ON-LINE MICROFLUIDIC SERS MESUREMENRS ON THE BASE OF SURFACE PLASMON-POLARITON EXCITATION

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Abstract

There are many methods that allow detection of complex analytes such as soil contaminants and explosives, which can be dispersed in the various of liquid and solid. Nevertheless, it remains a challenge to create a lab-on-a-chip (LoC) platform for on-line detection of small analytes volumes (below the few femtoliters), with high sensitivity, specificity and reliability. It is expected that the combination of microfluidics and plasmonic will create a highly sensitive and affordable lab-on-a-chip platform for the solving of above mentioned challenge. The proposed approach will utilize the unique advantages of microfluidics that explore and uses unusual behavior of microscale-restricted liquids and surface-enhanced Raman analytical method, which is able to recognize the single molecule of the targeted analyte. In this work, we demonstrated the model of a microfluidic micromixer incorporating with a plasmon active substrate. The design and realization of proposed experimental concept include the solving of following tasks: (i) utilization of Comsol software for mathematical simulation of possible processes in microfluidic mixer; (ii) preparation of microfluidic platform using 3D printing; (iii) application of excimer UV laser large-scale patterning and local gold deposition for creation of plasmonic active area. Our LoC platform allows detection of model analyte (R6G) at concentrations down to 10 fM (10^{-15} mol·L^{-1}). Proposed unique features are the key to new scientific experiments and innovations in the field of lab-on-a-chip devices and analytical approaches.

Keywords: Lab-on-a-chip, SERS, R6G, 3D printing, microfluidics system

1. INTRODUCTION

In recent years, many advances in science are associated with a reduction in the size of various analytical devices and the improvement of their characteristics [1-4]. One of the more promising trends in this area is microfluidic-based analytical platforms. Utilization of microfluidic allows managing the small volumes of liquids (of the order of micro-and nanoliter). Moreover, the microfluidics made it possible to develop a new class of devices - so-called lab-on-a-chip complex arrangement (LoC) [5-7]. The use of LoC modules in medicine, biology, pharmaceuticals, industry and other fields opens the new opportunities for significantly reducing the cost, complexity and timing of various analyzes and scientific research. Development of LoC can be closely attributed to the utilization of surface enhanced Raman spectroscopy (SERS). The SERS phenomenon is the result of localized surface plasmon resonance (LSPR). LSPR arises due to the excitation of a collective oscillation of electrons inside a metallic nanostructure induced by incident light, which leads to a huge optical amplification of the near field near the surface of metal nanostructures [8, 9]. It has been scientifically proven that the surface geometry of metallic nanostructures (size, shape, periodicity) [10-12] affects the intensity and distribution of the electromagnetic field on SERS substrates. This in its own way leads to the creation of a “hot spot” effect. Such a structure can be a nanoscale lattice.

So, SERS can be considered as a fundamental method for chemical analysis of small materials amounts, since it can be used to detect analytes adsorbed on metal structures at low concentrations [13-16]. The first priority to create the effective SERS-based component of microfluidic device is to increase the sensitivity of the

SERS signal, which can be implemented in a combination of Raman scattering and microfluidics. In this paper, we propose novel technique for the fabrication of periodic metal grille inside 3D microfluidic channel using femtosecond laser processing. The resulting 3D microfluidic SERS chip was tested using the model analyte (R6G). The results show that the microchips developed by us can work as 3D microfluidic SERS chip for super-sensitive online measurements with high performance.

2. EXPERIMENTAL

2.1. Materials

3D microfluidic model was formed with polymer Clear resin (purchased from Formlabs, USA). Isopropyl alcohol (≥98.5 %), deionized water, Rhodamine 6G (R6G) were purchased from Sigma-Aldrich and used without further purification. The target for Au deposition (purity of Au was 4 N) was purchased from Safina.

2.2. Sample preparation

The 3D model was made using 3D printing (the model is shown in **Figure 1**). Model for printing was performed in the program COMSOL Multiphysics. After the model printing the created samples were irradiated by UV-source for 30 min and dried at 24° C for 2 h.

