Electronic Supplementary Information (ESI)

Surface-Enhanced Raman Scattering on a Hierarchical Structural Ag Nano-Crown Array under Different Detection Ways

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1. Raman spectrum of PMMA.

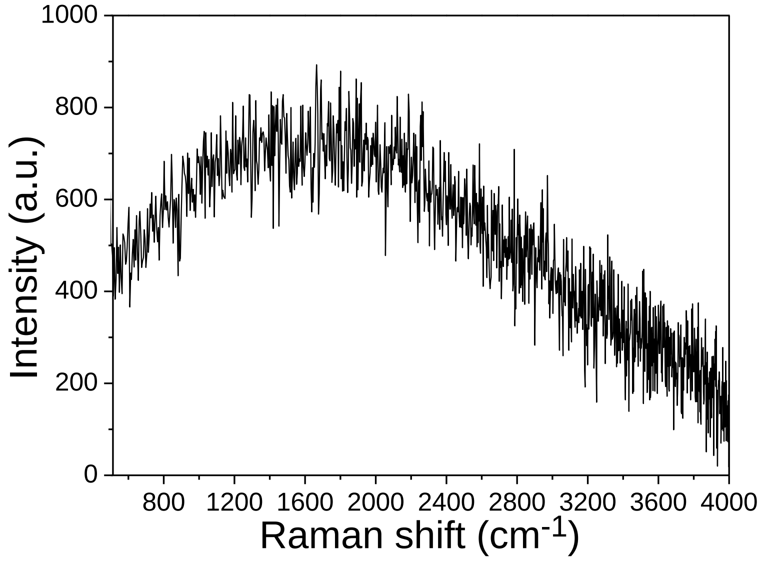

Fig. S2 A Raman spectrum of PMMA.

2. The comparison between planar Ag film and the nanostructured Ag film

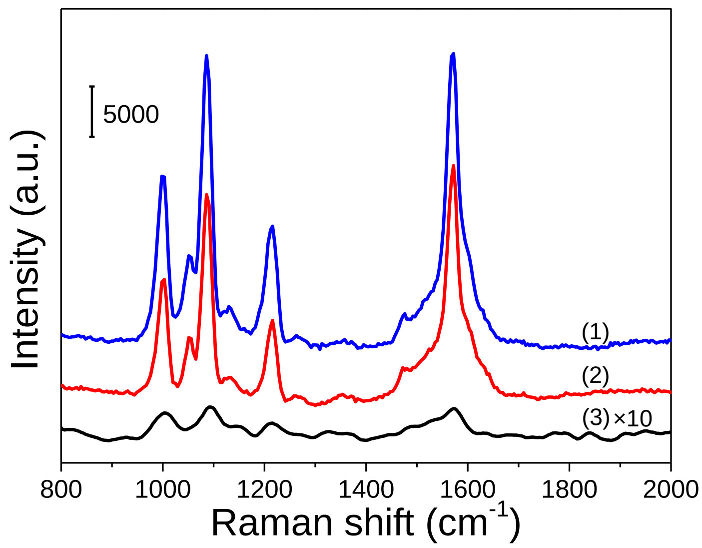

Fig. S2 The SERS spectra of 4-mpy aqueous solution (1.0×10^{-4} M) on the 20 nm Ag nano-crown substrate with detection mode of (1) type Ⅱ and (2) type Ⅰ, (3) on a planar Ag film with a thickness of 20 nm. The integration time of (1) and (2) was 1 s, (3) was 15 s.

A planar silver film was also fabricated and evaluated for comparison with Ag nano crown flexible substrate. The 20nm Ag film was prepared by vacuum evaporating Ag onto 1.0 cm × 1.5 cm quartz. 5.0 μL of 4-mpy aqueous solution was dropped on the planar Ag film. The enhancement of the 3D substrate is about 800 times greater than the planar Ag film.

