Electronic Supplementary Information for

Silver Nanoplates Prepared by Modified Galvanic Displacement for Surface-enhanced Raman Spectroscopy

Yongchao Lai, Wenxiao Pan, Dongju Zhang and Jinhua Zhan*

Key Laboratory for Colloid & Interface Chemistry of Education Ministry, Department of Chemistry, Shandong University, Jinan 250100 China

jhzhan@sdu.edu.cn

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1. Details of experiment and simulation

Synthesis of SERS substrates. Commercial copper foil was cut into flake (0.5×0.5 cm^2) and rinsed with ethanol and ultrapure water. Reaction solution was prepared by silver nitrate (1 mmol), 2-nitrobenzoic acid (1 mmol) and water (100 mL). Then small copper foil was immersed in the reaction solution. The color of copper foil changed in seconds and the reaction proceeded for 5 minutes to form uniform substrates. Then those flakes were taken out and rinsed three times with cupric acetate solution, ethanol, and ultrapure water in turn. The SERS substrate was dried at 60℃ and stored at room temperature for use. Dendritic silver nanostructures were prepared by dipping copper foil in silver nitrate solution (10 mM) overnight and rinsed three times with ethanol and ultrapure water in turn. Then they were dried at 60℃ and were attached to slide glass with double-sided Scotch tape.

SERS testing. Phorate and 4-aminothiophenol were dissolved in methanol to get the designed concentration. Bovine serum albumin (BSA) solution was prepared by dissolve BSA in ultrapure water. SERS substrates were dipped into probe solutions for 3 hours and rinsed three times with methanol or ultrapure water. Then SERS substrates dried at 60℃ and attached to slide glass with double-sided Scotch tape. Raman spectra were collected on confocal Raman systems and miniaturized Raman systems. For miniaturized Raman systems. The exciting laser was focused to sample by Raman coupled fiber probe.

Computational Details. Molecular dynamics simulations were carried out using the discover module of the software package Materials Studio 4.4 from Accelrys Inc.[1] To investigate the interface interaction between 2-nitrobenzoic acid molecules and the silver crystal plane, we chosen the COMPASS force field, which is specifically designed for non-bonded interactions in condensed phase materials.[2] Growth mechanism of silver nanoplates was studied by running molecular dynamics (MD) simulations in the NVT (constant atom number, volume and temperature) ensemble. This simulation method is similar to that described in the

reference.[3] Both the Ag (100), Ag (110) and Ag (111) crystal planes were composed of 77 silver atoms. NVT simulations for the three-dimensional models, which consist of ten 2-nitrobenzoic acid molecules on the silver surface, were performed for 100 ps with a time step of 1 fs. Energies of the three models were calculated: the silver crystal plane with 2-nitrobenzoic acid (E_{total}), the silver crystal plane only (E_{sur}), and 2-nitrobenzoic acid molecules only (E_{mol}). The interaction energy (E_{inter}) between 2-nitrobenzoic acid molecules and the silver crystal plane were obtained with the following formula: $E_{inter}= E_{total} -(E_{sur}+ E_{mol})$

Instrumentation. XRD patterns were recorded on the X-ray diffractometer (Bruker D8) with a graphite monochromator and Cu K_α radiation (λ =0.15418 nm) in the range of 10–80° at room temperature. The morphology of the products was characterized with transmission electron microscopy (JEM-100CXII) with an accelerating voltage of 80 kV and scanning electron microscopy (SEM, JSM-6700F). High resolution transmission electron microscopy (HRTEM) images were recorded on a JEM 2100 (JEOL, Japan) electron microscope operating at 200 kV. Diffuse reflection spectra were obtained using a TU-1901 UV-vis spectrophotometer (PGeneral, China). X-ray photoelectron spectra (XPS) were measured with X-Ray photoelectron spectroscopy (ESCALAB 250). All peaks were corrected by referencing the primary peak of the C (1s). Raman spectra were collected on LabRAM HR 800 system (HORIBA Jobin Yvon). A 17 mW air-cooled He-Ne laser with the 632.8 nm wavelength was used as the exciting source and focused onto the sample with a 50 objective (numerical aperture 0.5). All spectra were calibrated with respect to the silicon Raman mode at 520.7 cm^{-1}. Except especial explanation all spectra were recorded by LabRAM HR 800 systems. The miniaturized Raman system (Ocean Optics) was composed of a 300 mW semiconductor laser with the 532 nm wavelength, a QE 65000 Scientific-grade spectrometer and a Raman coupled fiber probe with SMA connector. TE cooled 2048 pixel Hamamatsu FFT-CCD worked as a Raman detector.

References

1 Accelrys Software Inc. (2008), *Materials Studio Release Notes, Release 4.4*, Accelrys Software Inc., San Diego, USA.

2 H. Sun, *J. Phys. Chem. B* **1998,** *102*, 7338-7364.
3 Q. H. Zeng, X. C. Jiang, A. B. Yu, G. Q. Lu, *Nanotechnology* **2007**, *18*, 035708.

