ESF Short Visit Grant – Scientific Report

Reference Number: 5408

Activity Title

New Approaches to Biochemical Sensing with Plasmonic Nanobiophotonics (PLASMON-BIONANOSENSE)

Title of the research project

Characterization of microfluidic devices for use with Surface Enhanced Raman Scattering

Applicant‘s Name and address

Virginia Merk, Science Institute, University of Iceland, Dunhagi 3, IS 107 Reykjavik, Iceland

Host name and address

Prof. Janina Kneipp, Humboldt-Universität Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany

1. Purpose of the visit

The purpose of the visit was to combine advantages of microfluidic channels, such as small sample volumes and the possibility of flow-through analysis, with the high sensitivity of Surface Enhanced Raman Scattering (SERS). To this end, gold nanostructures were fabricated by sequential metal deposition and thermal annealing at the home institute prior to the stay. These structures were afterwards incorporated inside microfluidic channels of different geometries and thicknesses.

To optimize the nanostructures as well as the microfluidic channels, information about the influence of the underlying substrate, annealing temperature and number of annealing steps, plasma treatment (which is necessary to fix the channels onto the glass) and the thickness of the microfluidic channel have to be obtained. For that, a short visit was arranged to the group of Prof. Janina Kneipp at Humboldt-Universität which has great expertise in the field of Surface Enhanced Raman Scattering and where a setup suitable to measure Raman spectra inside microfluidic channels is available.

2. Description of the work carried out during the visit

First, Raman spectra of different molecules (crystal violet, Adenine, p-Aminothiophenol) on the different gold nanostructures were measured at different excitation wavelength (633 nm and 785 nm). Attention was turned on determination of the enhancement factors as well on reproducibility of the Raman signal. Therefore areas of 100 x 100 μm^2 were mapped. After changing the wavelength the setup had to be realigned. Additionally to the Raman measurements UV/Vis measurements were performed to characterize the plasmonic properties of the different nanostructures. In a second step, the same molecules were measured in the microfluidic channels. Thereby different measurement geometries were tested. After the measurements all spectra were wavelength calibrated and the enhancement factors were determined by comparison with a normal Raman spectrum of crystal violet. 1½ days were used for travelling.

3. Description of the main results obtained

Characterization of the nanostructures

The gold nanostructures show a broad extinction in the range of 550 to 750 nm with a maximum at 645 nm which shifts to slightly shorter wavelength (630 nm) after plasma treatment for 30 s (Figure 1 a). This is quite promising for SERS at an excitation wavelength of 633 nm or 785 nm. The enhancement factors for these structures were found to be as high as 10^6 on a silicon wafer with a 100 nm silicon dioxide layer and 10^5 on glass microscope slides with high homogeneity of the enhancement on the microscopic scale (Figure 1 b). The difference in the enhancement can be explained by the cavity effect of the 100-nm SiO_2 layer. The plasma treatment has nearly no influence on the enhancement in the case of the structures on the silicon wafer and only small influence for the structures on the glass slides.