3. The SERS signal comparison under the detection ways of type Ⅰ and Ⅱ.

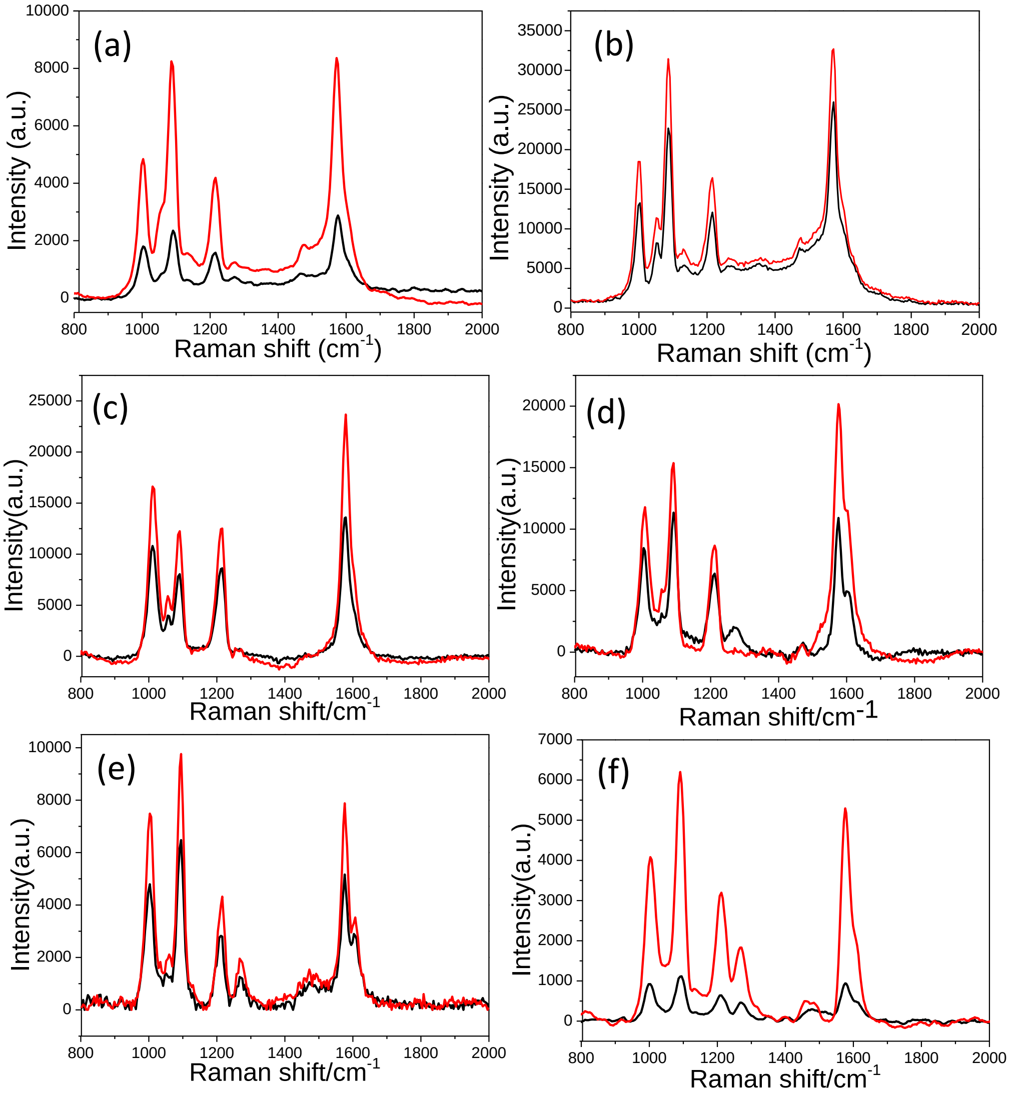

Fig. S3 SERS spectra of a 4-mpy aqueous solution (1.0×10^{-4} M) on hierarchical structural Ag nano-crown substrates with different thicknesses of Ag films excited using a 532 nm laser. Integration time was 1 s. (a) - (e) corresponds to 10, 20, 50, 100, 200 and 300 nm, respectively. The top curves were detected as type II mode while the bottom curves were detected as type I mode.

