Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Localized and Propagating Surface Plasmon Co-Enhanced Raman Spectroscopy Based on Evanescent Field Excitation

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1. LSPs effect caused by the vacuum deposition silver film

The silver film prepared by the vacuum deposition method is not an absolutely flat film, and has a certain level of roughness. The AFM image of the silver film is shown as follow. The roughness (RMS) is 2.141nm. So we should consider the contribution of rough silver film induced local surface plasmons on the SERS enhancement factor (EF).

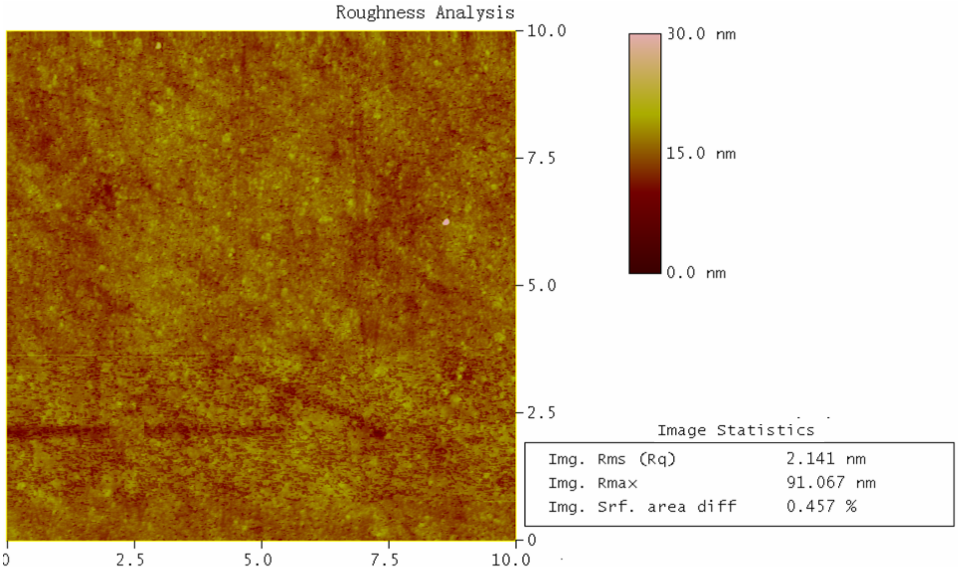

Figure 1S. The AFM image of the silver film prepared by the vacuum deposition method.

We measured the SERS EF come from the LSPs caused by rough silver via excitation of the 4-Mpy adsorbed on the silver film from the air side (figure 2S (b)). In this excitation way, the propagating SPR effect can be ignored due to without a prism as a coupling element. So the LSPs effect plays a main role. This SERS EF reflects the contribution of the LSPs located at the surface of the vacuum-deposited silver film.

The SERS enhancement factor is calculated by comparing the SERS signal excited the 4-Mpy adsorbed on the silver and the Raman signal of 4-Mpy. Sample for SERS measurements was prepared by the drop-coating of the 4-Mpy (10 μL, 10^{-6} mol/L) aqueous solution onto silver film deposited on the bottom of prism, and then the substrate was dried in room temperature. After the solvent evaporating (2 hours later), the solution formed a circular deposit with the diameter of 4.0 (±0.5) mm. The average surface coverage was calculated to be 4.63×10^{13} molecules/cm^2. Thus, the average occupied area of per 4-Mpy molecule is supposed to be about 2.2×10^{-14} cm^2, which is obviously larger than the maximum surface area per 4-Mpy (about 7.0×10^{-15}cm^2).[1] So, we can infer that the 4-Mpy deposited film was a monolayer. Sample for the normal Raman measurement was prepared by dropping the 4-Mpy (10 μL, 10^{-3} mol/L) aqueous solution onto a normal K9 prism. The solution formed a circular deposit with the diameter of 3.1 (±0.5) mm.

