Electronic Supplementary Information

Gap-Tunable Ag-nanorod Arrays on Alumina Nanotip Arrays as Effective SERS Substrates

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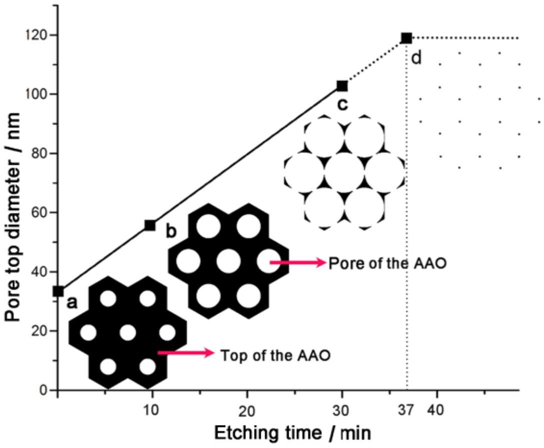
Part S1. Preparatory conditions for ordered alumina nanotips



Scheme S1 Schematic diagram of the pore top diameter of the conical-pore-AAO template achieved by a repeated multistep of anodization and pore-widening process as a function of etching time.

Conical-pore-AAO templates with alumina nanotips were fabricated by multistep oxalic acid anodizing (pore growth) and phosphoric acid etching (pore widening) processes. It has been reported that the pore diameter of AAO changes linearly with the etching duration,[1] so the diameter of the conical-pores on the top of AAO template (the pore open diameter) changes linearly with the etching time (Scheme S1). The first step anodization process produces nanopores with a diameter of about 33 nm (Scheme S1a). And the adjacent conical-pores began to connect with each other on the top of the AAO template at the etching time of about 30 min (Scheme S1c). For further increasing of the etching durations, the upper walls on the conical-pores would disappear and the nanotips at the joints of the nearest three conical-pores gradually formed (Scheme S1d). The nanotips were achieved at the etching time of about 37 min. Then the morphology of the nanotips would not change for increasing of the anodizing and etching cycles.

In order to obtain sharp alumina nanotips, the step etching duration should be far below 7 min. But it will be time-consuming to achieve nanotips if the etching duration is too short. It was chosen to be 2 min in the experiment (for the first 13 steps). Additionally, to save time we reduced cyclic times by prolonging the anodization and etching durations by 3 times in the last third steps

(14-16 steps). This will not affect the morphology of the upper half conical-pores, thus not affecting the Raman enhancement of the prepared SERS substrate.

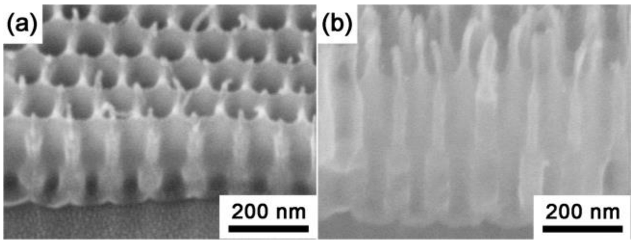


Fig. S1 Cross-sectional view SEM images of the conical-pore-AAO templates with step anodization durations of (a) 50 and (b) 60 s.

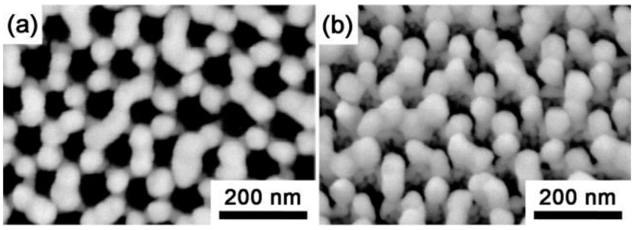


Fig. S2 SEM images of Ag-NR arrays with Ag-sputtering duration of 20 min. (a) is top view. (b) is tilted view at 30 deg.