4. The reproducibility of the SERS substrate.

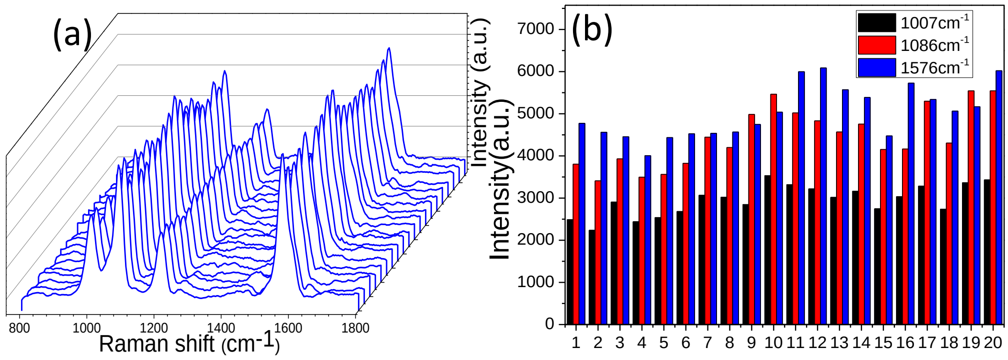

Fig. S4 (a) SERS spectra from randomly selected 20 points. (b) The intensities of three different peaks at 20 points on the same substrate.

Reproducibility is an important factor to evaluate the stand or fall of a SERS substrate besides sensitivity. This substrate with precise pattern is highly ordered since it replicated the morphology of a honeycomb-like AAO template. This should enable an even distribution of SERS “hot-spots”, bringing good reproducibility. To investigate this, we compared SERS signals of 4-mpy from 20 random points. Three peaks at 1007, 1086, 1576 cm^{-1} were chosen to evaluate its reproducibility, with the relative standard deviations (RSD) of Raman signals calculated to be 12.1%, 15.5% and 12.2%, which can meet the standard of a high-performance SERS substrate (in which the RSD is less than 20 %).

5. The spread Ag in the gaps of nanocrowns.

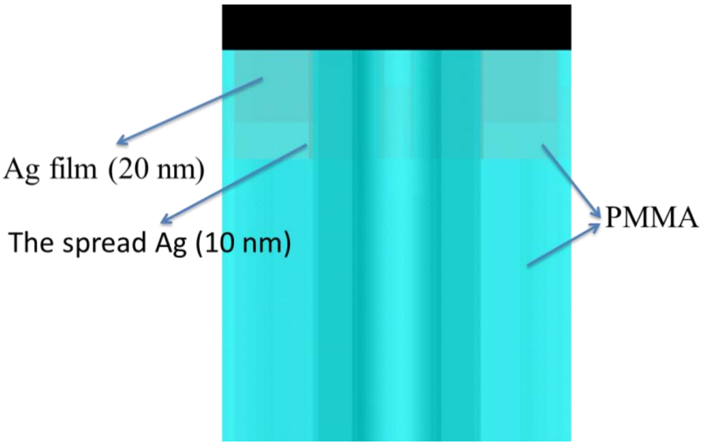

Fig. S5 The cross sectional view of the model in the FDTD simulation.

6. The calculation of Ag film thickness.

Because of the unique morphology of nano-crown and the uncertainty about the nucleation sites in the process of vacuum evaporating, the thickness of the deposited Ag was nonuniform at different sites. It prefers to locate at prominence sites rather than the sunk parts. So, it forms discrete Ag deposited islands, not a continuous and uniform film. We used the average thickness value to represent the sample trials for convenience. The thickness value was measured in every vacuum evaporation deposition process by using a Quartz Crystal Monitor (QCM), which had been equipped in the vacuum evaporation deposition box (Beijing Technol Science, China). We had calibrated the thickness of metal film by measuring the changes of resonant frequency of crystal oscillator for comparison of the surface profiler (DEKTAK 150) results. In our experiment conditions, a standard of 37 Hz/nm was set to fabricate the deposited silver film above the hierarchical structural nano-crown. The values of crystal oscillator frequency corresponding to the average thickness of silver film are 370 (10 nm), 740 (20 nm), 1850 (50 nm), 3700 (100 nm), 7400 (200 nm), and 11100 (300 nm) Hz, respectively.