

Strong surface enhanced Raman scattering from gold nanoarrays obtained by direct laser writing

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Abstract. We report for surface enhanced Raman scattering (SERS) from arrays of gold nanoparticles produced by 2-photons photo-reduction of the metallic precursor (HAuCl₄) hosted in a Poly-Vinyl Alcohol (PVA) matrix, on glass substrates. Samples with the same pattern but featuring different nanoparticles size and density were obtained by varying the writing laser power and scanning speed. The Raman spectra were recorded from samples immersed in a solution of rhodamine-6G (R6G), as well as, after exposure of the samples in xylene. SERS enhancement factors of up to $\sim 10^4$ were obtained for both analytes. The measurements show that the SERS enhancement is maximized on golden strips produced at higher writing laser power and lower scanning speed, where closer nanoparticles packing is obtained..

1. Introduction

Surface-Enhanced Raman Scattering (SERS) is a powerful analytical technique for detection of trace amounts of chemical and biological active molecules adsorbed on rough metallic surfaces or on metallic nanoparticles. Currently, different mechanisms of SERS have been identified [1], the major one being the electrodynamic enhancement of the local electric field due to surface plasmon resonance (SPR) [2,3]. The most favourable conditions for SPR enhancement are met on specific “hot spots” of the surface, which are usually associated with nanoscale metallic tips [4,5] (tip hot spots) or the gap between two closely spaced metallic nanoparticles, the so called “gap hot spots” [6,7]. Much of the efforts in SERS research in recent years have been focused on fabrication of artificial plasmonic structures in order to maximize the electrodynamic enhancement, as well as to accurately tune the SPR in a desired spectral range [8].

The 2-Photon Direct Laser Writing (2-PDLW) is a promising technique for tailoring of 2D and 3D structures on a sub-wavelength scale in photosensitive materials [9]. The method has been successfully applied for fabrication of mechanical and photonic devices [10–12]. Recently 2-PDLW has been utilized for production of 1D periodic gratings of gold nanoparticles (GNP), by the Au³⁺ photo-reduction, in a Poly-Vinyl Alcohol (PVA) matrix doped with HAuCl₄ [13]. It has been demonstrated



that the width of the gold strips can be finely tuned by choosing appropriate writing laser power and scanning speed. More interestingly for SERS applications, however, the GNP diameter distribution and surface density can also be controlled by the laser exposure parameters. Thus, at higher laser power and lower scanning speed larger density of GNPs could be achieved, which eventually can give rise to a formation of gap hot spots due to maximization of the close particle-particle contacts. Here we report for a strong SERS effect from the gold nanoarrays obtained by 2-PDLW on PVA+ H₂AuCl₄ matrix. The SERS properties of the structures have been tested against rhodamine-6G and xylene, and enhancement factors (EF) superior to 10^4 have been quantified.

2. Samples and methods

A batch of 50 gold 1D arrays was produced by 2-PDLW on a glass substrate by following the procedure described in reference [13]. Arrays were organized in a 5×10 matrix of a size $400 \times 600 \mu\text{m}$, as schematically shown in figure 1, with the laser power increasing in the range 2.5–22.5 mW along the columns with a step of 5 mW, and the scanning speed increasing from 10 to $100 \mu\text{m/s}$ along the rows with a step of $10 \mu\text{m/s}$. The period of the parallel gold strips within a single array is $4 \mu\text{m}$.

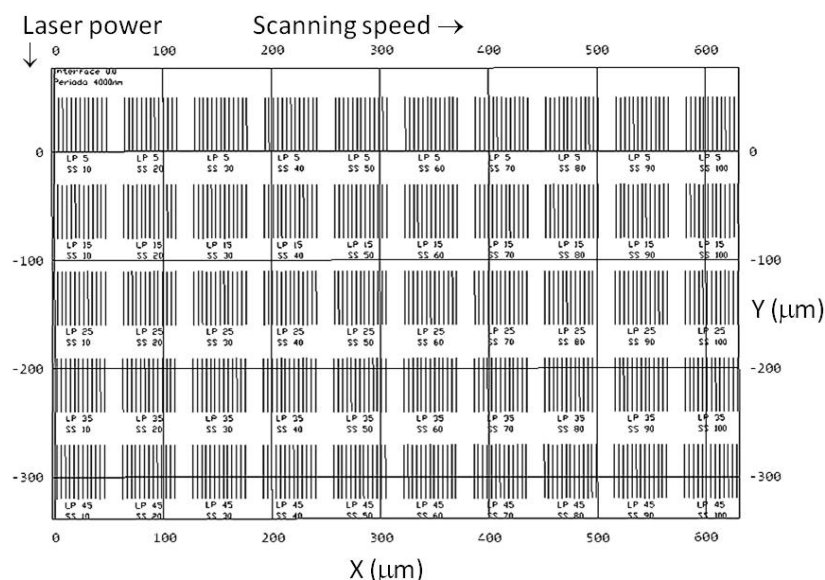


Figure 1. A scheme of the spatial organization of the gold arrays on the glass substrate. The laser power increases from top to bottom with a 5-mW step. The scanning speed increases from left to right with a step of $10 \mu\text{m/s}$.