Here, we adopted the estimation of the SERS enhancement factor (G) reported by Gupta and Weimer[2] as:

$$G = \frac{I_{Surf} / N_{Surf}}{I_{Raman} / N_{Raman}} = \frac{I_{Surf}}{N_{Surf}} \times \frac{N_{Raman}}{I_{Raman}} \qquad (1)$$

where the N_{Raman} and N_{surf} denote the number of probe molecules which contribute to the normal and SERS signals, while the I_{Raman} and I_{surf} denote the corresponding normal Raman and SERS intensities. In our experiment, because the 4-Mpy adsorbed onto the sliver was a monolayer, the G can be written in the following form,

$$G = \frac{I_{Surf}}{A\times\frac{M_{Surf}}{s_{Surf}}} \times \frac{A\times\frac{M_{Raman}}{s_{Raman}}}{I_{Raman}} = \frac{I_{Surf} \times s_{Surf} \times M_{Raman}}{I_{Raman} \times s_{Raman} \times M_{Surf}} \qquad (2)$$

where the M_{surf} *and* M_{Raman} are the number of 4-Mpy molecules dropped onto a sliver film coated prism and a normal prism. The S_{Surf} and S_{Raman} are the geometrical areas of the 4-Mpy casting film. A is the recorded area of a laser spot. Since SERS and Raman spectra were obtained under same excitation angle, the laser spot area of normal Raman can be ignored. The representative band at 1012 cm^{-1} due to ring-breathing (the band is at 992 cm^{-1} in the normal Raman spectrum.[3]) was selected to calculate the *G*. The SERS signal intensity at 1012 cm^{-1} is 127.7 cps and normal Raman signal intensity at 992 cm^{-1} is 16.5 cps (see Figure 2S (a)). The S_{Surf} and S_{Raman} are 0.13 and 0.08 cm^2. We calculated the EF by using the expressions (2) in the Supplementary Information. The value of EF is 1.3×10^4. The SERS EF obtained on the silver film by above method further approved that the silver is a rough one.

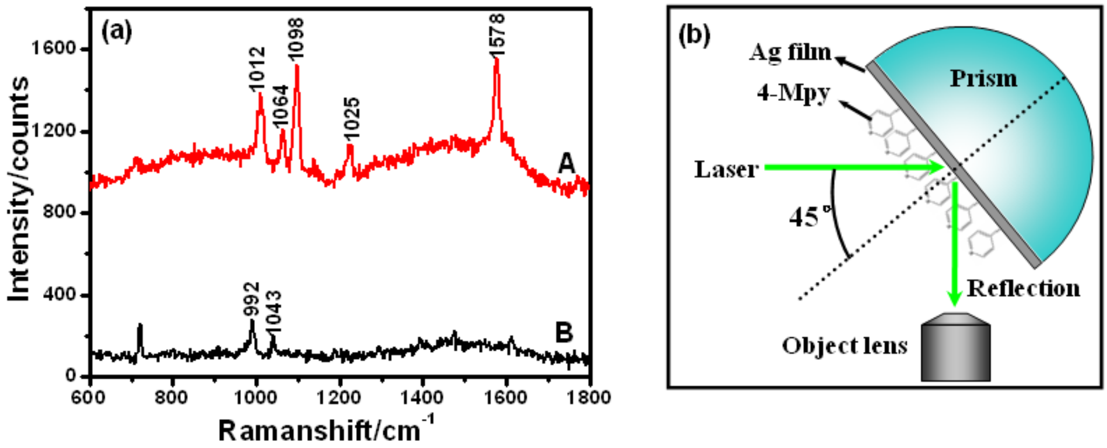

Figure 2S. (a) The SERS spectrum of 4-Mpy on silver film (Spectrum A, the integration time is 3s.) and normal Raman spectrum of 4-Mpy absorbed on a prism (Spectrum B, The integration time is 10s). All the spectra were measured by a 532 nm laser with the power of 8 mW. (b) The schematic diagram of measuring the SERS EF via excitation from the air side.