2. SEM image of commercial copper foil

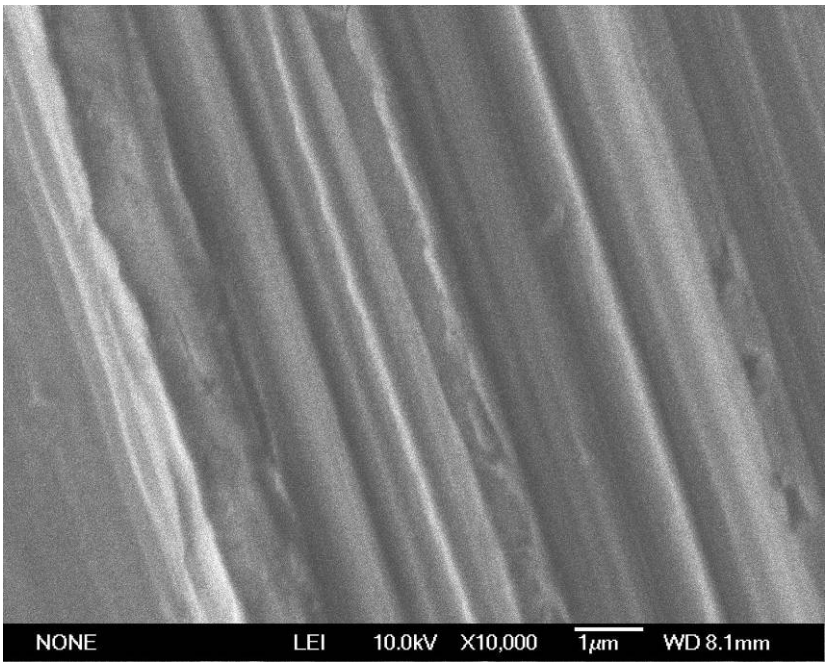


Figure S1. Typical SEM image of commercial copper foil.

3. SEM image of silver dendrites on commercial copper foil

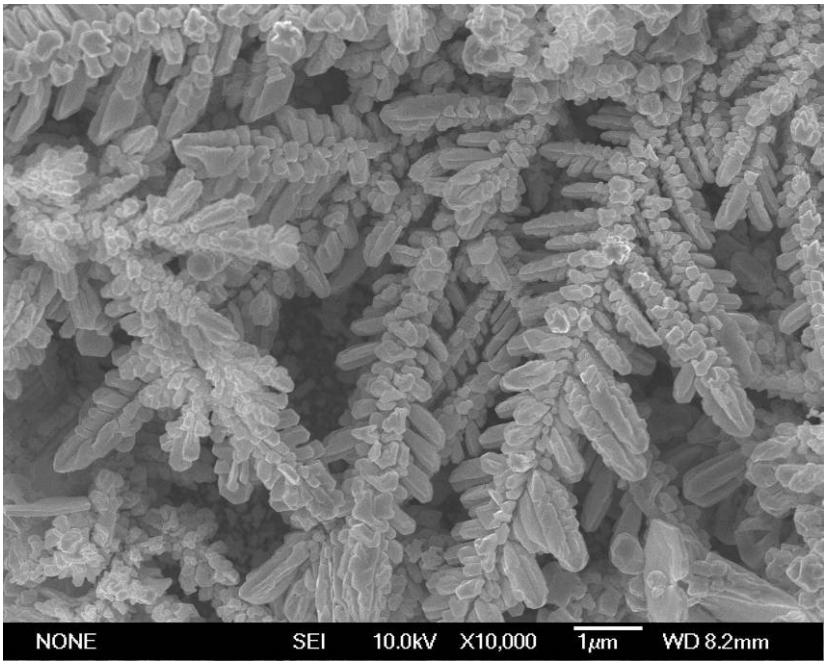
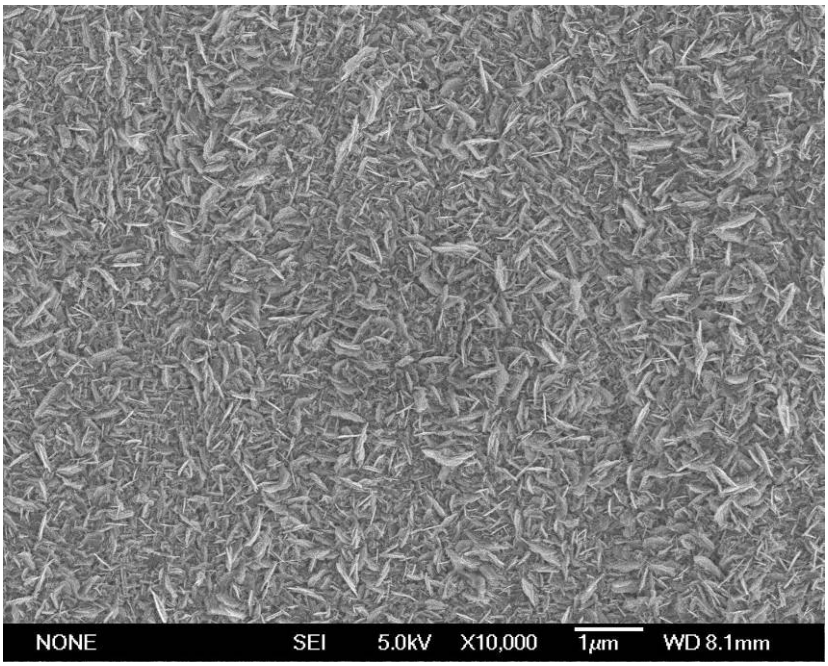


