Electronic Supplementary Information

Urchin-like Au-nanoparticles@Ag-nanohemisphere Arrays as Active SERS-substrates for Recognition of PCBs

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. Experimental Section

Fabrication of the urchin-like Au-NPs@Ag-NHS nanodot arrays: The AAO templates with large-scale highly ordered and hexagonally arranged nanopores were prepared via a two-step anodization of Al foil in 0.3 M oxalic acid under DC 40 V at 8 ℃.[15] The nanopores were widened for different durations to achieve desired pore-wall thickness in 5% (wt.) phosphoric acid at 40 ℃. Ag was sputtered onto the top surface of the AAO template to achieve Ag-NHSs within the pores by using an ion sputter (EDT-3000) for 20 min with a current of 5 mA, vacuum of 1.2×10^{-1} mBar. Then, wax was smeared on the top surface of the Ag-film by using an electrothermal board setting at 125 ℃, and a Si wafer (or glass slide) was attached to fix and support the Ag-NHS arrays. Next, the AAO template was removed in 1M NaOH solution for 20 min, achieving uniform Ag-NHS arrays supported on Si-wafer. Finally, small Au-NPs were sputtered onto the Ag-NHS surface for 10 s (EMITECH K550) with a current of 40 mA, vacuum of 1.0×10^{-1} mBar, to achieve 3D uniformly arranged urchin-like Au-NPs@Ag-NHS nanodot arrays.

Characterization: The wafer-scale aligned nanodot arrays were characterized by using SEM (SIRION 200). The Raman scattering spectra were recorded by a confocal Raman system (Renishaw, inVia). The excitation wavelength was 532 nm from an air-cooled argon ion laser, and the laser power was 0.5 mW used in the experiments. In the Raman characterization, the as-prepared substrates were immersed in R6G solution with different concentrations for 4 hours. For the identification of PCB-3, 2 uL of PCB-3 ethanol solutions from 10^{-3} M to 10^{-5} M were dropped onto the as-prepared substrate, and followed by Raman characterization after drying in the laboratory fume hood.

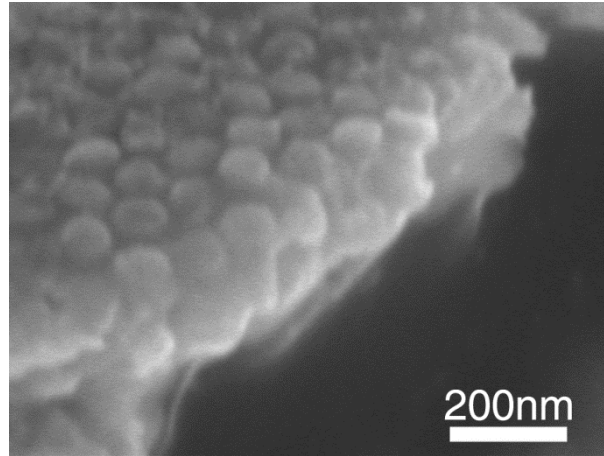**Part S1. The side-view SEM image of the Ag-NHS array to show the height of the Ag-NHS**

Figure S1. The side-view SEM image of the Ag-NHS array

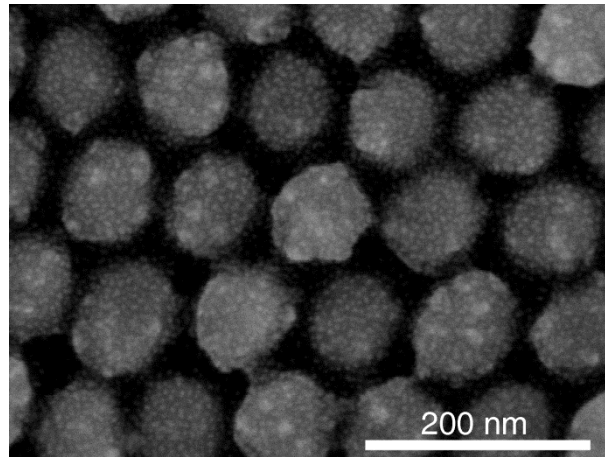**Part S2. The high-resolution SEM image of the Au-NPs@Ag-NHS array**