In addition, the SERS EF of 4-Mpy adsorbed on the silver film is as large as 10^6 based on the evanescent field excitation due to the effect of PSPs and LSPs. For a flat silver film, the enhancement factor (EF) is about 10^2 based on a Kretschmann configuration excitation.[4] While for a rough silver film, the SERS EF based on the Kretschmann configuration excitation originates from both the PSP resonance and the localized SP effects. For the Kretschmann configuration excitation, the electromagnetic field located at the silver film surface was enhanced by the PSP resonance effect.

And the localized SPR effect of rough silver film made the electromagnetic field further increased. Thus, the enhancement factor can reach 10^6 for a prism/silver film/air three layers structure based on Kretschmann configuration excitation.

In summary, we think the silver film used in our experiment is a rough silver film and the LSPs (caused by the rough silver film) increased the SERS signal obtained on a vacuum-deposited silver film based on evanescent field excitation. The SERS signal obtained on vacuum deposited silver film is come from the contribution of PSP effect and LSPs a certain extent LSPs on such a silver film.

2. Synthesis of silver nanoparticles

Silver colloid was prepared by Lee's method. [5] A 27.8 mg of $AgNO_3$ (Beijing Beihua Fine Chemical Co. Ltd.) was dissolved in 150 mL of distilled water and then the mixture was heated to boil. A 3 mL of sodium citrate solution (1 wt %) was added to above solution. The solution was kept boiling for 1 h under vigorously stirring. Then it was cooled to room temperature before use. Silver colloid shows yellow green color. The band position of its extinction spectrum (Figure 3S) locates at 416 nm.

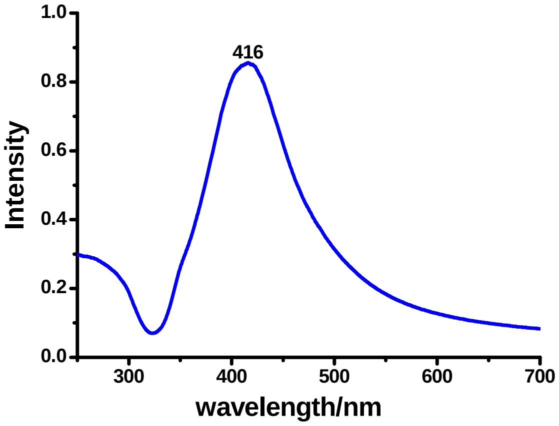

Figure 3S. Extinction spectrum of the silver colloid in present study.

3. Preparation of three different substrates (corresponding to Fig.2)

To prepare Substrate (a), a silver film was deposited on the bottom of a K9 prism (the refractive index is 1.52 at 532nm) via the vacuum evaporation method at the pressure of 8.0×10^{-4} Pascal. The thickness of the silver film is 45 nm.

Substrate (b) was prepared by self-assembly of probes on Substrate (a). In present study, 4-mercaptopyridine (4-Mpy, 95%, Sigma Co.) was used as a probe. Most 4-Mpy molecules can be bound to the silver film surface by their mercapto groups. The procedures are as follows. Different concentration of 4-Mpy aqueous solution was injected into a flow cell and mixed for half an hour. Then we injected water to remove the unadsorbed 4-Mpy.

Substrate (c) presents the formation of a silver film/4-Mpy/silver nanoparticles sandwich structure. Silver colloid was injected into the flow cell. Silver nanoparticles was captured by 4-Mpy and immobilized onto the silver film surface. The reaction was kept for an hour. After that, we injected water to wash the silver film surface. Most SERS measurement of 4-Mpy was carried out in the water surrounding except for the measurement of the enhancement factor, which was conducted in air.