Figure S2. SEM image of silver dendrites on commercial copper foil.

4. SEM images of silver nanoplates on the SERS substrate



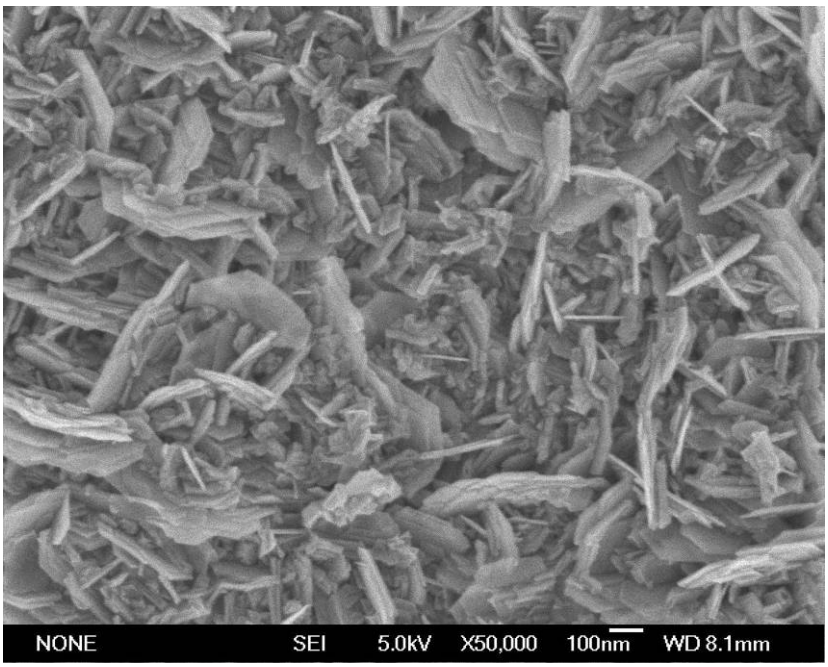


Figure S3. SEM images of silver nanoplates on the SERS substrate.