Figure S2. The high-resolution SEM image of the as-prepared Au-NPs@Ag-NHS array

Part S3. The diameter tailoring of the Ag-NHSs and the consequent neighboring gaps by tuning the pore-widening duration.
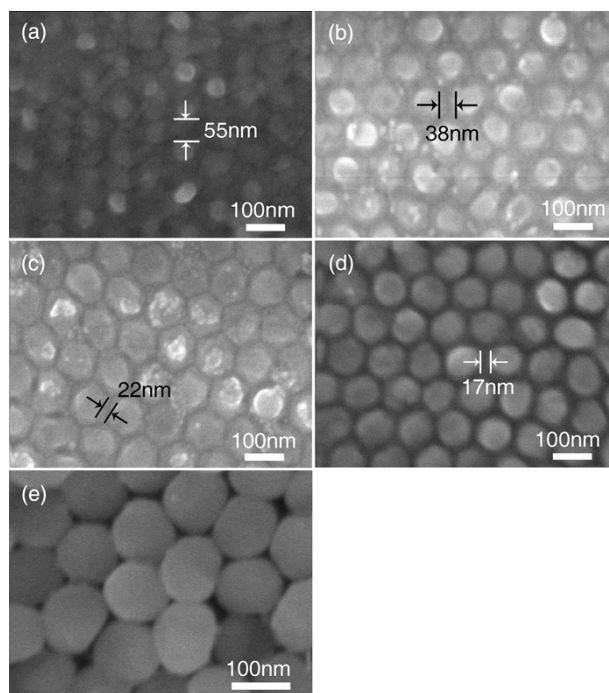

Figure S3. The SEM images of Ag-NHS arrays fabricated via sputtering Ag onto the surface of AAO templates with different pore-widening durations: (a) 0 min; (b) 5 min; (c) 10 min; (d) 15 min; (e) 25 min.

Part S4. The calculation of the dependence of enhancement factor (EF) on the gaps between the neighboring Ag-NHS
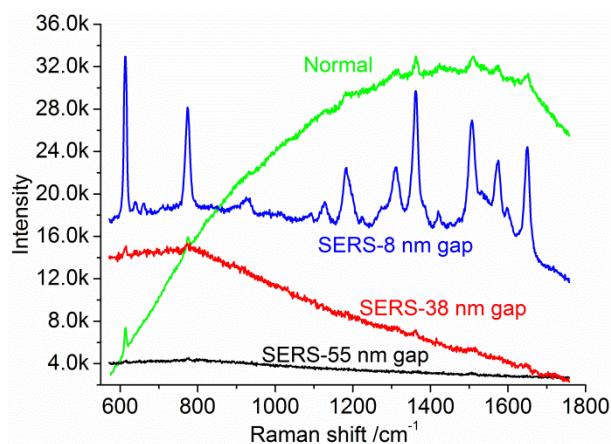

Figure S4. The Raman spectrum of 10^{-3} M R6G molecules on glass plate (denoted as "Normal") and the SERS spectrum of 10^{-9} M R6G molecules dropped on the Ag-NHS arrays with 8 nm neighboring gap (denoted as "SERS-8 nm gap", the laser power is 0.5 mW and integration time is 10 s), and the SERS spectrum of 3×10^{-7} M R6G molecules dropped on the Ag-NHS arrays with 38 and 55 nm neighboring gap (denoted as "SERS-38 nm gap" and "SERS-55 nm gap", respectively, the laser power is improved to 1mW and integration time is 10 s)

The EF can be calculated by

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{Nor}/N_{Nor}}$$

where I_{SERS} and I_{Nor} represent the intensity of the same band of R6G (here, 611 cm^{-1}) of SERS spectrum and normal Raman spectrum, and N_{SERS} and N_{Nor} represent the corresponding number of molecules in the focused incident laser spot.

In the experiment, 2 uL of 10^{-3} M R6G ethanol solution was dripped on a glass substrate, and diffused into a circle area with a diameter of 10 mm. Repeated 6 times to achieve uniform signal response. Then, on the assumption that all the molecules uniformly distributed on the substrate, there were 1.27×10^{19} molecules in per unite area. So, in the area of incident laser spot of 5 μm in diameter (×20 object lens,

Renishaw), there was 1.8×10^9 molecules, i.e. the N_{Nor} was 1.8×10^9. On the other hand, I_{Nor} is 1740 unites as shown in Figure S4.

For the as-prepared Ag-NHS arrays with different gaps were immersed in 3×10^{-7} M R6G solution for 4 hours to achieve uniform signal response in the SERS characterization, it's difficult to calculate accurately the number of R6G molecules adsorbed on the substrate. Here, as an estimation method, we use the similar experimental method to estimate the EF of the Ag-NHS array with 8 nm neighboring gap. 5 uL of 10^{-9} M R6G aqueous solution was dripped on the as-prepared Ag-NHS arrays substrate, and diffused into a circle area with a diameter of 5 mm. Then, the N_{SERS} was calculated to be 3010. On the other hand, I_{SERS} is 14640 unites as shown in Figure S3.