4. Incident angle-dependent SERS spectra of 4-Mpy

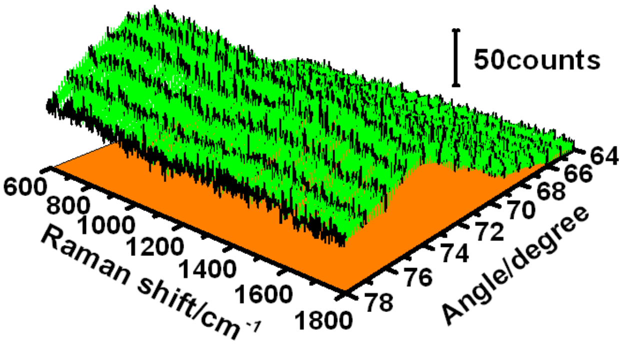

Figure 4S. Incident angle-dependent spectra of Substrate (a).

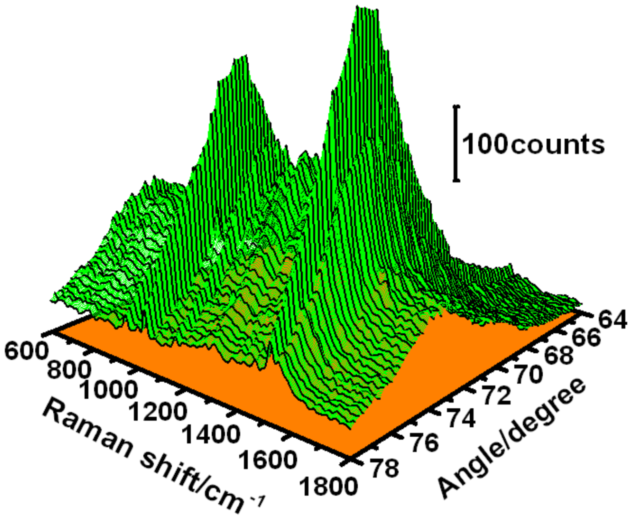

Figure 5S. Incident angle-dependent SERS spectra of Substrate (b).

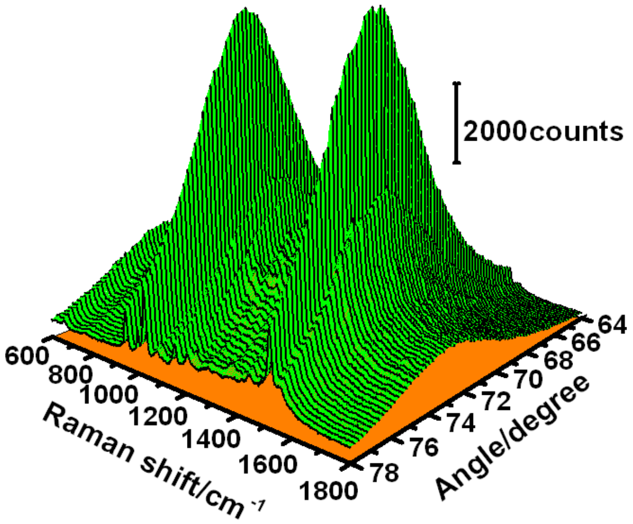

Figure 6S. Incident angle-dependent SERS spectra of Substrate (c).

