Field Enhanced SERS on Silver Nano-Particles Substrate Covered with a SiO2 Buffer Layer

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Abstract—The field enhanced Raman scattering of crystal violet (CV) molecules, excited by localized electromagnetic field of silver (Ag) nano-particles, is elucidated. In the study, a SiO2 buffer layer with a gradient thickness is employed to prevent the electron-transfer from the Ag nano-particles to the CV molecules. Using a laser beam of 532nm to probe the CV dye, the Raman scattering intensity was a function of the thickness of the SiO2 buffer layer. The maximum intensity of Raman signal was observed at the thickness of 8.5nm, where revealed a 61% increase of Raman scattering than that on an Ag nano-particles substrate without SiO2 buffer layer. The field enhanced Raman scattering leads to a potential to improve the sensor sensitivity.

Keywords—field enhancement; surface plasmon; sensor

I. INTRODUCTION

Surface Plasmon Resonance (SPR) of novel metallic nano-particle has been widely studied for sensor application. The resonance leads to an intense localized electromagnetic (EM) around metallic nano-particles and that strongly enhanced the Raman scattering of molecules or bio-molecules, as well known as surface enhanced Raman scattering (SERS). Based on SERS, it becomes convenience to sensing molecules or bio-molecules. Even a weak scattering from an individual molecule is detectable owing to the SERS of metallic nano-particle. However, the SERS mechanism is not clear due to the complicated interaction between the sensing target and the metallic nano-particles. A well understanding to SERS mechanism is important to advance sensor application.

Charge-transfer and electromagnetic field enhancement are two main mechanisms for SERS. In the study, we fabricated substrates of silver (Ag) nano-particles covered with or without a SiO2 film as sensing base to discriminate the two SERS mechanisms. The crystal violet (CV) dye as the sensing target was then coated on the substrates. The Ag nano-particles substrate without and with SiO2 cover represented the mechanism of the charge-transfer and field enhancement, respectively. With a probe of 532nm laser beam, the SERS signal of CV dye was excited and measured by a detector. In addition, a SiO2 layer with a gradient thickness was used to understand, in detail, the mechanism of field enhancement. The experiment and result will go with in the following sections.

II. EXPERIMENT

A. Sample preparation

Figure 1 (a) ~ (e) show the fabrication of sensing substrate of silver nano-particle, covered with a SiO2 buffer layer. The thickness of the SiO2 layer exhibits a gradient variation. In Fig. 1(a), a 6-nm silver film is thermally deposited on a glass substrate. After an annealing process of 250°C for 3 min, silver nano-particles (in Fig. 1(b)) form on the substrate. Then, an L-shaped plate as a mask is attached on the substrate, as shown in Fig. 1 (c). During the deposition process of the SiO2, a SiO2 layer with a gradient thickness is obtained by rotating the substrate from the z axis. The rotating speed was 0.14 degree per second. Figure 1 (d) shows substrate of silver nano-particles covered with a SiO2 buffer layer and the thickness of the SiO2 film gradually increases from position a to position b. The distance between two points is 10 mm. The CV dye doped in Polyvinyl Alcohol (PVA) is eventually spin-coated on the substrate, as shown in Fig. 1(e). It is well known that the surface plasmon resonance of Ag nano-particles depends on the surrounding environment. Herein, the SiO2 buffer layer with a gradient thickness results in a spatially-gradient modulation on the SPR of Ag nano-particles to affect the enhanced Raman signal of crystal violet (CV) dye.

Figure 1. The fabrication of sensing substrate of silver nano-particle, (a) a 6nm-thick silver film coated on a glass substrate, (b) silver nano-particles formed on the glass plate through annealing process, (c) L-shape plate as a mask and rotating the substrate for controlling the deposition of SiO2 film (d) a tapered SiO2 film obtained on the substrate, (e) CV/PVA was eventually coated on the substrate.
B. Experiment Setup

Figure 2 (a) shows the cross section of silver nano-particle substrate covered with a SiO$_2$ layer. The photo was shot by a Transmission Electron Microscope JEM-2100JEM (JEOL Inc.). A graphic layer was deposited on SiO$_2$ layer for improving TEM analysis. The silver nano-particle in the figure is located at the point c (5mm far from point a) on the substrate in Fig. 2 (b). It was found that the silver nano-particles were homogeneously covered by the SiO$_2$ buffer layer. The size of silver nano-particle was ~50nm and the thickness of SiO$_2$ layer was ~8.5 nm. The TEM pictures also showed that the thickness (d) of the SiO$_2$ buffer layer was gradually increased from position a (d = 0nm) to position b (d=18nm). Fig. 2 (c) reflects the section at around point c. It should be noted that the electron-transfer between CV molecules and silver nano-particles was prevented as a result of the SiO$_2$ buffer layer.

![Figure 2](image)

Figure 2. TEM analysis of silver nano-particle substrate, (a) TEM images of SiO$_2$/Ag nano-particle, (b) the probed position at point c on the substrate, and (c) the cross section of the substrate.