5. SEM images of Ag structures grown for different times

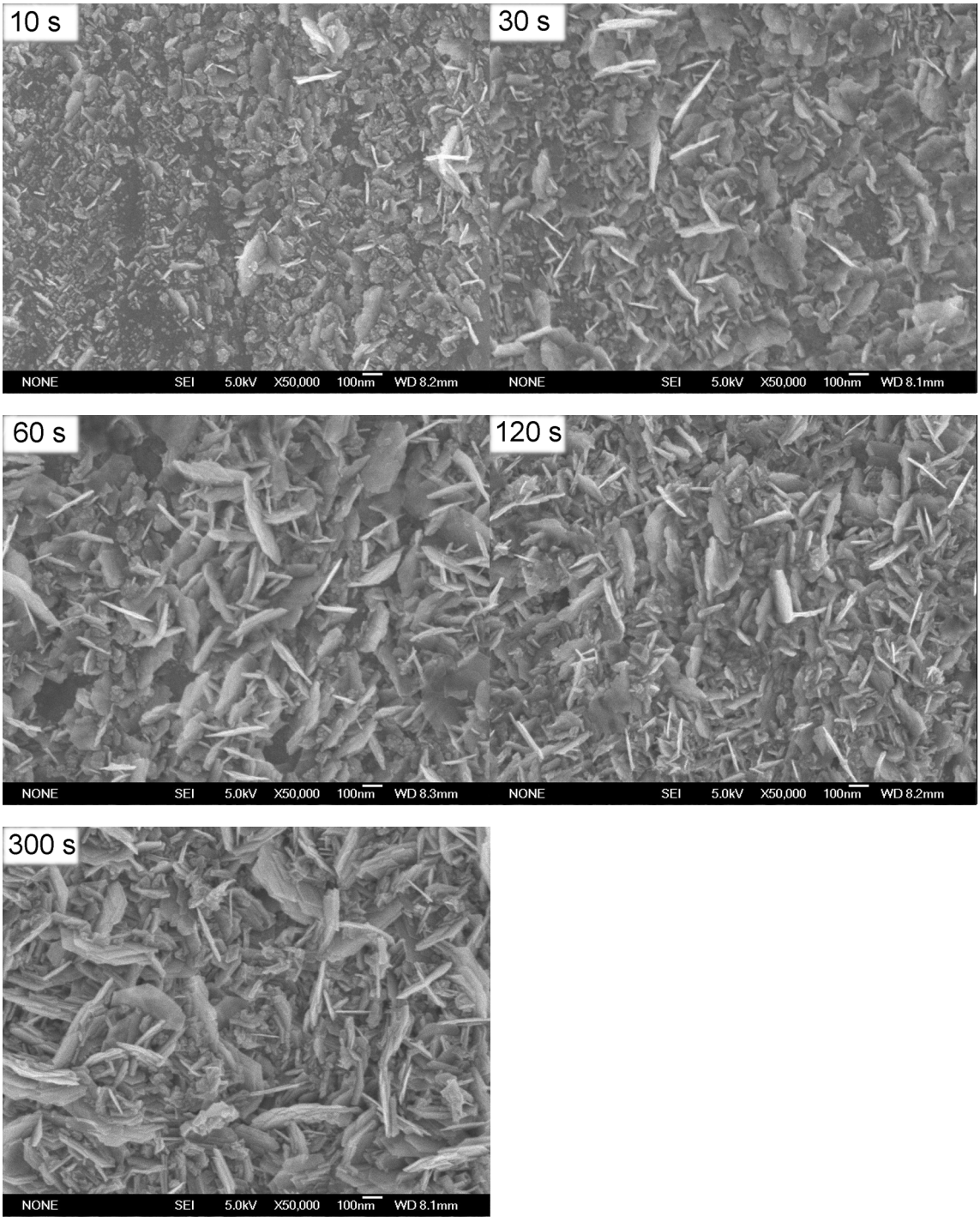


Figure S4.SEM images of Ag structures grown for different times.

6. Photograph of a piece of commercial copper foil (left) and a SERS substrate

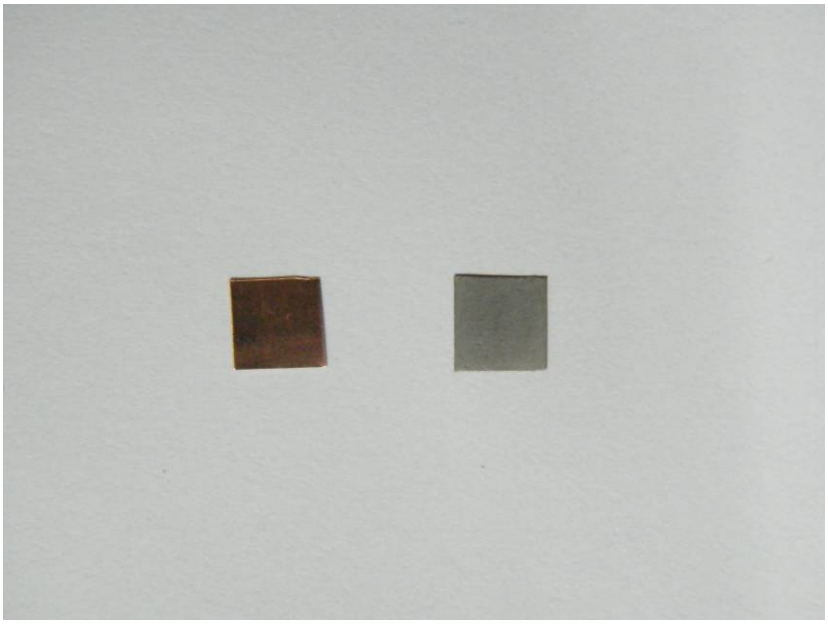


Figure S5. Photograph of a piece of commercial copper foil (left) and a SERS substrate (right).

7. Energy dispersive X-ray spectroscopy (EDS) of the SERS substrates

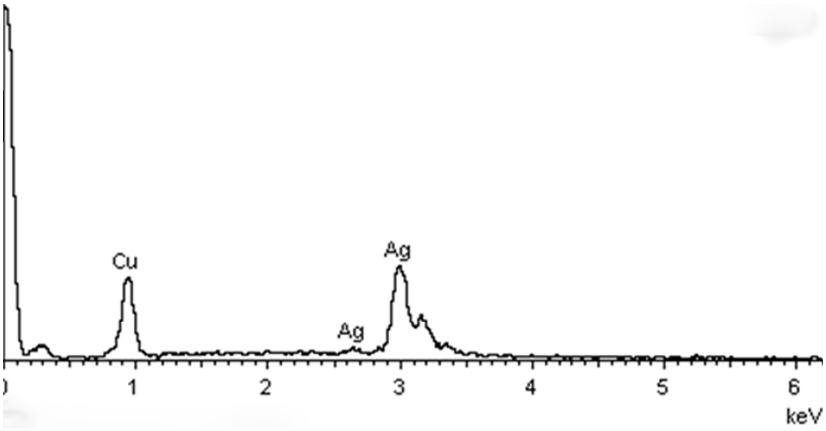


Figure S6. Energy dispersive X-ray spectroscopy (EDS) of the SERS substrates.