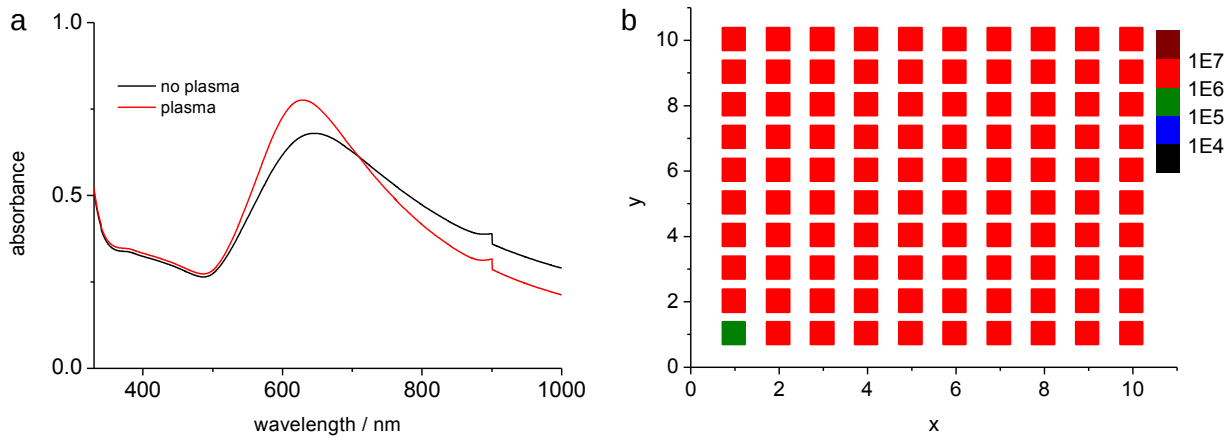

Figure 1: a) UV/Vis absorbance spectra of gold nanostructures before and after plasma treatment. b) schematic distribution of the SERS enhancement at different spots on gold nanostructures fabricated by sequential metal deposition and annealing.

It is known from the literature that annealing leads to a change in crystallinity which can result in a decrease in the SERS enhancement. When the nanostructures used here were not annealed after the last metal deposition step the enhancement of the structures on the silicon wafer decreased by one order of magnitude ($1 \cdot 10^5$ compared to $1 \cdot 10^6$). This might be explained by a change in the structure which could be observed by scanning electron microscopy. Without annealing the nanostructures are much smaller. The annealing temperature also has an influence on the enhancement. When the annealing temperature was decreased from 500°C to 250°C the enhancement was found to be as high as 10^5.

SERS measurements in microfluidic channels

It was possible to obtain SERS spectra of different molecules like Adenine, p-Aminothiophenol (PATP) and crystal violet (CV) inside the microfluidic channels. Additionally to the analyte signals the spectra also contains bands that can be attributed to the polymer. When the thickness of the polymer is decreased from 6 mm to 2.5 mm the intensity of the signals from the analyte increases and is comparable to the intensity of the analyte without the microfluidic channel whereas the intensity of the polymer signals decreases (Figure 2).