C. Experiment Setup

Figure 3 shows the experimental setup for measuring the SERS signal of CV molecule on sensing substrates. A cooling CCD (1024x256 pixels, Horiba Jobin Yvon Inc.) combined with a monochromator (with a 1200 lines/mm grating) is employed to measure the SERS signal of CV molecules. The Raman scattering spectra ranged from 400 to 2000 cm$^{-1}$ were obtained by continuously accumulating the Raman signals within 90 seconds per spectrum. A notch filter was used to eliminate the signal from light source (a 532nm laser, CVI MG Inc.). A fiber collimator collected the signal of Raman scattering emerged from the CV molecule. The spot size and intensity of probe laser beam was 2 mm in diameter and 17 mW, respectively. Using the prepared SiO$_2$/Ag nanostructure as a sensing substrate for SERS, the excited SPR field of Ag nano-particle depended on the probed position on the substrate. The position dependent SPR also affected the SERS of CV molecule.

![Figure 3](image)

Figure 3. Experiment setup for SERS measurement.

III. EXPERIMENT RESULT

Figure 4 shows the intensity of Raman scattering of CV molecule. The blue, red, and orange line, respectively, represents the Raman signal of CV molecule on sensing substrates (blue-line: Ag film without SiO$_2$ coverage; red-line: Ag nano-particle substrate without SiO$_2$ coverage, and orange-line: Ag nano-particle substrate with SiO$_2$ coverage). Comparing blue and red lines, it was found that the CV molecule on Ag nano-particles substrate revealed stronger Raman signal than that on Ag film. The result was attributed to the occurrence of SPR of Ag nano-particles, which enhanced the CV Raman signal. Additionally, the comparison of red and orange lines, the Raman signal on the Ag nano-particles substrate with SiO$_2$ coverage was enhanced 61% at the peak of 1170 cm$^{-1}$ than that on substrate without SiO$_2$ coverage. The intense EM field due to the excited SPR of Ag nano-particles may be the cause to the stronger enhancement in Raman signal.

![Figure 4](image)

Figure 4. SERS spectra of the CV molecules absorbed on silver film and SiO$_2$/Ag nanostructure at positions point c.

Figure 5 shows the intensity of the Raman spectra of CV molecule at probed position of 1, 3, 5, 7, and 9 mm on Ag nano-particles substrate with SiO$_2$ coverage. The intensity of the Raman signals was at 1170 cm$^{-1}$ in the spectrum. It was noted that the intensity of the Raman’s signals was a function
of probed position. The SERS intensity increased as the position was shifted from point a to point c. Then, the signal decreased. The maximum intensity of SERS occurred at point c, where the thickness of SiO$_2$ coverage was ~8.5 nm. It had to be noted that the thickness of the SiO$_2$ buffer layer depended on the probed position. The SiO$_2$ thickness varied from 0 to 18 nm between point a and b. The result showed that the gradually increased thickness of the SiO$_2$ buffer layer affected the SERS enhancement of CV molecule.

![Figure 5](image-url)

Figure 5. Intensity of Raman scattering at 1170 cm$^{-1}$ was plot against probed position. Units

Since the enhancement due to the charge-transfer transition was neglected because of the SiO$_2$ buffer layer, the enhanced Raman scattering of CV molecule was attributed to the EM field enhancement. In the study, it was noticed that two major factors could affect the magnitude of the SERS lights, which are the local EM field, the SP resonant wavelength. When the thickness of dielectric SiO$_2$ coverage on the Ag nano-particle was increased, the SP resonant wavelength of the Ag nano-particle shifted to red band. As the SPR was closed to the excitation wavelength of CV dye, we could observed the maximum enhancement of the SERS of CV molecule.

The decay of the SERS intensity for the thickness of the SiO$_2$ coverage beyond 8.5 nm was considered due to the cause of the nature decay of localized EM field. In our case, the decay increased far than 10 nm from the nanoparticle’s surface. The power decay of the EM fields due to the distance from the surface of the Ag nano-particle eventually overcomed the increase when the excited SPR of Ag nano-particle closed to the wavelength of the Raman modes of CV molecule. So that the increase of SERS intensity was declined when the SiO$_2$ coverage was beyond 8.5 nm. It should be reminded that the SPR field intensity of Ag nanoparticle decay from the surface of the Ag nano-particle. The decay induced a decrease of SERS signal.

IV. CONCLUSION

In conclusion, the field enhanced Raman scattering of crystal violet (CV) molecule had been demonstrated by using an Ag nano-particle substrate with a SiO$_2$ cover of a gradient thickness. The field enhancement was stronger than the effect of electron-transfer between the CV molecule and the Ag nano-particle. Besides, the enhanced signal depends on the probed position of sensing substrate. The maximum intensity of SERS occurred at point c, where the thickness of SiO$_2$ coverage was ~8.5 nm. The sensing substrate of metallic nano-particle revealed potential applications of large-area sensing biosensor and of molecular structure analysis. The SiO$_2$ also prevent some demolition on sensing target as the electron-transistion occurred.

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REFERENCES