8. HRTEM image of a single silver nanoplate and corresponding FFT of the HRTEM image

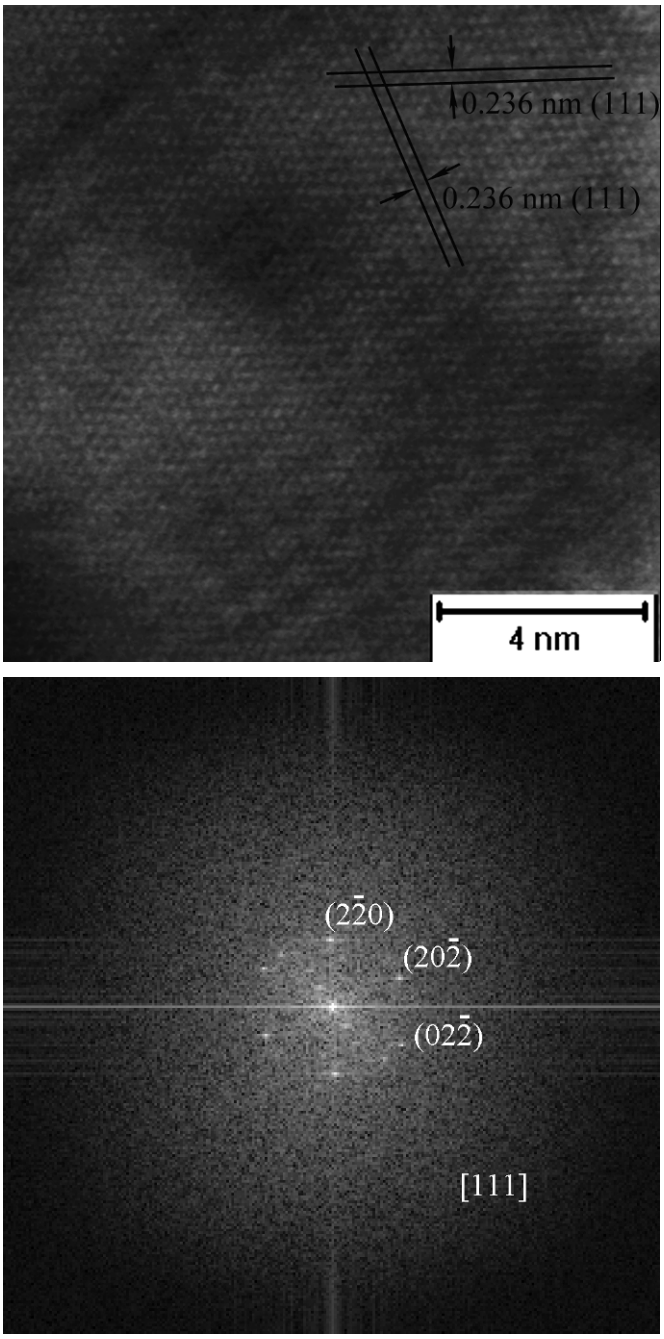


Figure S7. HRTEM image of a single silver nanoplate and corresponding FFT of the HRTEM image.

9. The XRD patterns of copper foil before and after reacting with silver complex

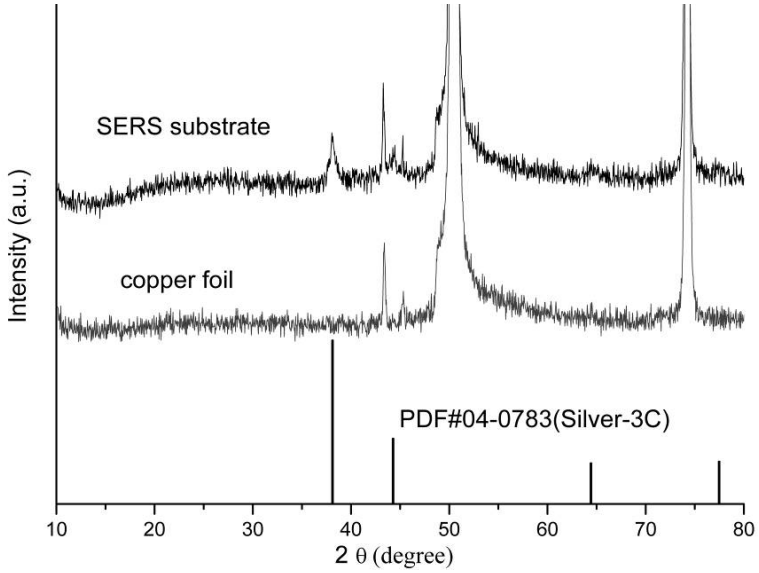


Figure S8. The XRD patterns of copper foil before and after reacting with silver complex.

