Influence of silver-core gold-shell nanoparticle parameters on the variation of surface-enhanced Raman spectra

Maciej S. Wróbel*[a], Katarzyna Karpienko[a], Marcin Marzejon[a,b], Filip Sadura[a], Soumik Siddhanta[c], Ishan Barman[c, d], Janusz Smulko[a]

[a]Faculty of Electronics, Telecommunications and Informatics, Gdansk University of Technology,
G. Narutowicza 11/12, 80-233 Gdansk, Poland;
[b]Institute of Physical Chemistry, Polish Academy of Sciences,
Kasprzaka 44/52, 01-224 Warsaw, Poland;
[c]Department of Mechanical Engineering, Johns Hopkins University, Latrobe Hall 223,
3400 N Charles St, Baltimore, MD 21218, USA;
[d]Department of Oncology, Johns Hopkins School of Medicine, Baltimore, MD, USA

ABSTRACT

The detection of molecules by surface-enhanced Raman spectroscopy (SERS) is dependent on the nanomaterial used to induce the enhancement effect. This depends on a variety of parameters of the substrate such as the metal used for their creation, their shape, size and size distribution, concentration, as well as the parameters of the solution, such as packing of the nanoparticles, the complexity of the sample, the solvent, etc. It is most crucial, that the parameters are kept constant to provide uniformity of the enhancement. this is crucial for the development of SERS as a reliable and quantitative technique for bioanalysis. Here, we have developed the silver-core and gold-shell nanoparticles, to serve as the enhancement material. The fabrication phase involved constant concentrations of chemicals stability of the solution physical parameters like stirring and heating, and differed only in the perturbation of the reagents addition kinetics. These nanoparticles were investigated further with their ability to measure the solutions of 2-naphtalenethiol in DMSO, as model for testing the variability of the signal due to the enhancement and the kinetics of the nanoparticle-sample solution during a routine Raman measurement procedure. The results indicate vast difference in the preference of the 2-naphthalenethiol to come into contact with the nanoparticles and the partial enhancement of DMSO in most cases, with an almost complete by-pass of the solvent and direct detection of the 2-naphthalenethiol in one case. Moreover, the kinetics of the measurement solution, or its stability during measurement, is provided.

Keywords: surface-enhanced Raman spectroscopy, nanoparticles, metrology, biophotonics.

1. INTRODUCTION

The surface-enhanced Raman spectroscopy (SERS) is a molecular spectroscopy technique which enables to observe vibrational bands of analyte molecules. The biggest advantage, in comparison with the classical Raman spectroscopy, is a great measurement signal enhancement. SERS enables detection of molecules at trace levels due to the electromagnetic and chemical enhancement of the Raman signal of the molecule. The SERS signal's enhancement factor is of the order of 10^6 or more[1]. Pivotal in the achievement of high enhancements are the nanomaterials[2–5] used to induce such enhancement. Their physical parameters (like shape, size, size distribution), as well as the chemicals used in preparation method define their characteristics. Especially in the case of nanoparticles, which are suspended in a solution, the stabilization agents (such as polyethylene glycol[6], CTAB[7] or sodium citrate[8,9], among others[10,11]) play an important role. The precision of the fabrication method is of utmost importance for achievement of high enhancement factors[12], accurate tuning of their plasmon resonance to desired wavelengths[13,14], and to ensure their uniformity[15,16]. The latter characteristic is very important, possibly even more important from the metrological point of view, than the achievement of record-high absolute enhancement factor with hot-spots[17].

*maciej.wrobel@pg.edu.pl; phone: +48 58 347 2482

The hot-spots are localized areas of immense enhancement due to the overlapping of the electromagnetic fields, mostly dependent on sharp features and assemblies of nanoparticles. Should the molecule come into the close vicinity of the hot-spot its signal is enhanced much more than from other areas over the nanoparticle or the nanoparticle cluster[18]. The reasoning is such that the variation causes differences in the SERS spectra of molecules, resulting in different dependence of the recorded SERS signal on the concentration of the investigated molecule. Such behavior of the nanoparticle-molecule system causes nonlinearities in signal concentration-intensity response, and is highly volatile, by increasing the variance of the spectra[19].

