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Surface Enhanced Raman Scattering Sensing with Nanostructures Fabricated by Soft Nanolithography

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The nanospike structures formed with femtosecond laser irradiations have been successfully replicated on the surface of a polyurethane (PU) polymer using a low cost soft nanolithography method. The surface enhanced Raman scattering (SERS) of rhodamine 6G (Rh6G) and dinitrotoluene (DNT) molecules have been measured with silver coated PU nanospike surfaces by a simple portable Raman spectrometer. Compared to a flat silver coated surface, where no Raman Scattering of the molecules can be detected by the simple portable Raman spectrometer, the Raman spectra are enhanced by more than 4 orders of magnitudes. This indicates that the high area/volume ratio and small size of the PU nanospikes can be used for SERS sensing.

Keywords: Surface enhanced Raman scattering, sensing, nanospike, soft nanolithography

1 Introduction

Raman spectroscopy is a powerful tool that provides the fingerprint for the unique chemical identification of molecules. However, for most of the molecules the Raman scattering signals are very weak, which limits its potential applications. Surface enhanced Raman scattering (SERS) method can be used to enhance the weak Raman scattering signals because of the local plasma resonance modes produced by irradiations on a microscopically rough metal surface (1). The magnitude of the enhancement can be obtained up to the order of $\sim 10^6$ (2–5), and even the order of $\sim 10^{14}$ for the single molecule measurement (6, 7). The silicon nanospikes, with a diameter of 50∼150 nm, can be formed with the femtosecond laser irradiations (8–10). Such nanospiked structures have high area-to-volume ratio and small size, which is applicable for the SERS sensing. The soft nanolithography, based on the replica molding in polymers from the masters, is an important technique for nanoscience and technology (11–13). In this work, by combining the femtosecond laser irradiation with the soft nanolithography technology, we have successfully replicated the silicon nanospike structures with polymer, and fabricated the SERS sensing systems on the polymer nanospike substrates at very low cost.

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2 Experimental

As described in previous papers (8–10), silicon nanospikes were fabricated by irradiating the surface of the silicon substrate in water by a femtosecond laser with a frequency-doubled output (400 nm wavelength, 100 fs pulse, 1 kHz frequency) from an amplified Ti:sapphire laser. The soft nanolithography (12) fabrication procedure of nanospikes is shown in Figure 1. First, the as-fabricated silicon wafers with nanospikes were rinsed in HF solution to remove the oxide layer, oxygen plasma treated for about 5 min, and coated with 1H,1H,2H,2H-perfluorooctyltrichlorosilane (Fluka) in a vacuum chamber. Then, the poly(dimethylsiloxane) (PDMS) mold was made with a spin-coated hard-poly(dimethylsiloxane) (h-PDMS) (∼100 μm thick) as the contact layer with the nanospike surface, and a layer of soft-poly(dimethylsiloxane) (s-PDMS) (∼2 mm thick) as a back layer. Finally, the nanospike structures were replicated on the surface of the UV-curable polyurethane (PU) polymer by lightly pressing the PDMS mold onto the PU glue (Norland Optical Adhesives, NOA 73; Cranbury, NJ) on a glass substrate and UV-curing for about 5 min. In our experiment, tens of PU replicas were fabricated from each PDMS mold. For measurement of the SERS signal, an approximately 100 nm thick silver layer was thermally evaporated on the nanospiked PU surface. The Raman-scattering measurements were conducted on a portable Raman measurement system (Raman Systems R-3000, the resolution is about 10 cm^{-1}) equipped with a semiconductor laser of a 785 nm excitation wavelength and an adjustable power of 90∼290 mW.

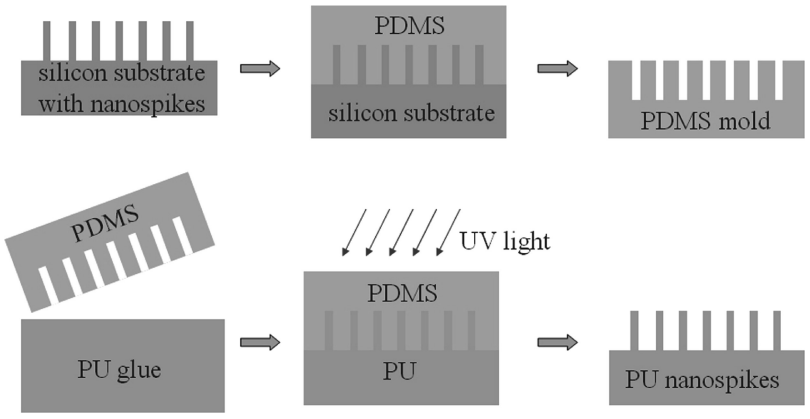

Fig. 1. Schematic illustration of the soft nanolithography fabrication procedure for replicating the nanospike structures.

3 Results and Discussions

The morphologies of the as-fabricated PU nanospikes were analyzed using a field emission scanning electron microscope (FESEM) (JOEL JSM-7401F). The typical FESEM images of the PU nanospike structures 1st and 10th replicated from the same PDMS mold are shown in Figure 2 at two different magnifications. To better observe the effect of the replications, we used the TEM copper grids (SPI, hexagonal, 200 mesh) as the mask during fabricating the silicon nanospikes. As shown in the left images at 2000× magnification of Figure 2, we can see that both the 1st and 10th replicas have the same profile of the hexagonal structure, and even the featured defects of the structure have been replicated. Their FESEM images at higher magnification are shown in the right of Figure 2. We can clearly observe and compare each nanospike in the 1st and 10th PU replicas. The images show that every corresponding nanospikes in the two replicas have the same shape and the deviations of the edge are less than 5 nm. It indicates that the nanospike structures can be replicated within 5 nm deviation for more than 10 times. Furthermore, we believe that such replication using just one PDMS mold can be made many times without change of the feature of the nanospikes.