10. The diffuse reflection spectra of copper foil before and after reacting with silver complex

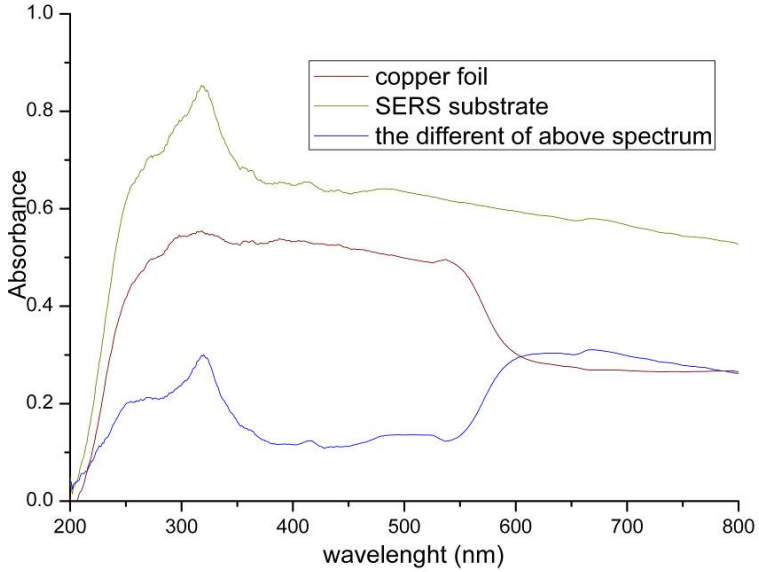


Figure S9. The diffuse reflection spectra of copper foil before and after reacting with silver complex.

11. The models of molecular dynamics simulation for Ag (110) plane with 2-nitrobenzoic acid

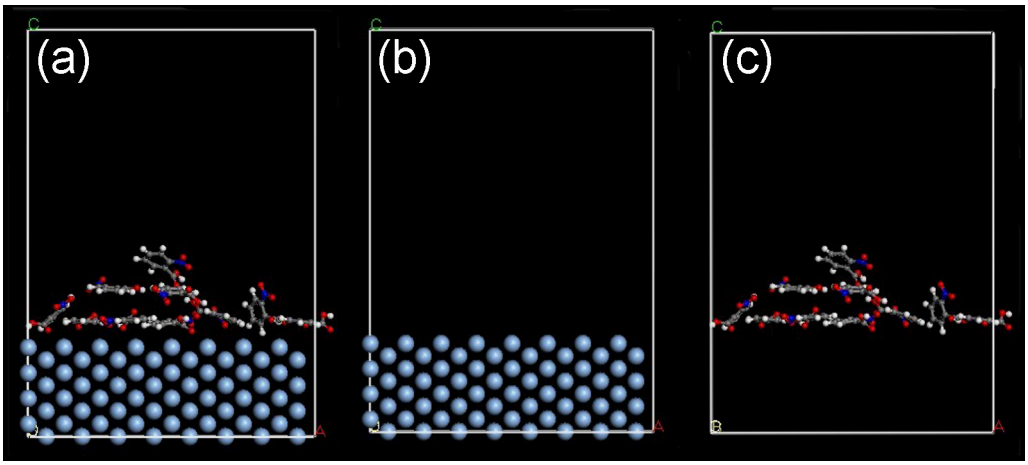


Figure S10. Ag (110) models of: (a) silver crystal plane with 2-nitrobenzoic acid, (b) silver crystal plane only, (c) 2-nitrobenzoic acid only.