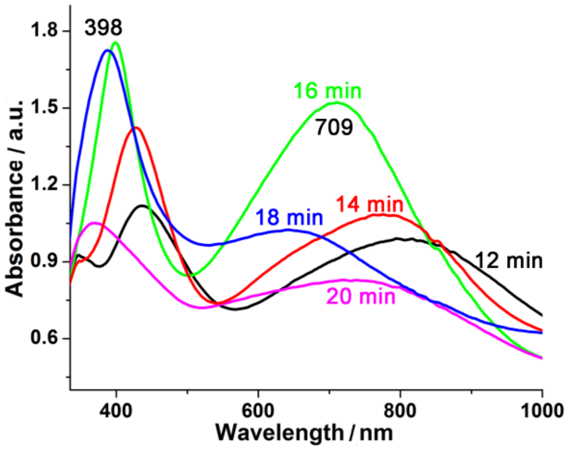


Fig. S3 The UV-vis absorption spectra of Ag-NR arrays with Ag-sputtering durations from 12 to 20 min.

Part S2. Enhancement factor (EF) of Ag-NR arrays

The average SERS EF is calculated by comparing the ratios of the peak intensities of R6G molecules on Ag-NR arrays to the corresponding normal signals from a pure R6G film, the EF can be calculated by

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{RS}/N_{RS}}$$

where I_{SERS} and I_{RS} represent the intensities of the same band of the SERS spectra and the normal Raman spectra respectively, and N_{SERS} and N_{RS} represent the number of molecules on the substrates and the films within the laser spot respectively.

In the experiments, a certain volume V_{SERS} and concentration C_{SERS} R6G aqueous solution was dispersed to an area S_{SERS} on the Ag-NR arrays. For normal Raman experiment, a certain volume V_{RS} and concentration C_{RS} R6G ethanol solution was dispersed to an area of S_{RS} on silicon wafer, and dried to form R6G solid thin film. Thus the foregoing equation can be rewritten as follows:

$$\mathrm{EF} = \frac{\mathrm{I_{SERS}}}{\mathrm{I_{RS}}} \cdot \frac{\mathrm{S}_{SERS} V_{RS} C_{RS}}{S_{RS} V_{SERS} C_{SERS}}$$

For estimation the EF of the Ag-NR arrays with Ag-sputtering duration of 16 min, 8 μL of 10^{-10} M R6G ethanol solution was dispersed on an area of about 24 mm^2 for the Ag-NR arrays and 10 μL of 10^{-3} M R6G ethanol solution was dispersed to an area of about 9 mm^2 for the silicon wafer. Fig. S4 shows representative Raman and SERS signal from the silicon wafer and the Ag-NR arrays. The intensities for the C-C-C ring in-plane vibration mode at 612 cm^{-1} are 199 cps for the Ag-NR arrays and 209 cps for the silicon wafer substrate, respectively.[2] The EF is calculated to be 3.2×10^{7}.

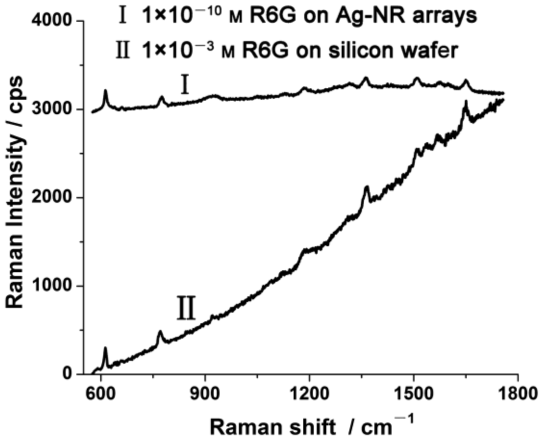


Fig. S4 (I) The SERS spectrum of 8 μL 10^{-10} M R6G ethanol solution dispersed on 24 mm^2 Ag-NR arrays with an Ag-sputtering duration of 16 min. (II) Raman spectrum of R6G obtained by dispersing 10 μL 1×10^{-3} M R6G ethanol solution on 9 mm^2 silicon wafer. cps: counts per second.