The SERS characteristics of the rhodamine 6G (Rh6G) and dinitrotoluene (DNT) molecules have been measured on the replicated PU nanospike structures and the flat PU surfaces which are both coated with a 100 nm thick silver layer. The Raman spectra of Rh6G molecules (14, 15) are shown in Figure 3. The concentration of the Rh6G in water we used in the experiment is about 10^{-7} mol/L. We can see that there is no Raman scattering signal of Rh6G molecules on the flat PU surfaces because of the low concentration. However, the Raman signals of the Rh6G molecules can be clearly observed using the replicated nanospiked PU surface. The sharp peaks indicate that the Raman signals of

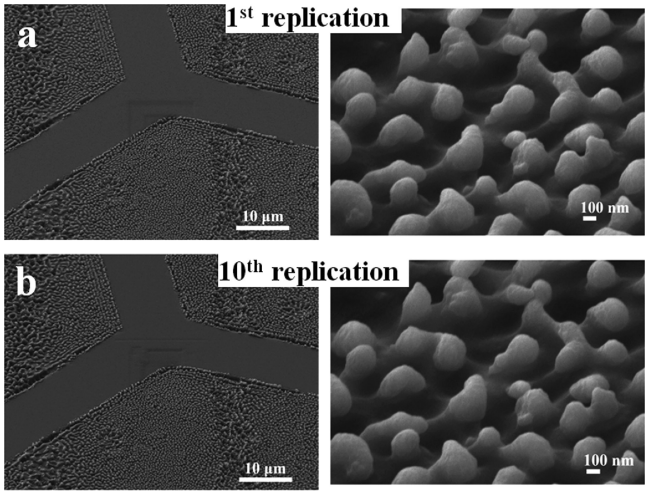

Fig. 2. The SEM images of PU nanospikes at two different magnifications, which were replicated from the same nanospiked silicon surface. (a) The 1st replication; (b) the 10th replication.

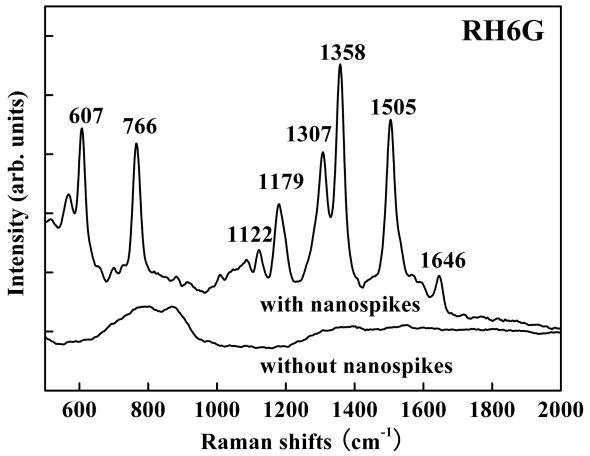

Fig. 3. The Raman spectra of Rh6G molecules measured with the replicated PU nanospike structures and the flat PU surfaces. The Raman data collection time is 10 s and the laser excitation power is about 90 mW.

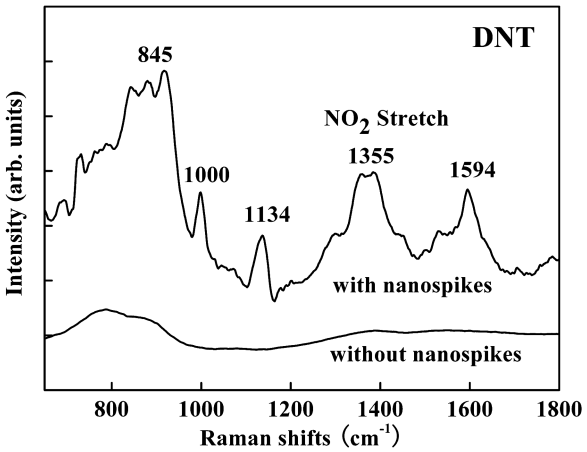

Fig. 4. The Raman spectra of DNT molecules measured with the replicated PU nanospike structures and the flat PU surfaces. The Raman data collection time is 10 s and the laser excitation power is about 90 mW.

the Rh6G molecules have been enhanced by more than 4 orders of magnitudes with the silver coated PU nanospike structures. This is because of the high area/volume ratio and small size of the PU nanospikes, which will increase the number of molecules close to the surface and produce many more plasma modes on the surface. The 2,4-dinitrotoluene (2,4-DNT) is one of the precursors and manufacturing impurities of the TNT, which is important for the detection of explosives. In this experiment, the concentration of the DNT in methanol is about 5×10^{-5} mol/L. The Raman spectra of DNT molecules (16) are obtained and shown in Figure 4. The results are similar to that of Rh6G molecules, which indicates that the SERS characteristic of the PU nanospike structures can be applied to variety of materials such as a protein (17). The Raman spectra of the Rh6G and DNT molecules have been also measured using different replicated PU nanospike structures and the same results were obtained. This indicates that the characteristics of sensing are repeatable during the replication process.

4 Conclusions

In conclusion, the SERS signals of Rh6G and DNT molecules are successfully obtained from the PU nanospike structures which are replicated by the soft nanolithography method. The Raman signals have been enhanced by several orders of magnitudes because of the high area/volume ratio and small size of the PU nanospikes. It demonstrates that the highly sensitive, repeatable and low-cost SERS sensing systems can be easily fabricated by using the nanospike structures formed by femtosecond laser irradiation and the soft nanolithography.

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