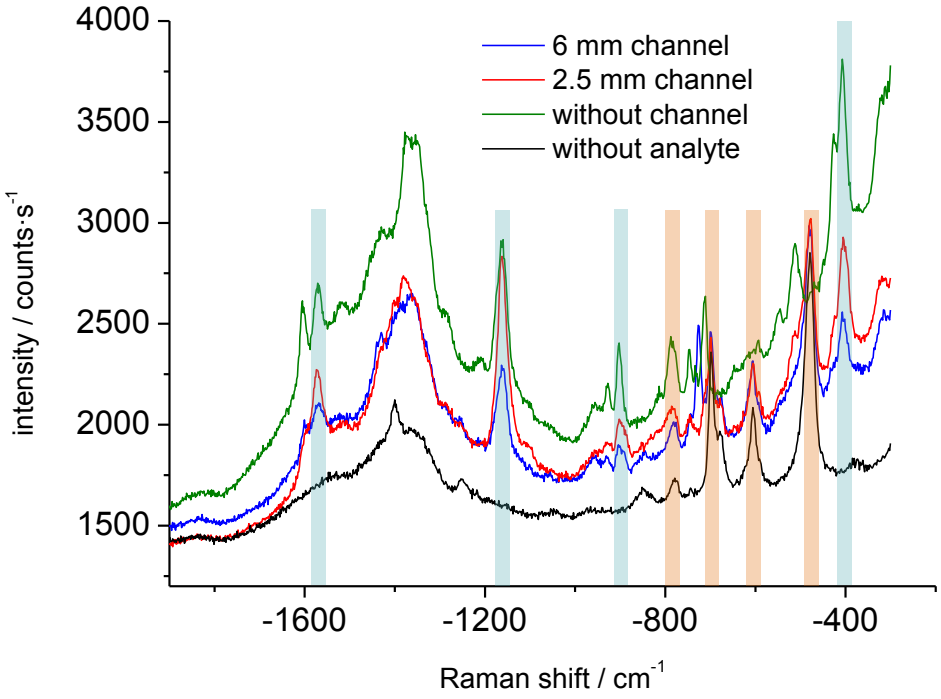

Figure 2: SERS spectra of 10^{-5} crystal violet (CV) inside microfluidic channels of different thickness excited through the polymer. For comparison the black line shows a spectrum of the microfluidic channel itself and the green line shows a spectrum of 10^{-5} crystal violet on the same structures without a microfluidic channel (λ = 785 nm, 1s). The signals marked with blue originates from the analyte (CV) and the signals marked with orange originates from the polymer.

To completely remove the polymer signals from the spectra the excitation was donef rom the backside (through the glass). In this case a huge background signal (probably due to scattered light from the glass) occurs (Figure 3).

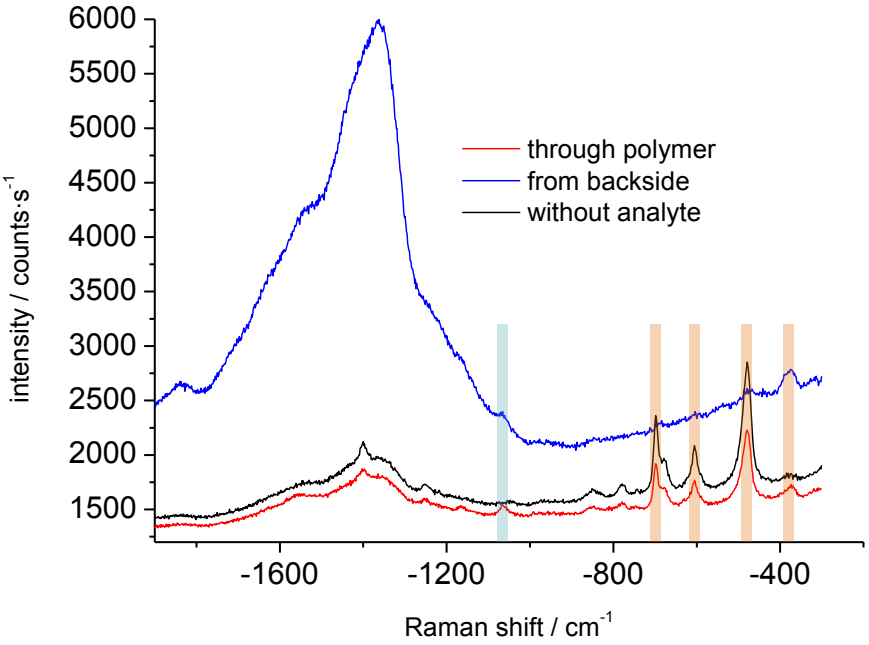

Figure 3: SERS spectra of 10^{-4} p-Aminothiophenol (PATP) inside a 6 mm thick microfluidic channel excited through the polymer and through the glass (backside). For comparison the black line shows a spectrum of the microfluidic channel itself (λ = 785 nm, 1s). The signals marked with blue originates from the analyte (PATP) and the signals marked with orange originates from the polymer.

4. Future collaboration with host institution

The results show that the generated nanostructures are suitable for SERS measurements inside microfluidic channels. The thickness of the polymer as well as the way of excitation has thereby a remarkable influence on the obtained spectra. It would be interesting to continue the collaboration with the host institution to make further investigations. After optimization of the geometry of the microfluidic devices and the measurement setup other molecules relevant for SERS sensors and reactions inside the microfluidic channels might be studied.

5. Projected publications/articles resulting or to result from your grant

The results obtained during the visit show the high potential of the combination of microfluidic devices with Surface Enhance Raman Scattering. With some further optimization the results of the work might be of sufficient impact for publication in a peer-reviewed journal.

6. Other comments

The applicant gratefully acknowledges assistance from Marina Gühlke and useful discussions with Prof. Janina Kneipp.