12. The SERS data of 4-aminothiophenol from fresh substrate and the aged substrate after three months

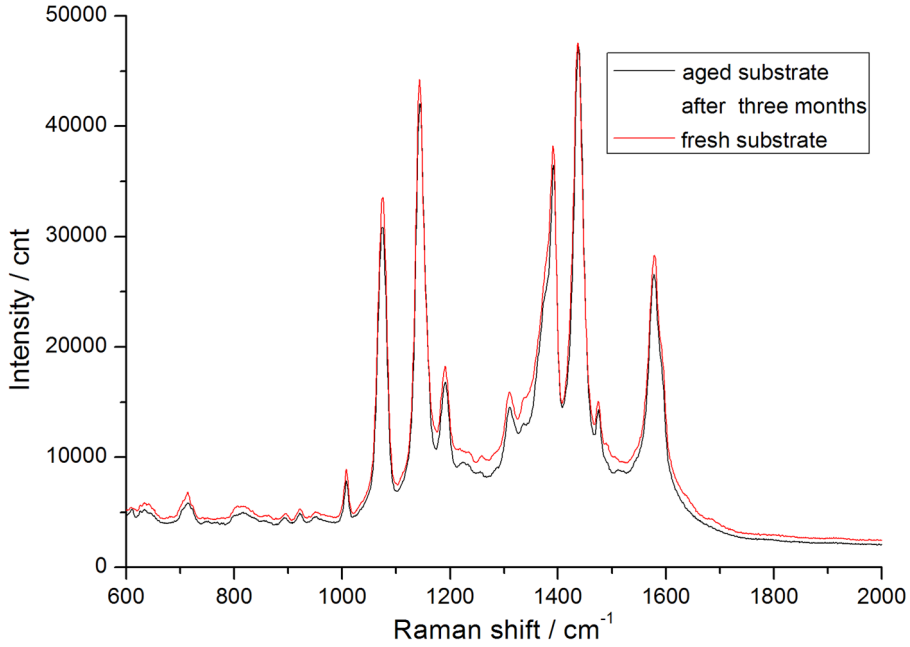


Figure S11. The SERS data of 4-aminothiophenol from fresh substrate and the aged substrate after three months.

13. Raman spectra of 4-aminothiophenol recorded by confocal Raman systems.

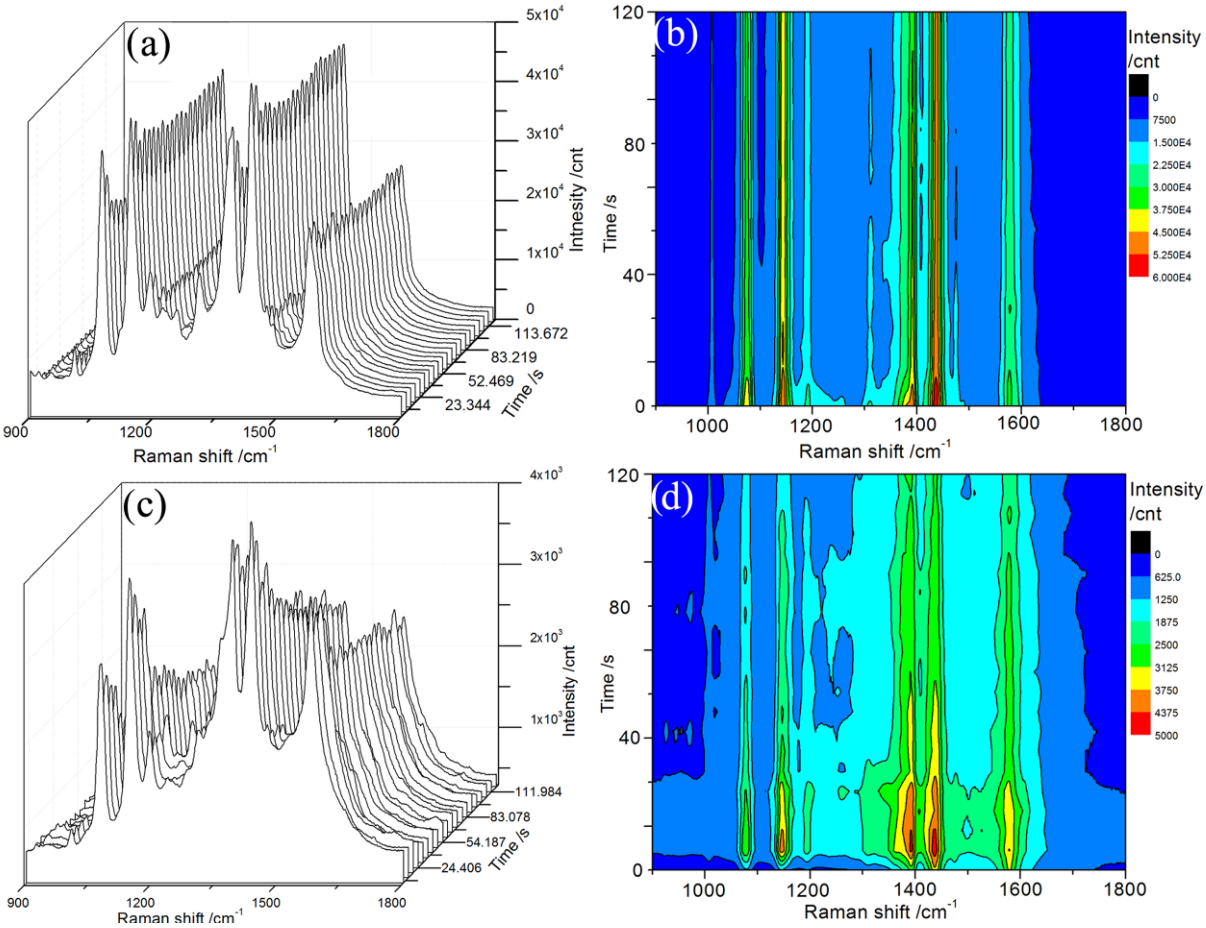


Figure S12. SERS spectra for the SERS substrates (a) and silver dendrites nano-structures (b) probed with 10^{-4} M p-aminothiophenol with continuous laser radiation. The integration time of each spectrum is 1 s.

