PDMS NANOSTRUCTURES FABRICATED BY TWO-STEP MOLDING PROCESS USED FOR TUNABLE SERS INTEGRATED WITH MICROFLUIDICS
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ABSTRACT
We present a two-step molding process to fabricate the polydimethylsiloxane (PDMS) nanospheres using PDMS nanowell as mould, which replicates from self-assemble polystyrene (PS) spheres on silicon substrate. Such nanostructures can control the Raman scattering enhancement factor (EF) under outer pressure via microfluidics continuously. The EF of the surface enhanced Raman scattering (SERS) for detection of Rhodamine 6G (R6G) on such nanostructures reach $10^8$ times higher than that on smooth substrate. The calculated results of finite-difference time-domain method (FDTD) agree with the experimental data. The repeatable soft lithography method, which is simply and low cost, is expected to be utilized to develop SERS-based analytical devices.

KEYWORDS: SERS, Nanofabrication, Microfluidics, PDMS

INTRODUCTION
Despite numerous previous reports demonstrating the surface enhanced Raman scattering (SERS) effect for different molecules and substrates, there is still an ongoing search for better substrates for SERS-based chemical sensors. Indeed, as an ideal sensitive and widely applied optical detection for chemical and biological detection, SERS is known as ‘optical fingerprint’ for its representing the chemical and biological molecule’s unique vibrational frequencies which based on the inelastic scattering of photons by chemical entities [1, 2]. Such characteristic makes SERS successfully utilized for distinguishing different molecules. And, as a solution to the low efficiency of Raman scattering, SERS provides a significantly increase of Raman scattering. Such effects are achieved mostly by exploiting the electromagnetic resonance properties of Au nanoparticles or roughened surface. A reliable SERS substrate can have an extremely high enhancement factor. However, the SERS effect on a nano-structured substrate has not been fully understood yet, mainly because the nanogap between two nano-components, which is believed critical for plasmon coupling, cannot be continuously changed. To get a better understanding the mechanism of SERS, we fabricate a PDMS substrate that can change the spacing among nanostructures continuously under microfluidic pressure.

APPROACH
Previous experiments have shown that the spacing between two metal nanoparticles affects the EF of SERS [3, 4]. The lack of reliable techniques for controlling the properties of the local field at the metal surface has been a major experimental limitation in the quantification and understanding of SERS. Since the wavelength we use in this experiment is 633 nm, such length is greater than almost all the distances between the nanostructures, which is a typically near field situation. Near field situation will gradually turn into far field situation as distance arises, and it is expected to observe a declination in the Raman intensity as such distance increases slightly. To control the spacing among the nano-components continuously, a practical method for changing the distance among the nanostructures is to control the pressure of the microfluidics chamber. The pressure of the chamber can control the deformation of the PDMS substrate and then change the gap between two nano-structures. Based on such ideas, we propose a tunable nano-structured substrate, which enables tunable SERS and, therefore, offers an opportunity to reveal essence of SERS dependent on the spacing among nano-components on PDMS substrate. The schematic diagram of an integrated microfluidic chip is shown in Fig. 1.

Figure 1: Schematic diagram of the integrated microfluidic chip and the biomolecular Raman imaging system

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EXPERIMENTAL

We first dropped proper density of 400-nm polystyrene (PS) sphere ethanol solution on the silicon wafer to form monolayer polystyrene nanospheres by self-assemble. With the surface tension of ethanol during evaporation, PS spheres were automatically assembled into a highly-ordered structure (Fig. 2). The fabrication process of the Au/PDMS nanostructures is shown in Fig. 3. The nano-pattern of the self-assembled nanospheres was then transferred to the PDMS substrate using a two-step molding process. We fabricated PDMS nanowell using self-assemble PS sphere as mould first. The nanowells were replicated from self-assemble PS spheres (Fig. 4). We then fabricated PDMS nanostructure using the nanowell as mould (Fig.5). Such nanosphere-shaped structures can be used for SERS after evaporating a 50-nm thick Au film. Our soft lithography-based nanofabricated SERS substrate is batch-processed and mass-reproducible since it can be repeatedly replicated from only one master copy.

The different solutions of R6G were dropped on the PDMS nanostructures coated with Au film, and then water was pumped in the under chamber to control the spacing between the PDMS nanostructure. Meanwhile, the SERS was obtained.

RESULTS AND DISCUSSION

We started from 10 μg/mL R6G solution and increased the concentration gradually until 40 μg/mL. A much stronger signal of Raman spectroscopy was detected on such Au/PDMS nanosphere-shaped structures than on smooth substrate under different R6G solutions (Fig. 6). A tremendous difference of Raman signal was observed on two different substrates. Almost all the characteristic Raman peaks of R6G molecules were distinctive in the spectrum taken on the Au/PDMS nanosphere-shaped structures, while only a few peaks such as 1194, 1276, 1358 and 1645 cm⁻¹ peaks were strong in the spectrum. The EF could be up to 10⁸ times higher than that of the smooth Au/PDMS substrate.

Since PDMS is flexible, the distance between each unit of nanostructures can be changed as the micro-chamber pressure increase. Its Raman signal was detected when solutions of R6G flow through. Fig. 7 indicates the significant change of SERS signals with and without stretching the Au/PDMS nanostructures. Some reason for this change is that the distance between the PDMS nanostructure increasing maybe result the coupling of electric field between the sample and the Au/PDMS nanostructures.

Via FDTD method, the EF differences can be simulated for the near field of the nanowell-shaped and Au/PDMS nanosphere-shaped structures (Fig. 8). Seen from the results, two-step molding Au/PDMS nanosphere-shaped structures have a much higher EF than that of the complementary nanowell-shaped structures and, also, the one with enlarged gaps. Enlarging the gap width actually can change the EF to a much lower level. Such simulation results well fit the experimental results. The Au/PDMS nanosphere-shaped structure is an ideal highly active tunable method for SERS due to the PDMS nanostructure’s easily-controllable property.

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CONCLUSION
In summary, we have demonstrated the Au/PDMS nanoshpere-shaped structure as a highly active, tunable SERS substrate. The SERS intensity of sample molecules depends critically on the gap width. This kind of measurement, which allows mass production of identical SERS active sites on economical polymer substrates, will provide us a better understanding of the mechanism of single-molecule-SERS. Such large scale monolithic integration of the Au/PDMS nano-PDMS-sphere in microfluidics promises label free detections of biochemical reactions.

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