Such effects are thus increasing the error of prediction in quantitative analysis[20]. Moreover, the instabilities of nanoparticle fabrication procedure cause changes in the recorded spectra due to difference in the shape and size distribution, packing of nanoparticles etc., all contributing factors to the hot-spot formulation, and eventually, variance of the spectral response.

From the metrological point of view, it is crucial to ensure the stability and real applicability of the SERS technique for routine quantitative industrial measurements. Therefore, among other instrumental parameters affecting the sensitivity and precision of the method, like the noise levels, also the differences and variability in the spectra due to material properties should be established for the evaluation of effectiveness of the proposed SERS-based approach for quantitative detection.

Here, we investigate the case of silver-core gold-shell nanoparticles fabrication for their evaluation in biofluid analysis. The fabrication method is presented, along with the plasmon-tuning and resulting UV-VIS nanoparticle batches spectra. The SERS spectra of model solutions are presented, to evaluate the difference in spectral response as well as the difference in spectral variation between measurements, which describe the stability of the method. The kinetics of the measurement process are important, thus the spectra were recorded just after sampling, up to a couple of minutes of the measurement procedure, to show the kinetics of the molecule-nanoparticle system happening even in such simple environments as these.

2. MATERIALS AND METHODS

The stock silver nanoparticles were obtained by the Lee-Meisel method[21], by reduction of $AgNO_3$ with sodium tricitrate at 100°C while stirring. In 100 ml of pure water conductivity 0.05 µS the 18 mg of $AgNO_3$ was dissolved. The sodium citrate was added dropwise with various speeds and drop volume. The concentrations in two created stock solutions were identical.

Secondly, the gold shell was grown on the silver nanoparticles, created in the previous step. The shell was formed by reduction of gold(III) chloride trihydrate ($HAuCl_4H_7O_3$) by hydroxylamine hydrochloride (NH_2OH HCl) solution. The higher the amounts of the reagents the greater is the shell thickness, and therefore the red-shift of the plasmon resonance. The nanoparticles utilized in this study were fabricated from a single batch of the silver nanoparticles. Using different amounts of reagents, the final nanoparticle batches were created with plasmon resonance peak tuned to be blow, at and over the 830 nm. This was made to characterize the relationship between the maxima of plasmon resonances (while using the same excitation wavelength), and the metrological response of the measured SERS signal.

Optical parameters measurements of nanoparticles were performed using UV-VIS spectrophotometer (UV-VIS 9000 by Metash). The prepared samples (0.5 mL of nanoparticles solution and 2 ml of DI water) were placed into PMMA single-use cuvettes and the measurements in the spectra range from 300 nm to 1100 nm with 1 nm step were performed.

The surface-enhanced Raman spectra were recorded on a Raman spectrometer set-up with 830 nm excitation laser, axial-transmissive spectrograph and a CCD camera. The excitation light was guided to the sample by a fiber-optic probe with 2.5 cm working distance. Spectra were measured with 1s integration time for 3 minutes, to investigate the effect of sample changes over short time periods after mixing the analyte solution with nanoparticle solution during the measurements. It is important to define the time period for the validity of the measurement. Different samples might be more resilient to temporal changes, while for others it may be a very critical parameter .

The sample was loaded as a drop with 10 µl volume on an aluminum plate. The sample consisted of a concentrated solution of the nanoparticles 1:1:1 with 10^{-2} mM solution of 2-naphthalenethiol in dimethyl sulfoxide (DMSO), and H_2O or 5M NaCl in H_2O, as further indicated.

3. RESULTS

Four types of silver-core gold-shell nanoparticles were fabricated and used for the experiments. The differences in their fabrication included the concentrations of chemicals, with the same string and heating, and resulted in a variable size distributions of core-shell nanoparticles and different peak plasmon resonance. The resulting nanoparticles show different plasmon peak positions, varying between 750 – 850 nm, and show a different spread of their sizes.

