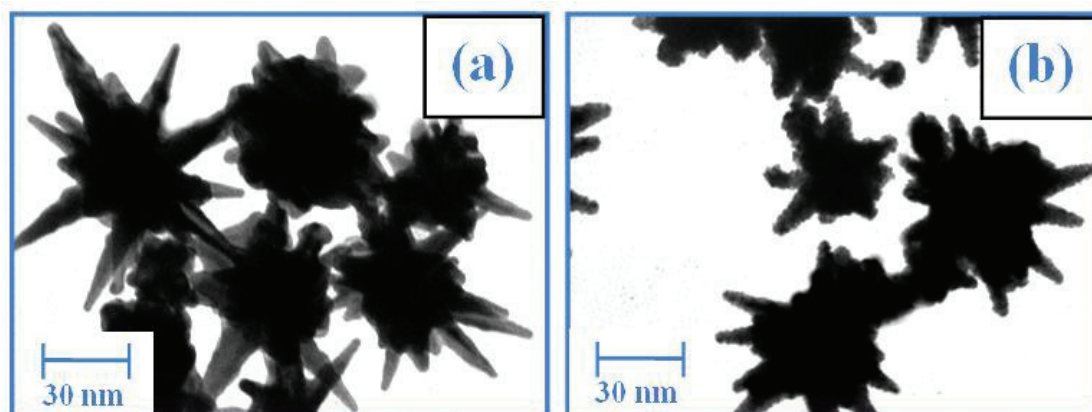


Figure 2 TEM images of (a) - AuMs; (b) - Au@PtNPs

3.1.2. X-ray photoelectron spectroscopy (XPS)

Concentration of elements on the surface of prepared samples was studied by X-ray photoelectron spectroscopy (XPS). Results are summarised in the **Table 1**. As expected, after thiol grafting the surface of samples contained elements typical for thiol grafting (sulfur), and elements of grafting Au@PtNPs (gold and platinum).

Table 1 Concentration of elements studied by XPS

Sample	Element concentration (At. %)				
	C (1s)	O (1s)	S (2p)	Au (4f)	Pt (4f)
Su-8/Au	56.1	24.5	-	-	-
Su-8/Au/ADT-SH	65.9	18.1	5.9	-	-
Su-8/Au/ADT-SH/Au@PtNPs	66.9	16.1	3.3	2.3	2.0
Su-8/Au/BDT	65.8	18.5	6.2	-	-
Su-8/Au/BDT/Au@PtNPs	67.1	16.3	4.3	1.9	1.5

3.1.3. Atomic force microscopy (AFM)

For characterization of the sample surface before and after surface AuMs immobilization, the peak force AFM technique was used. Surface mapping was performed with Icon (Bruker) set-up on $3 \times 3 \mu\text{m}^2$ samples area. In particular, **Figure 3** shows the different stage of the AuMs immobilization through the ADT-SH and BDT linkers. **Figure 3(a)** represents the grating structure before the samples immersing in the solution of Au@PtNPs. **Figure 3(b)** shows the surface morphology after the nanoparticles immobilization through the BDT spacer molecules (also during the 24 hours of entrapping procedure). Finally, **Figure 3(c)** shows the results of Au@PtNPs grafting after the 24 hours of sample immersing in the solution of ADT-SH, followed by the Au@PtNPs. As is evident, the entrapping of Au@PtNPs occurs, but the grating surface is not fully covered. The grating structure is fully screened by the attached Au@PtNPs, which indicate the complete covering of pristine surface during the reaction time.

