Supporting Information

Experimental Section

Materials

AgNO₃, citric acid, $H_2C_2O_4$, H_3PO_4 , H_2CrO_4 , $HClO_4$, ethanol, highly pure aluminum foils (99.999%), H_3BO_3 and $SnCl_4$ were obtained from Shanghai Chemical Reagent Company (Shanghai, China). p-Aminothiophenol (PATP) and crystal violet (CV) were purchased from Sigma company. All reagents were of analytical grade and used as received without further purification. Ultrapure water (>18.0 M\Omega.cm) was purified using a Millipore Milli-Q gradient system throughout experiment.

Characterizations

Morphologies and structures of the samples were characterized with SEM (Philips XL 30 FEG). SERS measurements were carried out with a confocal microprobe Raman system (LabRam HR800) using a laser of 532.06 nm and an objective lens $(50\times, \text{Numerical Aperturec (NA)} = 0.5)$ to reduce instrumental noise. The laser power was approximately 0.2 mW. UV/Vis absorbance spectra were recorded on a Solid spectrophotometers (3700DUV, Shimadzu).

Preparation of the self-assembled monolayer Ag nanoparticles

Ag sols were prepared according to the Lee-&-Meisel method.^[1] This method results in a grey-yellow solution which has a UV-Vis absorption maximum at 415 nm. The mean particle size is around 50 nm in diameter. The concentration of as-prepared Ag sols can be estimated to be $\approx 10^{11}$ colloids/ml.^[2] 100 ml of the Ag sols was concentrated to 1 ml by centrifugation at 8,000 rpm for 10 min.

The Si water was first cut into small pieces of about 1 cm×1cm, which were cleaned and hydroxylated by immersing in a freshly prepared piranha solution (a mixture of 98% H₂SO₄ and 30% H₂O₂, 7:3, v/v) for ~1 h, followed by extensive rinsing with distilled water and drying under a stream of nitrogen. Secondly, the hydroxylated Si was immediately immersing into a 10 mM APTS ethanol solution for 2 h to form a 3-aminopropyl monolayer on its surface, and then rinsed with ethanol and heated at 110°C for 1 hour. Finally, the as-prepared Si substrate was immersed

into the concentrated Ag sol (~50 nm in diameter, prepared according to the classical citrate reduction method) for 30 min. Then, the self-assembled monolayer Ag nanoparticles on Si substrate was obtained after extensively rinsing with water.

Preparation of the silver nanorods array

Nanoporous alumina template with pore diameters of about 80 nm were fabricated via a two-step anodization process as described in leteratures.^[3,4] Highly pure aluminum foils (99.999%) were degreased under ultrasonication by acetone, distilled water and anhydrous ethanol, respectively, and then annealed at 500 °C for 5 h in a Ar₂ gas atmosphere. Then the foils was electropolished under the constant voltage of DC 10 V in a mixture of anhydrous ethanol and HClO₄ (9:1 in v/v) until a mirror shining surface appeared. The treated aluminum sheets were firstly anodized in 0.3 M H₂C₂O₄ solution under constant voltage (40 V) at temperature of 5 °C. After anodization for 4 h, the formed alumina was moved into H₃PO₄ (6%) and H₂CrO₄ (1.8 wt%) solution at 60 °C for 6 h to remove the oxide membrane. And then after washed by distilled water several times, the Al sheets were anodized again in the same anodizing conditions for 10 h. Then the backside of Al layer was removed via a reaction with a saturated SnCl4 solution. The barrier layer at the bottom of the AAO membrane was removed by placing the sample in 6% H₃PO₄ until the barrier layer was dissolved. After washing and drying, a transparent and through-hole AAO template was obtained.