5. Calculation for SERS enhancement factor of 4-Mpy

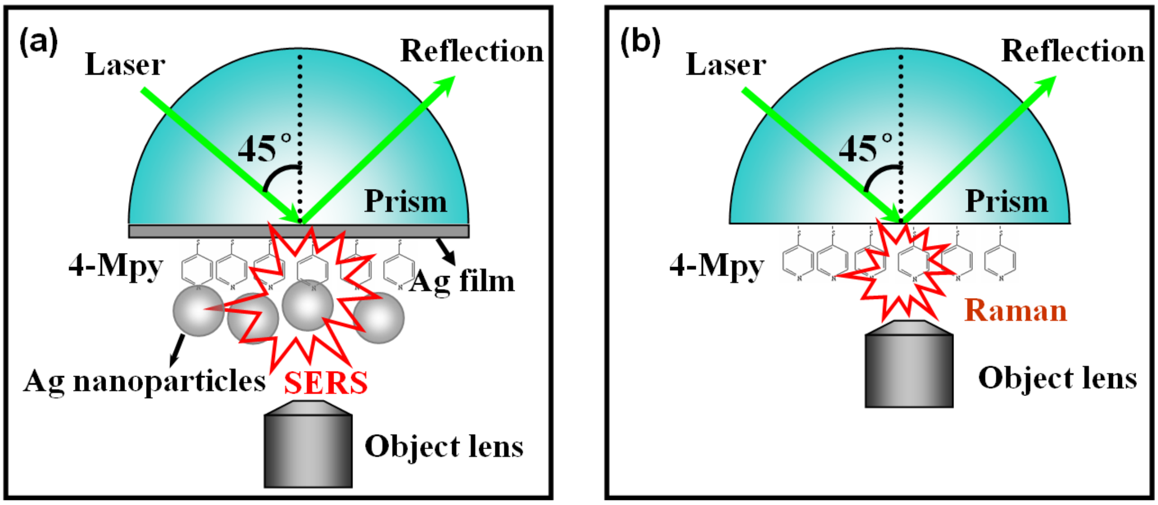

Figure 7S. (a) The schematic diagram of the setup of SPs enhanced SERS. (b) The setup of the measurement of normal Raman spectrum.

The SERS enhancement factor is calculated by comparing the SERS signal excited via evanescent field and the Raman signal excited via the total internal reflection. Sample for SERS measurements was prepared by drop coating of 10 μL of the 4-Mpy (10^{-8} mol/L) aqueous solution onto Substrate (a), and then the substrates were dried in room temperature. After the solvent evaporating (2 hours later), the solution formed a circular deposit with the diameter of 4.0 (±0.5) mm. The average surface coverage was calculated to be 4.8×10^{11} molecules/cm^2. Thus, the average occupied area of per 4-Mpy molecule is supposed to be about 2.1×10^{-12} cm^2, which is obviously larger than the maximum surface area per 4-Mpy (about 7.0×10^{-15}cm^2).[1] So, we can infer that the 4-Mpy deposited film was a monolayer. After that, silver colloid was injected into the flow cell to construct a silver film/4-Mpy/silver nanoparticles sandwich structure. We first measured SPR curve of this sandwich structure in air. The SPR curve indicates that the resonance angle is ~45°. Then we measured SERS signals at the resonance angle (~45°) to evaluate the effect of LSP and PSP co-enhancement. The schematic diagram of the setup of silver nanoparticles assisted LSP-PSP co-enhanced SERS is shown in Figure 7S (a).

Sample for the normal Raman measurement was prepared by dropping 10 μL of a 4-Mpy (10^{-3} mol/L) aqueous solution onto a normal K9 prism. The solution formed a circular deposit with the diameter of 3.6 (±0.5) mm. The setup of the measurement of normal Raman spectrum of 4-Mpy is shown in Figure 7S (b), which is a total internal reflection mode.

Here, we adopted the estimation of the SERS enhancement factor (*G*) by using the expression (2) in the part 1. Where the N_{Raman} and N_{surf} denote the number of probe molecules which contribute to the normal and SERS signals, while the I_{Raman} and I_{surf} denote the corresponding normal Raman and SERS intensities. The M_{surf} *and* M_{Raman} are the number of 4-Mpy molecules dropped onto a sliver film coated prism and a normal prism. The S_{Surf} and S_{Raman} are the geometrical areas of the 4-Mpy casting film. A is the recorded area of a laser spot. Since SERS and Raman spectra were obtained under same excitation angle, the laser spot area of normal Raman can be ignored. The representative band at 1007 cm^{-1} due to ring-breathing (the band is at 994 cm^{-1} in the normal Raman spectrum.[3]) was selected to calculate the G. The SERS signal intensity at 1007 cm^{-1} is 922 cps and normal Raman signal intensity at 994 cm^{-1} is 6 cps (see Figure 8S). The S_{Surf} and S_{Raman} are 0.13 and 0.10 cm^2. Thus, the value of G is 2.0×10^7.