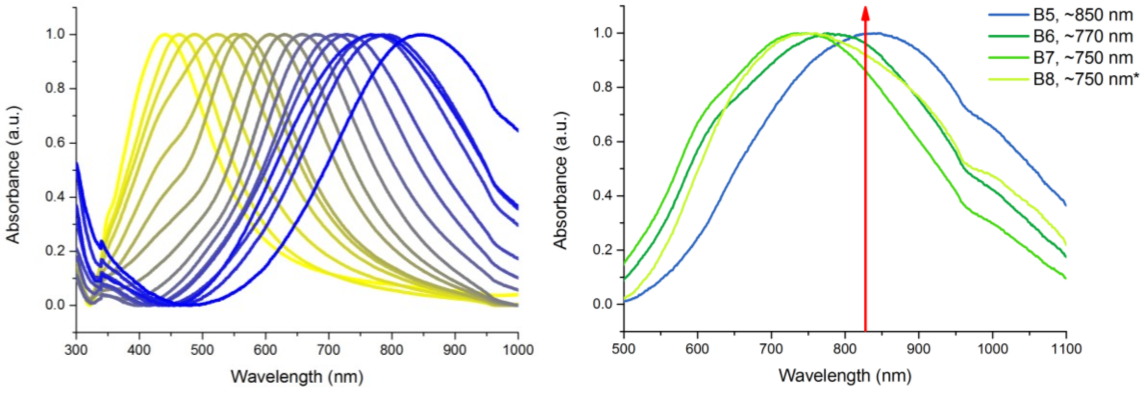

Figure 1. The UV-VIS spectra of the initial nanoparticles and the shell-growth process (left). The UV-VIS spectra of the resulting nanoparticles, with plasmon resonance about the excitation wavelength (right).

The resulting SERS spectra (figure 2) are presented for the nanoparticles with and without the additional NaCl which acts as an agglomerating agent and also increases the conductivity of the solution. The spectra indicate vast differences in the intensity of the signal. More importantly, some of the nanoparticles show greater preferential enhancement of the 2-napthalenethiol over the DMSO solvent. However, after the elapsed 3 minutes time the DMSO begins to influence their spectra, and diminishes the spectra of the 2-napthalenethiol. When comparing the effect of NaCl, the intensity is overall higher than without it, and the nanoparticles seem to be more tightly bound to the analyte rather than the solvent, and seem to have reduced the DMSO peak in comparison to the 2-naphthalenethiol peaks. The difference in the intensities of the signal between different nanoparticles also become more pronounced. The spectra after some time from sampling, in the case of added NaCl seem to have an improved temporal stability of the measurement. While the DMSO is more pronounced, still the analyte peaks are much clearly distinguishable. The nanoparticles with the largest size distribution, B8, show that the solvent peaks are much stronger, even at the very beginning of the measurement.