Part S3. EF of Ag nanocap arrays

The conventional AAO template was fabricated by a two-step anodization of Al foil.[3] The long-period first anodization was the same as the conical-pore-AAO template. The second anodization step was performed for 2 h. Then the nanopore diameter was enlarged to about 80 nm (Fig. S5a). The Ag-nanocap arrays were formed under different Ag-sputtering durations on the conventional AAO templates, a high SERS intensity was observed with Ag-sputtering duration for 12 min (Fig. S5b). For estimation the EF of the Ag nanocaps, 8 μL of 2×10^{-6} M R6G ethanol solution was dispersed to an area of about 30 mm^2 for the Ag nanocaps and 10 μL of 1×10^{-3} M R6G ethanol solution was dispersed to an area of about 9 mm^2 for the silicon wafer. Fig. S6 shows representative Raman and SERS signal from the silicon wafer and the Ag nanocaps. The intensities for the C-C-C ring in-plane vibration mode at 612 cm^{-1} are 11734 cps for the Ag nanocaps and 240 cps for the silicon wafer substrate, respectively.[2] The EF is calculated to be 1×10^5.

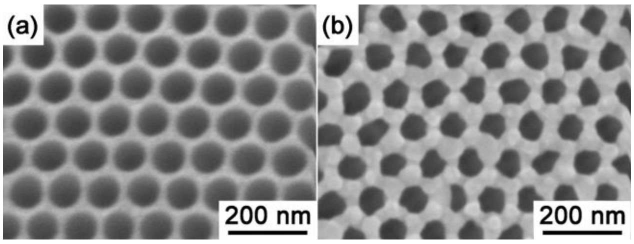


Fig. S5 SEM images of (a) the conventional AAO template and (b) Ag-nanocap arrays.

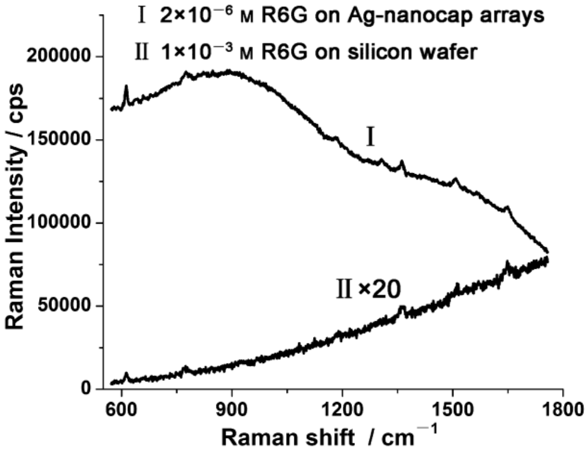


Fig. S6 (I) The SERS spectrum of 8 μL 2×10^{-6} M R6G ethanol solution dispersed on 30 mm^2 Ag-nanocap arrays. (II) Raman spectrum of R6G obtained by dispersing 10 μL 1×10^{-3} M R6G ethanol solution on 9 mm^2 silicon wafer. The Raman spectrum is magnified 20 times for clarity.

Part S4. Density of SERS "hot spots" between neighboring Ag-NRs

Fig. S7a shows hexagon-shaped nanopore arrays on the top of conical-pore-AAO template. The center distance between neighboring hexagons (the inter-pore distance) is about 103 nm (Fig. S7a) and the side-length of the hexagons is approximately 60 nm. So the nanopore density is calculated to be 1.1×10^{10} cm^{-2}. There are 6 "hot spots" around one nanopores with every "hot spots" shared between the adjacent two conical-pores (Fig. S7b). Thus the first kind of SERS "hot spots" density is approximately 3.3×10^{10} cm^{-2}.

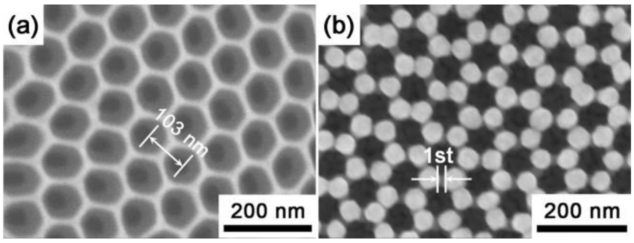


Fig. S7 SEM images of (a) the conical-pore-AAO template with the step anodization duration of 40 s and (b) Ag-NRs hexagonally distributed on the pore joints of the conical-pore-AAO template. The first kind of SERS "hot spots" is marked as "1st" in (b).