Raman spectra were recorded on a LabRAM micro-Raman spectrometer with a He-Ne laser excitation at 632.8 nm. The laser beam was focused onto the glass surface through microscope equipped with $\times 50$ objective of a long working distance onto a spot of typical diameter of $5 \mu\text{m}$, as shown in figure 2. Reference Raman spectra were taken from the substrate and the gold strips prior to any SERS measurements. After that Raman spectra were recorded with the sample immersed in a 10^{-5} M water solution of rhodamine-6G. Subsequently, the sample was washed in ethanol and exposed to a technical grade xylene (mixture of ortho-, meta-, and para- isomers) for 5 minutes, then washed again in ethanol, and finally Raman spectra were investigated for detection of trace amounts of xylene.

3. Experimental results and discussion

The reference spectrum, taken from the bulk of concentrated 10^{-3} M R6G solution, is shown in figure 3 (a). A typical spectrum taken from a gold strip, when the glass substrate was immersed in a 10^{-5} M R6G solution, is shown in figure 3 (b). The Raman lines of R6G significantly widen in the vicinity of gold strips and increase in intensity. When the integrated intensity of the Raman bands is normalized to the R6G concentration, as described in [1], the SERS enhancement factor (EF) accounts for $\approx 10^4$.

on average for the array written @22.5 mW/10 μ m/s during the 2-PDLW process (the left-bottom array in figure 1).

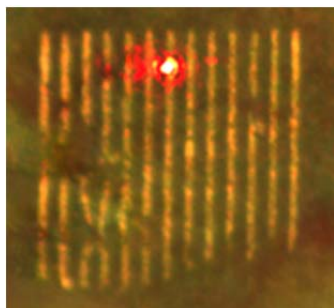


Figure 2. Gold strips as seen under optical microscope. The He-Ne laser focus on the sample is also visible as a bright spot.

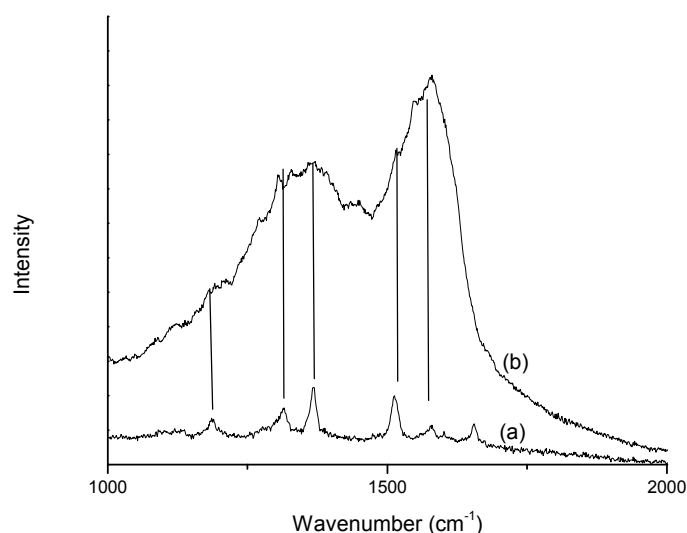


Figure 3. (a) A reference spectrum of a bulk 10^{-3} M R6G water solution. (b) Raman spectrum taken from a gold strip immersed in a 10^{-5} M R6G water solution. The intensity scale is the same for the two spectra.

Although a significant EF was evidenced for R6G, the quality of the SERS spectra is far from satisfactory due to the poor resolution of the spectral features. This fact could be explained by the strong enhancement of the wide photoluminescence (PL) background, which masks to a large extent the Raman signal. The physical origin of the PL enhancement is essentially the same as that of SERS, a SPR amplification of the local electric field around the metals surface [14]. According to [14] the PL background hampers the SERS signal at distances from the surface exceeding ≈ 10 nm. Thus, we may draw the conclusion that the R6G water solution does not penetrate effectively into the gaps between the gold nanoparticles, probably due to the large surface tension of water. Therefore, it would be instructive to test the SERS properties of our samples against organic solvents, which typically have about three times smaller surface tension than water.

We have chosen as a test substance the xylene, $C_6H_5(CH_3)_2$, which is a common organic solvent in many industrial applications. The toxicological hazard of xylene is well documented, which imposes

specific regulations on its content in the common-life products [15]. Therefore, it could be of a definite practical interest to develop analytical methods for detection of trace amounts of xylene.