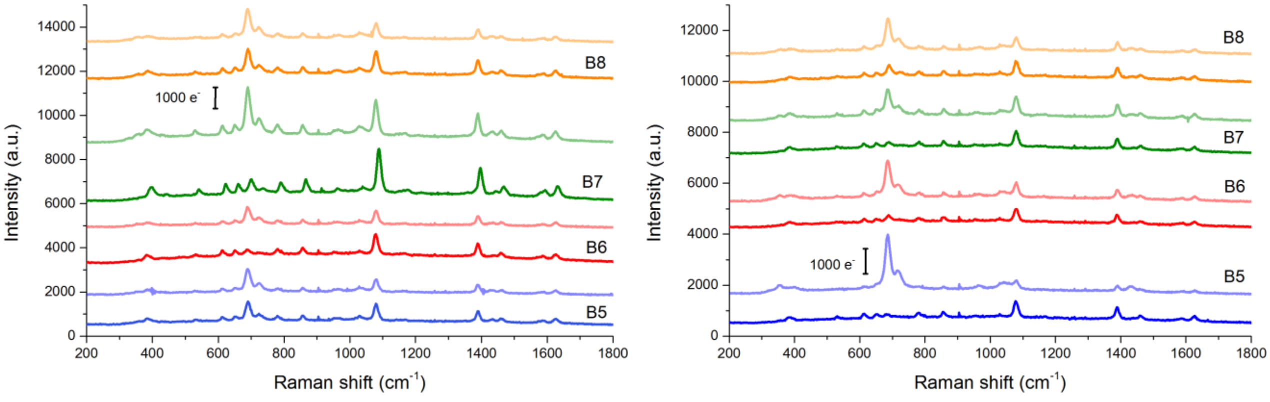

Figure 2. The SERS spectra of the nanoparticles just after initial sampling (darker colors), and after 3 minutes from sampling (light colors), for measurements with NaCl (left) and without (right). The scale bar marks intensity of 1000 counts.

4. CONCLUSIONS

Different types of nanoparticles were formed by following the same protocols for the creation of silver-core gold-shell nanoparticles. Their differences in the plasmon resonance peak position and its bandwidth are shown as an indicator of the crucial factor in SERS - the stability of material fabrication. However, even with much different parameters, all of the nanoparticles, even when shifted from the excitation wavelength, clearly show presence of the 2-naphthalenethiol peaks. Only after some time of measurements, the signal becomes overwhelmed by the DMSO solvent. In the case of NaCl, the nanoparticles are much more efficient in enhancing the signal, and are more stable over time. However, the difference in the intensity of the signal is higher between different batches of the nanoparticles.

This differences in the enhancement of the SERS spectra, and especially different preference of molecular species is of immense interest from the metrological point of view. The results suggest greater impact must be placed on the kinetics-preference mechanism of some molecules over the others in solutions, which may be an important problem in accurate quantification using the SERS method, arising simply due to a small time differences between the sampling and the moment of taking measurement.

ACKNOWLEDGEMENT

This study was partially supported by the National Science Center, Poland under the grants no. 2016/20/T/ST7/00380, and no. 2017/25/N/ST7/01366, the stipend START no. 95.2017 awarded by Foundation for Polish Science, as well as DS Programs of the Faculty of Electronics, Telecommunications, and Informatics, Gdańsk University of Technology, and the JHU Whiting School of Engineering Seed Funds.

REFERENCES

[1] Fang, Y., Seong, N.-H. and Dlott, D. D., "Measurement of the Distribution of Site Enhancements in Surface-Enhanced Raman Scattering," Science **321**(5887), 388–392 (2008).

[2] Mosier-Boss, P., "Review of SERS Substrates for Chemical Sensing," Nanomaterials **7**(6), 142 (2017).

[3] Asiala, S., Barrett, L., Mabbott, S. and Graham, D., "Advances in Biofunctional SERS-Active Nanoparticles for Future Clinical Diagnostics and Therapeutics," Frontiers of Plasmon Enhanced Spectroscopy Volume 1, American Chemical Society, 131–161 (2016).

[4] Banholzer, M. J., Millstone, J. E., Qin, L. and Mirkin, C. A., "Rationally designed nanostructures for surface-enhanced Raman spectroscopy," Chem. Soc. Rev. **37**(5), 885–897 (2008).

[5] Yaseen, T., Pu, H. and Sun, D.-W., "Functionalization techniques for improving SERS substrates and their applications in food safety evaluation: A review of recent research trends," Trends Food Sci. Technol. **72**, 162–174 (2018).

[6] Stiufiuc, R., Iacovita, C., Lucaciu, C. M., Stiufiuc, G., Dutu, A. G., Braescu, C. and Leopold, N., "SERS-active silver colloids prepared by reduction of silver nitrate with short-chain polyethylene glycol," Nanoscale Res. Lett. **8**(1), 47 (2013).