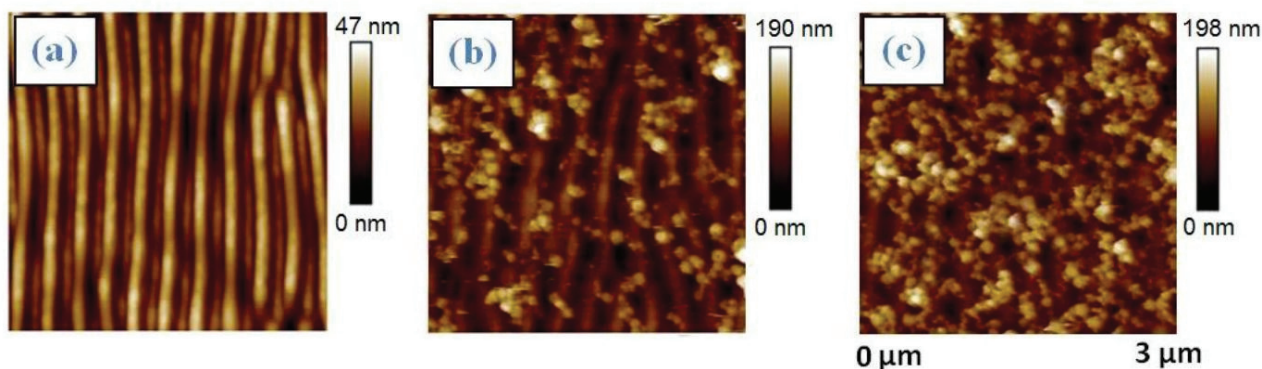


Figure 3 Surface morphology measured on the: (a) - patterned polymer surface covered by gold layer; (b) - patterned polymer surface covered by silver layer with grafted Au@Pt NPs after sample immersing in BDT solution during the 24 hours; (c) - patterned polymer surface covered by gold layer with grafted Au@Pt NPs after sample immersing in ADT-SH solution during the 24 hours

3.1.4. SERS

Raman scattering was measured on Nicolet Almega XR spectrometer (Laser power 30 mW) Raman spectrometers with 780 nm excitation wavelengths. Spectra were measured 10 times, each of them with 30 s accumulation time. As analytical standart the Rhodamine 6G was used (supplied from SigmaAldrich, dissolved in methanol (10^{-11} mol·L⁻¹ solution) and added by dropping solution onto samples surface before SERS measurement).

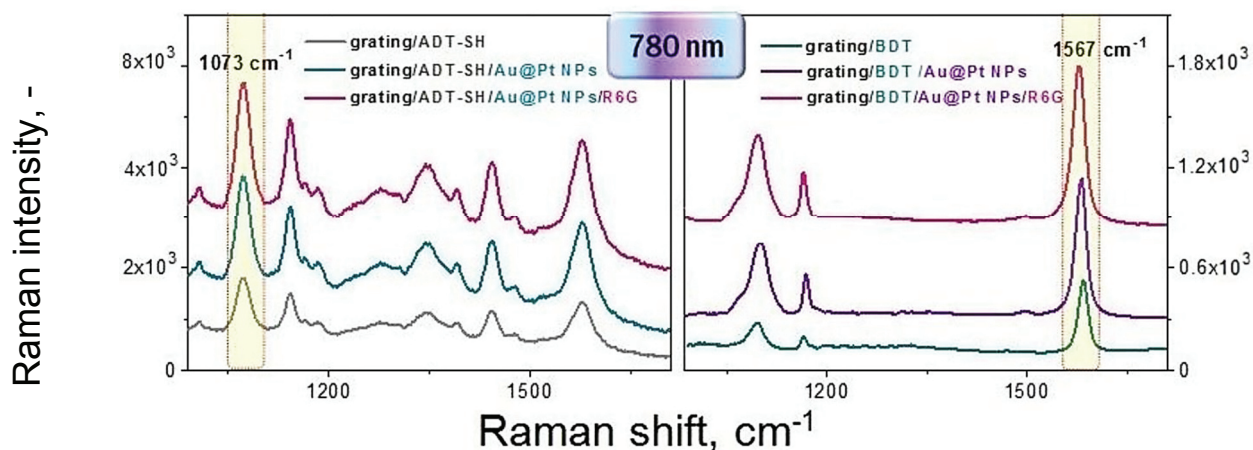


Figure 4 SERS spectra from the samples consisting of gold gratings grafted through ADT-SH and BDT linkers with Au@PtNPs and additionally covered with R6G molecules

In the SERS experiments, the Au@PtNPs were grafted to the surface of silver gratings through ADT-SH and BDT linkers. Raman excitation was performed using 780 nm. It must be noted that in proposed system two molecules, able to give significant SERS response are presented: the BDT (or ADT-SH) and R6G. As is evident from the **Figure 4** the apparent SERS responses were observed from both molecules. But in the case of SERS excitation with 780 nm, the R6G peaks disappear (or becomes insignificant), and the BDT or ADT-SH response is dominant. This fact indicates that the plasmon intensity is distributed differently: when the excitation wavelength is closed to the plasmon maximum of the both kind of metal nanostructure the plasmon energy is focused in the gap between the Au@PtNPs and gold grating. In the case of ADT-SH, the better Au@PtNPs grafting density and high SERS enhancement factor were achieved. This approach implements the light focussing at the nanometer scale between the gold surface and grafted gold nanourchins.

4. CONCLUSION

The plasmonically coupled SERS substrates were prepared by the creation of gold grating (supported the SPP excitation) followed by the grafting of Au@PtNPs to the gold surface. Prepared structures were checked using the AFM and Raman spectroscopy techniques. Plasmon coupling and SPP-LSP interplay allows to achieve high SERS enhancement, compare to the array of Au@PtNPs, deposited in the dielectric environment or on the metal films. More detailed experiments show that in the case of ADT-SH, the better Au@PtNPs grafting density and high SERS enhancement factor were achieved. Moreover, the produced structure allows SERS measurements with a portable Raman spectrophotometer. From the viewpoint of sensitivity and reproducibility prepared SERS substrates to have key advantages for the various analytical applications.