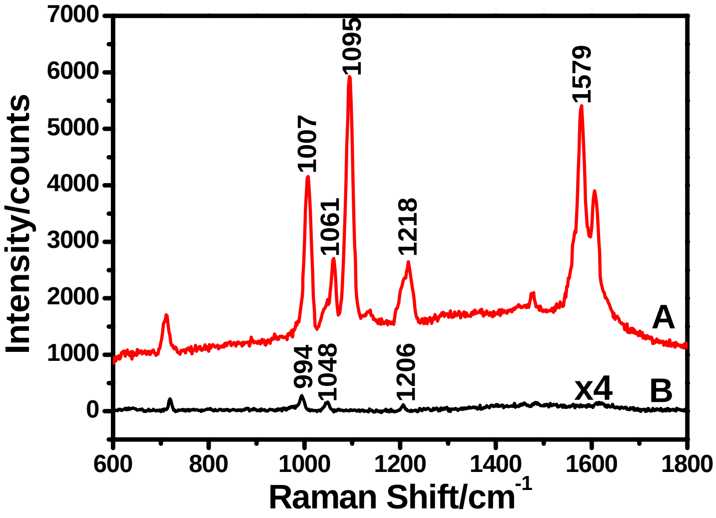

Figure 8S. A) The SERS spectrum of 4-Mpy on Substrate (c). The integration time is 3s. B) Normal Raman spectrum of 4-Mpy absorbed on a prism. The integration time is 10s. All the spectra were measured by a 532nm laser with the power of 8 mW.

6. The comparison between the evanescent field and bright field excitation.

The SERS spectra excited via evanescent field and bright field was compared. The schematic diagram of the SPs enhanced SERS based on the evanescent field and bright field excitation were show in figure 9S. The spectrum a and the spectrum b in the figure 9S (c) were the spectra excited via evanescent field excitation and bright field excitation. We found that the background signal of the spectrum a was restrains, which implied the evanescent field excitation can depress the background signal. The result indicated the SERS spectra excited and collected in an evanescent field restrains the background signal and gets high signal-to-noise SERS signals, which is an important advantage for the evanescent field excitation. In addition, the SERS signal excited via evanescent field excitation is about 15 fold of the SERS signals excited by bright field.

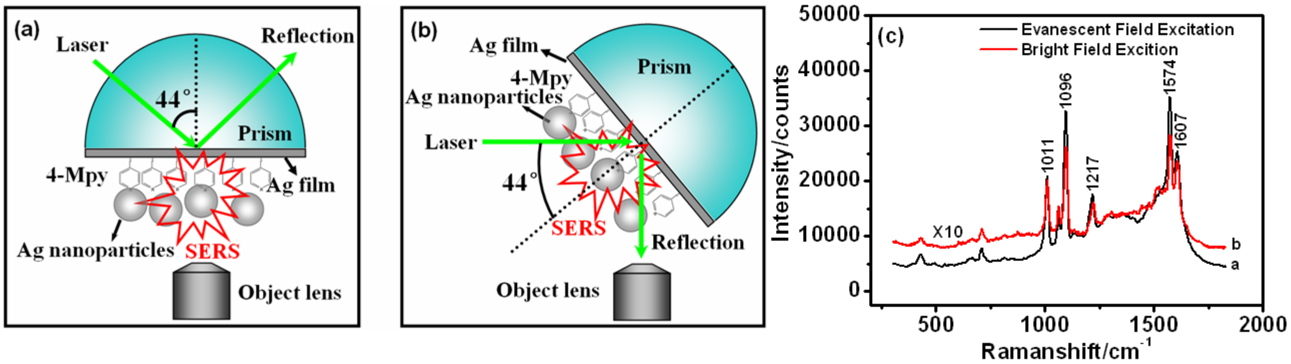

Figure 9S. The schematic diagram of the SPs enhanced SERS based on the evanescent field excitation (a) and bright field excitation (b). (c). The SERS spectra excited via the evanescent field and bright field. The incident angle is 44°。

References

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