[7] Meng, J., Tang, X., Zhou, B., Xie, Q. and Yang, L., "Designing of ordered two-dimensional gold nanoparticles film for cocaine detection in human urine using surface-enhanced Raman spectroscopy," Talanta **164**, 693–699 (2017).

[8] Bastús, N. G., Merkoçi, F., Piella, J. and Puntes, V., "Synthesis of Highly Monodisperse Citrate-Stabilized Silver Nanoparticles of up to 200 nm: Kinetic Control and Catalytic Properties," Chem. Mater. **26**(9), 2836–2846 (2014).

[9] Dong, X., Ji, X., Wu, H., Zhao, L., Li, J. and Yang, W., "Shape Control of Silver Nanoparticles by Stepwise Citrate Reduction," J. Phys. Chem. C **113**(16), 6573–6576 (2009).

[10] Zeng, J., Zheng, Y., Rycenga, M., Tao, J., Li, Z.-Y., Zhang, Q., Zhu, Y. and Xia, Y., "Controlling the Shapes of Silver Nanocrystals with Different Capping Agents," J. Am. Chem. Soc. **132**(25), 8552–8553 (2010).

[11] Doctor, E. L. and McCord, B., "Comparison of aggregating agents for the surface-enhanced Raman analysis of benzodiazepines," Analyst **138**(20), 5926–5932 (2013).

[12] Israelsen, N. D., Hanson, C. and Vargis, E., "Nanoparticle Properties and Synthesis Effects on Surface-Enhanced Raman Scattering Enhancement Factor: An Introduction," Sci. World J. **2015,** 124582 (2015).

[13] Okamoto, K., "Tuning of the Surface Plasmon Resonance in the UV-IR Range for Wider Applications," Frontiers of Plasmon Enhanced Spectroscopy Volume 2, American Chemical Society, 247–259 (2016).

[14] Siddhanta, S., Wróbel, M. S. and Barman, I., "Integration of protein tethering in a rapid and label-free SERS screening platform for drugs of abuse," Chem. Commun. **52**(58), 9016–9019 (2016).

[15] Gupta, R., Siddhanta, S., Mettela, G., Chakraborty, S., Narayana, C. and Kulkarni, G. U., "Solution processed nanomanufacturing of SERS substrates with random Ag nanoholes exhibiting uniformly high enhancement factors," RSC Adv. **5**(103), 85019–85027 (2015).

[16] Meng, W., Hu, F., Jiang, X. and Lu, L., "Preparation of silver colloids with improved uniformity and stable surface-enhanced Raman scattering," Nanoscale Res. Lett. **10,** 34 (2015).

[17] Wei, H., McCarthy, A., Song, J., Zhou, W. and Vikesland, P. J., "Quantitative SERS by hot spot normalization – surface enhanced Rayleigh band intensity as an alternative evaluation parameter for SERS substrate performance," Faraday Discuss. **205**, 491–504 (2017).

[18] Itoh, T. and Yamamoto, Y. S., "Near-Field Interaction between Single Molecule and an Electromagnetic Field at 'Hotspot' Generated by Plasmon Resonance," Frontiers of Plasmon Enhanced Spectroscopy Volume 1, American Chemical Society, 23–37 (2016).

[19] Ansar, S. M., Li, X., Zou, S. and Zhang, D., "Quantitative Comparison of Raman Activities, SERS Activities, and SERS Enhancement Factors of Organothiols: Implication to Chemical Enhancement," J. Phys. Chem. Lett. **3**(5), 560–565 (2012).

[20] Bell, S. E. J. and Sirimuthu, N. M. S., "Quantitative surface-enhanced Raman spectroscopy," Chem. Soc. Rev. **37**(5), 1012–1024 (2008).

[21] Rycenga, M., Cobley, C. M., Zeng, J., Li, W., Moran, C. H., Zhang, Q., Qin, D. and Xia, Y., "Controlling the Synthesis and Assembly of Silver Nanostructures for Plasmonic Applications," Chem. Rev. **111**(6), 3669–3712 (2011).