14. Raman spectra of bovine serum albumin (BSA) and phorate recorded by confocal Raman systems.

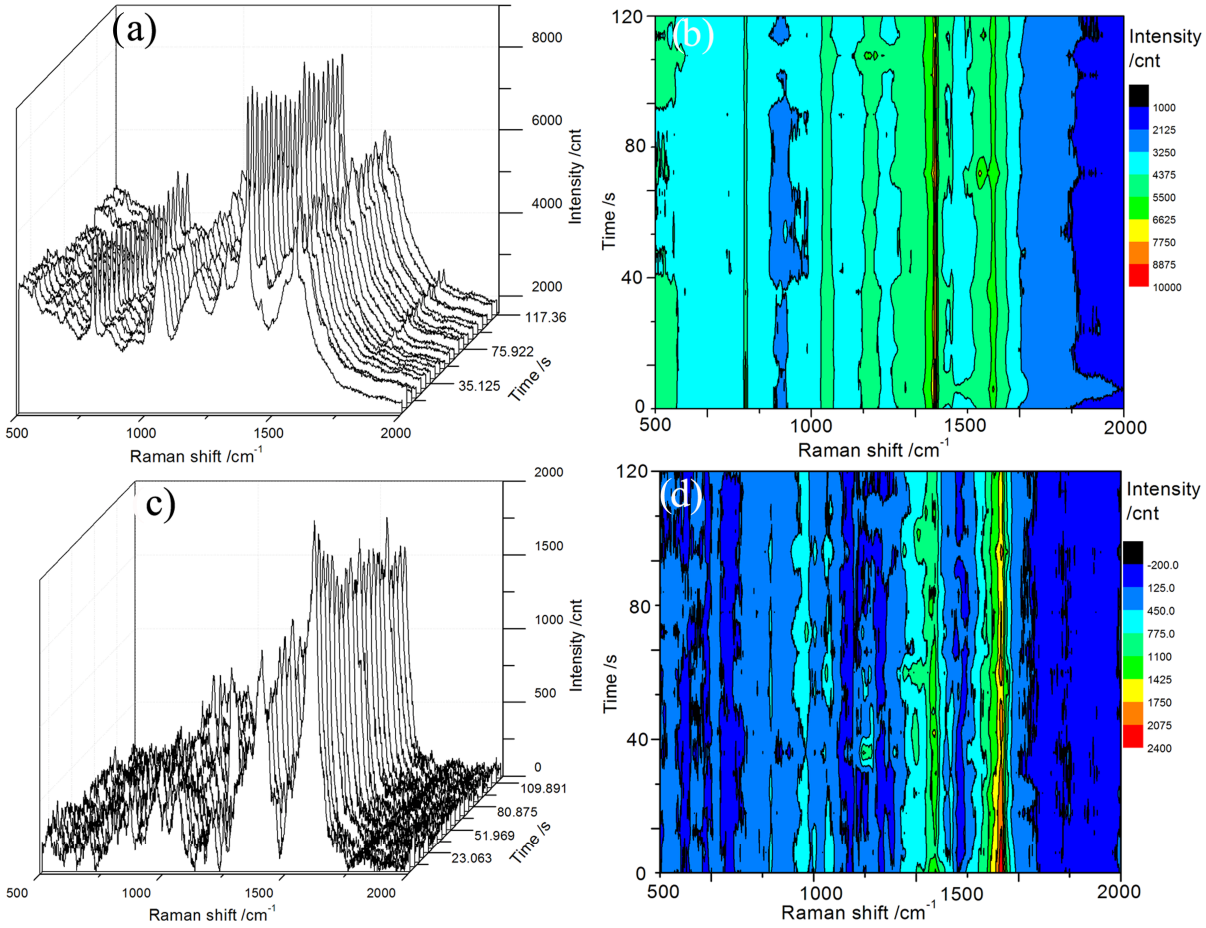


Figure S13. The acquisition time of all spectra was 1 s and the interval time between two spectra was 5 s; Laser power was decreased by D 0.6. (a) Raman spectra of BSA (10^{-5} M) from the SERS substrates with continuous laser radiation in the air; (b) The color contour map of (a); (c) Raman spectra of phorate (10^{-4} g/ml) from the SERS substrates with continuous laser radiation in the air; (d) The color contour map of (c).