Electrochemical deposition was performed in a three-electrode electrochemical cell by the use of a Model LK2005 electrochemistry workstation(LANLIKE, China). Briefly, one planar surface side of the AAO template was firstly deposited a thin layer of Au (about 25 nm), serving as working electrode. A Ag/AgCl electrode, and a Pt plate were used as the reference electrode and the counter electrode, respectively. The template was immersed in the 10g/L AgNO₃, and 10g/L H₃BO₃ electrolyte. The Ag nanowire arrays were obtained by Constant Current Electrodepositing in the pores of the AAO template at 0.5 mA for different times (e.g. 1 min or 10 min) at room temperature. After deposition, the as-prepared samples were taken out from the electrolyte, and rinsed several times with ultrapure water, and then dried in air. The SERS substrate was fabricated as follows: The template sides coated with Au layer was potentiostatically electroplated at 4.0V, in the solution of 100g/l CuSO₄, to protect the base of Ag array. After that, the array was dipped into 6% H₃PO₄ at temperatures of 40°C to remove the AAO template. Following that, the Ag array was rinsed several times with ultrapure water, and then dried in air.

Calculation of the enhancement factor (EF)

Assuming that the excitation volume as a cylinder, the diameter (d) and the height (h) of the laser spot were determined by the following equations:

$$d = \frac{1.22\lambda_{laser}}{NA} = 1.29\mu m \tag{1}$$

$$h = \frac{2.2n\lambda_{laser}}{\pi (NA)^2} = 2.38\mu m \tag{2}$$

where *n* is the refractive index of neat PATP crystal powder ($n \approx 1.6$).

The absolute magnitude of the enhancement factor (EF) for reversible hotspots was estimated according to the following equation:

$$EF = \frac{I_{SERS} / N_{SERS}}{I_{bulk} / N_{bulk}}$$
(3)

 I_{SERS} represents the Raman intensities at 1428 cm⁻¹ collected from the NR array-L. I_{bulk} represents the Raman intensities at 1428 cm⁻¹ collected from the crystalline powder, which is about 10 cnts under the similar experimental setup. N_{bulk} is the molecule number of the neat crystal of PATP in the laser excitation volume $(\pi (d/2)^2 h=3.1\times 10^{-12} \text{ cm}^3)$, and can be calculated to be about 1.7×10^{10} by the use of the density of 1.18 g/cm^3 . N_{SERS} is the average number of adsorbed molecules in the scattering volume for the SERS measurements. As shown in Fig. S1, we used 1 ml 1×10^{-9} M PATP to modify the NR array-L located in the polymethyl methacrylate (PMMA) holder. In this case, the PATP molecules with thiol group can strongly bind to the Ag surface and can hardly adsorb onto other surfaces such as the PMMA surface. After 30 min incubation, we assumed that all PATP molecules could adsorb onto the surface of the NR array-L ^[5] and all PATP molecules were uniformly distributed over the NR array-L surface. The diameter (*D*) of the NR array-L round piece is 10 mm, while the diameter (*d*) of the laser spot is 1.29 μ m (Eqn. 1). Therefore, N_{SERS} can be estimated to be about 10⁴. A conservative EF for the PATP molecules on the NR array-L can be calculated to be about ~1.7×10⁸.

Supplementary Figures (S1-S5)



Fig. S1. (Left) The as-prepared round piece of the NR array-L and (Right) the polymethyl methacrylate (PMMA) holder used for the modification of NR array.



Fig. S2. SEM images of (a) the prepared NR array-S, (b) enlarged details and (c) the lateral view of the NR array-S (the upper inset shows gold-sputtered alumina templates, and the arrows indicated the template hole and the cracked nanorods); And SEM image of (d) the prepared NR array-L, (e) enlarged details and (f) the lateral view of the NR array-S (the lower inset shows SEM image of the individual nanorods liberated completely from an alumina template).



Fig. S3. The structures of SERS signal molecules: p-aminobenzenethiol (PATP) and crystal violet (CV).



Fig. S4. Five circles of the SERS area mapping on NR array-L.



Fig. S5. (a) Time-course SERS mapping of the intensity of 1428 cm⁻¹ peak on NP SAM under dry conditions using 1×10^{-6} M PATP as the SERS reporter. (b) Time-course SERS mapping of the intensity of 1428 cm⁻¹ peak on NP SAM for three cycles of evaporating 50 µL ethanol.

References

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