Figure 4 (a) shows a reference Raman spectrum of xylene, while spectra (b)-(e) were recorded on gold strips after exposure of the sample in xylene, as described in section 2. The Raman spectrum of bulk xylene overlays a wide PL background, which makes the Raman lines poorly resolvable. It is noteworthy that the spectrum (a) is multiplied by a factor of 5000 in order that its characteristic Raman features fit the intensity scale of the spectra (b)-(e).

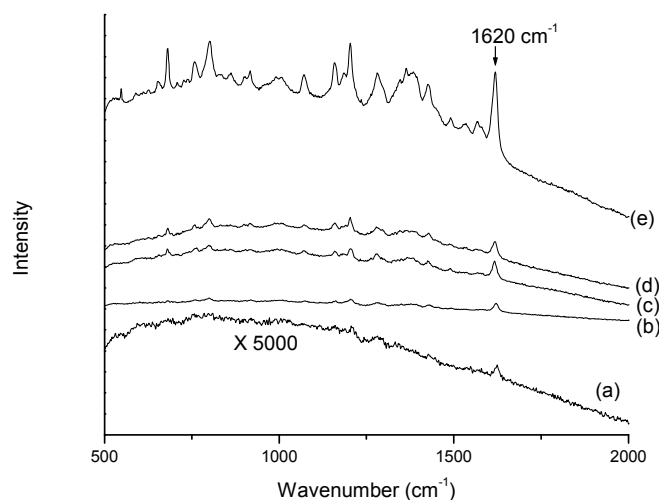


Figure 4. (a) Reference spectrum from bulk xylene; (b)-(e) SERS spectra recorded on gold strips written at a laser power of 22.5 mW and a scanning speed of 100, 70, 40, 10 $\mu\text{m/s}$ respectively.

Therefore, the spectra presented in figure 4 evidence for a large SERS enhancement of xylene Raman features on the gold strips. The PL backgrounds enhances as well, but to a much lesser extent than the Raman spectrum. According to [14] this fact implies close proximity between xylene molecules and the gold nanoparticles.

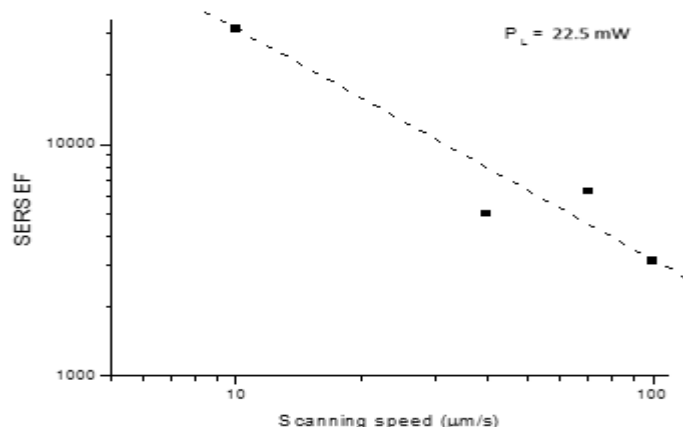


Figure 5. A log-log plot of the estimated SERS EF for the xylene line at 1620 cm^{-1} versus scanning speed, at a constant laser writing power $P_L = 22.5\text{ mW}$.

The SERS EF estimated for the strongest xylene line at 1620 cm^{-1} (see figure 4) correlates with the scanning speed (SS) in the process of laser writing, as shown in figure 5. The same order of magnitude EF have been estimated also for the other Raman lines present in the spectrum. Roughly, the SERS EF scales as $1/\text{SS}$, i.e. in a proportion to the deposited laser energy per unit length. As reported in [13] the surface density of GNPs increases at smaller scanning speeds. Thus, our data correlate the SERS EF to the GNP density, which corroborates the assumption for formation of gap hot spots upon closer GNP packing.

4. Summary and conclusions

We established that the arrays of GNPs obtained by 2-PDLW process can serve as effective SERS substrates. We recorded SERS enhancement factors close or superior to 10^4 both for R6G solution and for xylene. The photoluminescence undergoes enhancement as well, which is comparable to the SERS enhancement in the case of R6G water solution. For xylene, however, the SERS signal overwhelms by two orders of magnitude the photoluminescence background. We attribute the different SERS behavior of the two analytes to the different surface tension of water and xylene. More concretely, the smaller surface tension of xylene allows the xylene molecules to fill-in the gap hot spots formed between closely packed GNPs.

We quantified that the SERS EF for xylene is maximized on GNP arrays written at highest laser power and smallest scanning speed. We explain this fact by the maximization of GNP density, and the formation of a large number of gap hot spots thereof, at highest laser exposures.

Acknowledgments

This work was sponsored by the Project INERA (GA316309) of the 7-th Framework Program of the European Union. Authors gratefully acknowledge also the scientific and technological support of the CNR user facility "Beyond Nano" – Pole of Cosenza, as well as the financial aid by the Bulgarian Scientific Fund through the grant FNI-TO2/26.

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