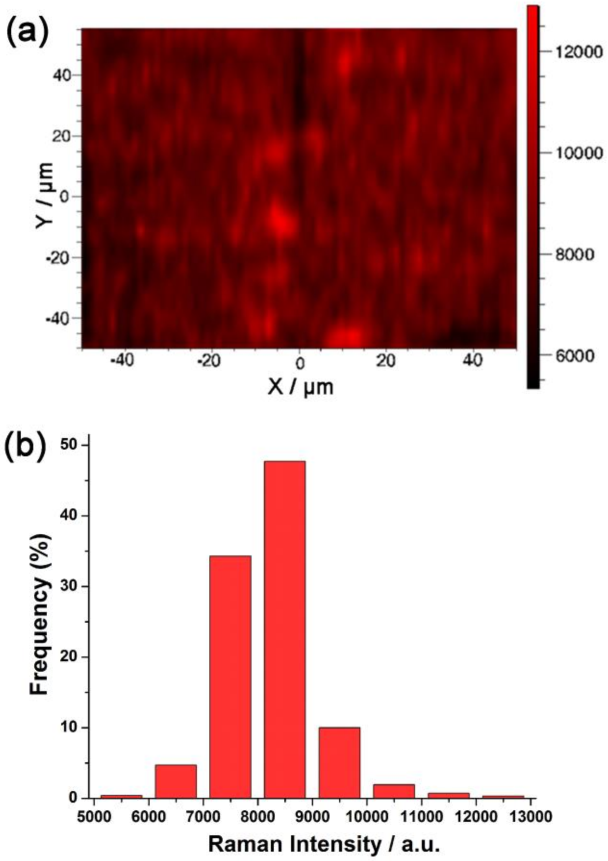


Fig. S8 (a) Streamline SERS mapping of the Ag-NR arrays with Ag-sputtering duration of 16 min. (b) The 612 cm^{-1} relative SERS peak intensity distribution of the Ag-NR arrays shown in (a).

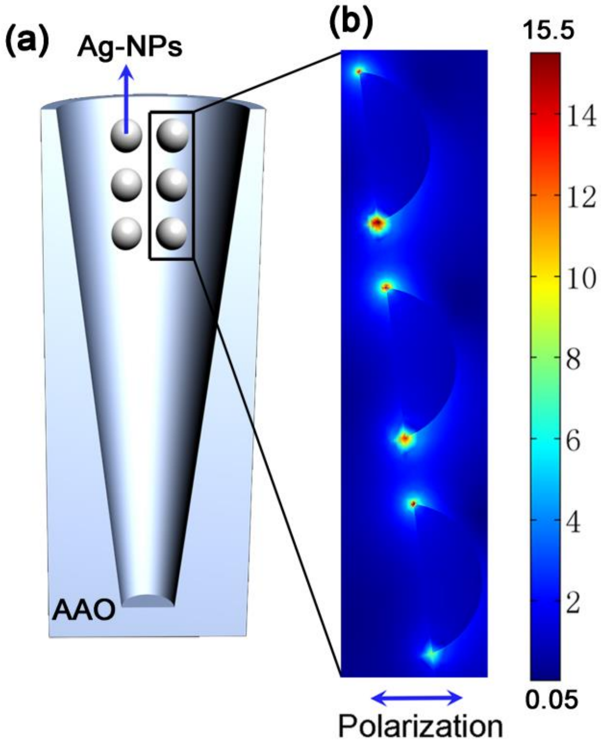


Fig. S9 (a) Schematic of Ag-NPs in the conical-pore of the AAO template for FEM calculation, with gap size of about 8 nm between the nearest NPs. (b) Simulated electric-field intensity distribution in the vertical plane across the middle of the selected NPs. The polarization of the incident light is shown on the lower section.

References

1. K. Choi, S. H. Park, Y. M. Song, Y. T. Lee, C. K. Hwangbo, H. Yang and H. S. Lee, *Adv. Mater.*, 2010, **22**, 3713.
2. Y. C. Liu, K. H. Yang and T. C. Hsu, *J. Phys. Chem. C*, 2009, **113**, 8162.
3. T. Qiu, W. J. Zhang, X. Z. Lang, Y. J. Zhou, T. J. Cui and P. K. Chu, *Small*, 2009, **5**, 2333.