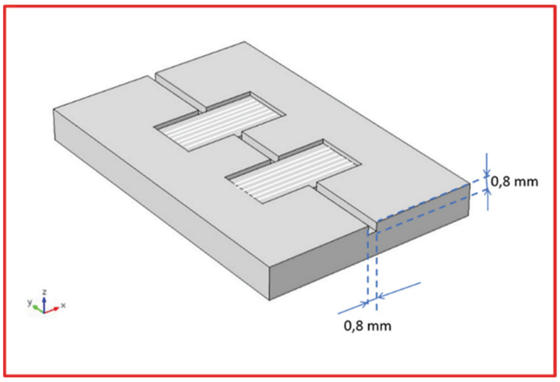

Figure 1 The 3D model of microfluidic chip, used for further 3D printing and deposition of surface plasmon-polariton areas

Grating preparation

Polymer films (Solution of epoxy resin, photoresist Su-8, purchased from Microchem, Germany) were spin-coated (1000 rpm, 10 min) from a solution onto 3D microfluidic SERS chip surface. The prepared samples were dried at 60°C for 24 h, irradiated by UV-source for 30 min and annealed at 90°C for 2 h. Pattering procedure of Su-8 film was performed using the excimer laser irradiation (KrF excimer laser, COMPexPro 50F, Coherent, Inc., wavelength 248 nm, pulse duration 20-40 ns, repetition rate 10 Hz) [15]. The laser beam was polarized linearly with a cube of a UV-grade fused silica with an active polarization layer. The samples were irradiated with 3000 laser pulses with laser fluencies above 9 mJ cm^{-2}. The angle of laser beam incidence with respect to the sample surface normal was 45° and the periodic surface structures were created on the Su-8 surface with 1×2 cm^2 patterned area size. The Au was deposited onto a patterned surface by vacuum sputtering (DC Ar plasma, gas purity of 99.995 %, a gas pressure of 4 Pa, a discharge power of 7.5 W, sputtering time 200 s, resulted thicknesses 25 nm). The deposition of Au was accomplished from Au target (purity of 99.99 %, provided by Safina, Czech Republic).

Surface measurement techniques

For characterization of sample surface, the peak force AFM technique was applied. Surface mapping was performed with Icon (Bruker) set-up on the areas of 8×8 $μm^2$.

Microfluidic SERS investigations- concentration dependence

In the 3D microfluidic SERS chip was to filed water solutions of R6G in different concentrations 10^{-6} M, 10^{-8} M, 10^{-10} M, 10^{-12} M, 10^{-14} M and the SERS response was on-line collected from the gold grating surface. Raman scattering was measured on portable ProRaman-L spectrometer (Laser power 20 mW) Raman spectrometer with 785 nm excitation wavelengths. Spectra were measured 120 times, each of them with 3 s accumulation time.

3. RESULTS AND DISCUSSION

The morphology of excimer-created gold grating was measured using the AFM technique and typical periodical surface pattern is presented in the **Figure 2A**. As is evident the surface topography represents a well ordered grating array, with sinusoidal shape. As was proven in our previous work such geometry of metal surface is favorable for the excitation and propagation of so-called surface plasmon-polariton. At the other word, photon entrapping the metal grating surface will lead to the appearance of plasmon waves, which focused the light energy near the surface and allow the efficiently exciter the SERS phenomenon. To evaluate the SERS performance of nanostructure the typical Raman analyte, R6G was used. In particular, the SERS spectra were acquired in the microfluidic chip at ambient temperature, using a customized microscopic Raman spectrometer equipped with a 780 nm excitation laser and a spectrometer grating having 500 grooves per mm. During the test, the R6G solutions of varied concentration were loaded into a syringe and then injected into the microfluidic microchannel with SERS active area using a syringe pump. (**Figure 2B**) **Figure 2C** shows the typical SERS spectra of R6G solutions of with different concentrations (from 10^{-6} to 10^{-14} mol·L⁻¹). Characteristic R6G SERS bands can be clearly distinguished in the **Figure 2C**: 605, 771, 1185, 1310, 1355, 1505, 1602, and 1645 cm $^{-1}$ are identified [17]. As can be expected the intensities of the peaks of Raman scattering gradually decrease with the decreasing of R6G concentration The SERS signal becomes almost unnoticeable at a concentration below 10^{-14} mol·L⁻¹.