ACKNOWLEDGEMENTS

This work was supported by the GACR under the project 15-33459A.

REFERENCES

- [1] LAL, S., LINK, S., HALAS, N. J. Nano-optics from sensing to waveguiding. *Nature photonics*, 2007. vol. 11, 641.
- [2] PEKSA, V., LEBRUSKOVA, P., SIPOVA, H., STEPANEK, J., BOK, J., HOMOLA, J., PROCHAZKA, M. Testing gold nanostructures fabricated by hole-mask colloidal lithography as potential substrates for SERS sensors: sensitivity, signal variability, and the aspect of adsorbate deposition. *Physical Chemistry Chemical Physics*. 2016. 18, no. 29, pp. 19613-19620.
- [3] KALACHYOVA, Y., ERZINA, M., POSTNIKOV, P., SVORCIK, V., LYUTAKOV, O. Flexible SERS substrate for portable Raman analysis of biosamples. *Applied Surface Science*. 2018. vol. 458, pp. 95-99.
- [4] GUSELNIKOVA, O., POSTNIKOV, P., ERZINA, M., KALACHYOVA, Y., SVORCIK, V., LYUTAKOV, O. Pretreatment-free selective and reproducible SERS-based detection of heavy metal ions on DTPA functionalized plasmonic platform. *Sensors and Actuators B: Chemical*. 2017. vol. 253, pp. 830-838.
- [5] KHOURY, C. G., VO-DINH, T. Gold nanostars for surface-enhanced Raman scattering: synthesis, characterization and optimization. *The Journal of Physical Chemistry C*. 2008. vol. 112, no. 48, pp. 18849-18859.
- [6] EVCIMEN, N. I., COSKUN, S., KOZANOGLU, D., ERTAS, G., UNALAN, H. E., ESENTURK, E. N. Growth of branched gold nanoparticles on solid surfaces and their use as surface-enhanced Raman scattering substrates. *RSC Advances*. 2015. vol. 5, no. 123, pp. 101656-101663.
- [7] DONASONG, H., INAYANG, Y. Solution based, on chip direct growth of three-dimensionally wrinkled gold nanoparticles for a SERS active substrate. *Chemical Communications*, 2015. vol. 51, no. 1, pp. 213-216.
- [8] DUAN, H. W., KUANG, M., WANG, D. Y., KURTH D. G., MOHWALD, H. Colloidally stable amphibious nanocrystals derived from poly {[2-(dimethylamino) ethyl] methacrylate} capping. *Angewandte Chemie*, 2005. vol. 44, pp. 1717-1720.
- [9] XU, J., ZHANG, L., GONG, H., HOMOLA, J., YU, Q. Tailoring plasmonic nanostructures for optimal SERS sensing of small molecules and large microorganisms. *Small*. 2011. vol. 7, no. 3, pp. 371-376.
- [10] ZHENG, P., LI, M., JUREVIC, R., CUSHING, S. K., LIU, Y., WU, N. A gold nanohole array based surface-enhanced Raman scattering biosensor for detection of silver (I) and mercury (II) in human saliva. *Nanoscale*, 2015. vol. 7, no. 25, pp. 11005-11012.
- [11] KALACHYOVA, Y., MARES, D., JERABEK, V., ULBRICH, P., LAPCAK, L., SVORCIK, V., LYUTAKOV, O. Ultrasensitive and reproducible SERS platform of coupled Ag grating with multibranching Au nanoparticles. *Physical Chemistry Chemical Physics*. 2017. vol. 19, no. 22, pp. 14761-14769.
- [12] GUO, Dao-Jun; MIRKHALAF, Fakhradin. *Modification of nano-objects by aryl diazonium salts*. Wiley-VCH: Weinheim, Germany, 2012. pp. 103-124.
- [13] ALVAREZ-PUEBLA, R. L., LIZ-MARZAN M., GARCIA DE ABAJO, F. J. Light concentration at the nanometer scale. *The Journal of Physical Chemistry Letters*, 2010. vol. 1, pp. 2428-2434.
- [14] RODRIGUES-LORENZO, L., ALVAREZ-PUEBLA, R. A., PASTORIZA-SANTOS, I., MAZZUCCO, S., STEPHAN, O., KOCIK, M., GARCIA DE ABAJO, F. J. Zeptomol detection through controlled ultrasensitive surface-enhanced Raman scattering. *Journal of the American Chemical Society*. 2009. vol. 131, no. 13, pp. 4616-4618.