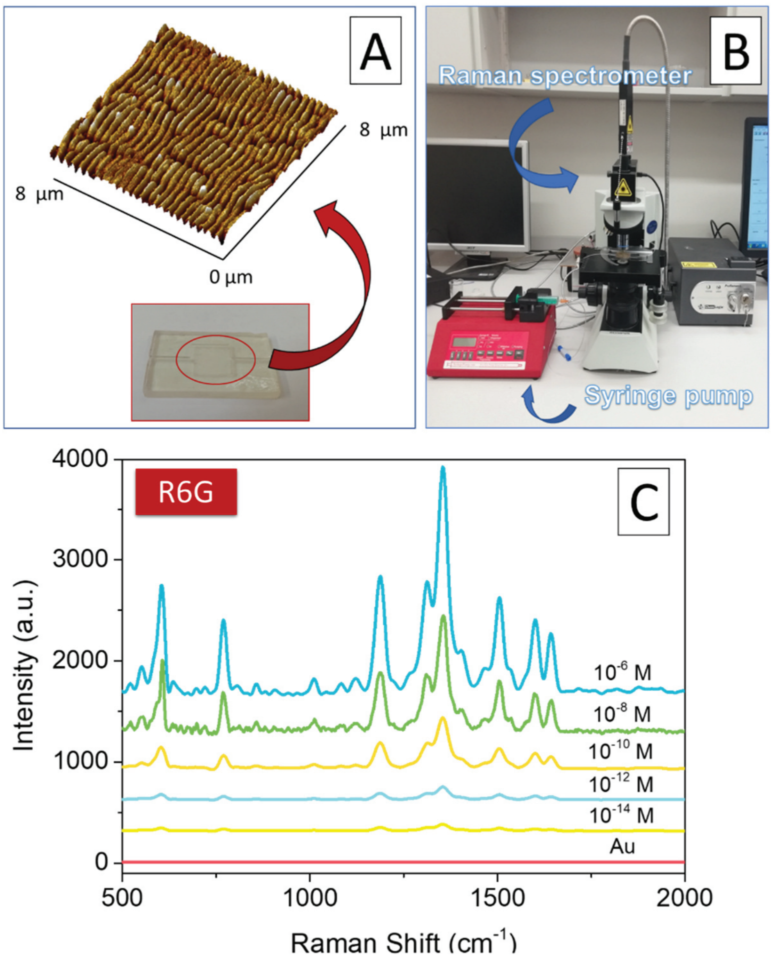

Figure 2 A) The photo of SERS-active microfluidic chip and the AFM-characterized periodic metal grating surface; B) the experimental setup used to perform the on-line SERS measurements in the microchannel; C) Raman spectra of R6G water solutions with varying concentrations, measured using proposed microfluidic SERS-active chip.

The enhancement factor (EF) of the SERS signal was determined by calculating the analytical gain using the following equation: $(EF) = (I_{sers} * N_{ref})/(I_{ref} * N_{sers})$ [18] (10^{-6} M concentration of the

R6G solution was used). The I_{SERS} and I_{ref} are the Raman intensities from the sensor and a reference measurement from a bulk sample; N_{SERS} and N_{ref} are the number of molecules contributing to the corresponding Raman intensity, respectively. In our case, calculations were made for a microfluidic SERS chip with and without a grid. Since the molecule numbers are the same in our case, the Raman intensities were used directly for SERS EF calculations. To determine the EF parameter, a peak of 1355 cm^{-1} was chosen and the EF was found to be equal 10^8. So, in our case, the microfluidic SERS chip with a lattice shows a pronounced enhancement of SERS in the combination with the possibility to analyze the small samples volume.

4. CONCLUSION

In this paper, we proposed a novel technique for the fabrication of plasmon-active SERS component inside 3D microfluidic channel using femtosecond laser surface pattering, followed by the deposition of thin metal film. An experimental model of a microfluidic channel was made using 3D printing. The created structures were applied for real-time surface-enhanced Raman spectroscopy (SERS) measurements of small samples volumes. Created microfluidic SERS platform allows detection of model analyte (R6G) at concentrations up to 10 fM (10^{-15} mol·L^{-1}). Proposed unique features are the key to new scientific experiments and innovations in the field of lab-on-a-chip devices and analytical approaches.

ACKNOWLEDGEMENTS

This work was supported by the Grant Agency of Health Ministry 15-33459A

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