So, the EF of the Ag-NHS array with 8 nm neighboring gap can be calculated to be 0.5×10^7. For the case of the other Ag-NHS array substrates with different neighboring gaps, the EF can be achieved by proportioning Raman intensity of the sample with 8 nm gap to the other samples. Then, based on the intensity shown in Figure 2(a), the EF of the Ag-NHS array with 17 nm, 22 nm and no gap (with pore-widening time of 25 min) is 2.8×10^6, 1.2×10^6, and 3.4×10^5, respectively. For the case of Ag-NHS arrays with 38 and 55 nm neighboring gap, the intensity is too low to distinguish in Figure 2(a). Via improving the incident laser power, the SERS spectra are shown in Figure S4. Based on the intensity ratio to the Ag-NHS arrays with 8 nm gap, the EF of the Ag-NHS array with 38 nm and 55 nm gap is 4.5×10^5 and 1.3×10^5, respectively.

Part S5. The morphology evaluation of the Au-NPs@Ag-NHS arrays after different Au-sputtering duration.
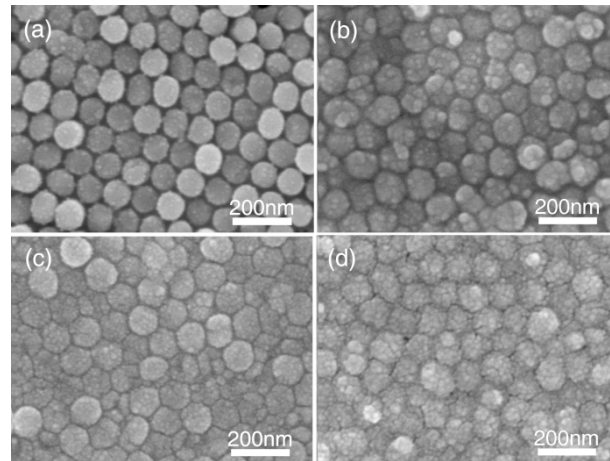

Figure S5. The SEM images of the as-prepared Au-NPs@Ag-NHS arrays after Au-sputtering of (a) 20s; (b) 1min; (c) 1.5 min; (d) 2 min.

Part S6. The localized electrical field distribution with FDTD simulation between the bare Ag-NHSs with 17 nm neighboring gaps.
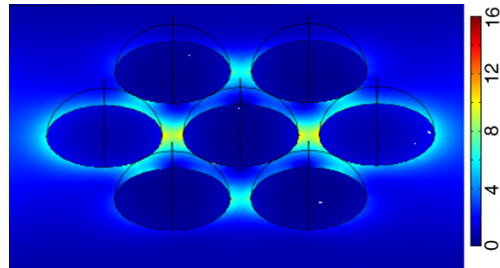

Figure S6. The localized electrical field distribution with FDTD simulation between the bare Ag-NHSs with 17 nm neighboring gaps.

Part S7. The calculation of the enhancement factor of the as-prepared urchin-like Au-NPs@Ag-NHS hybrid nanodot arrays.
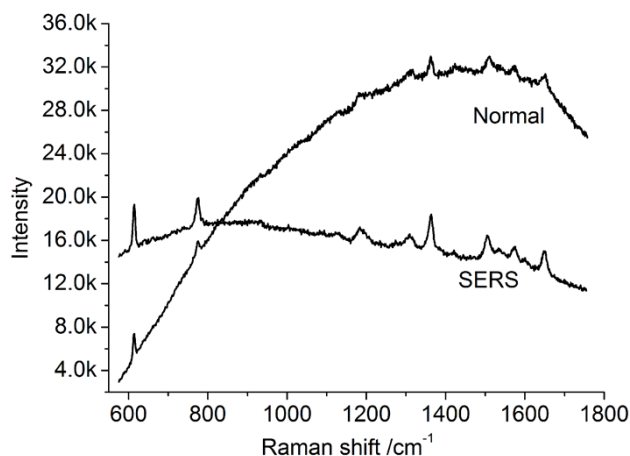

Figure S7. The Raman spectrum of 10^{-3} M R6G molecules on glass plate and the SERS spectrum of 10^{-10} M R6G molecules dropped on the urchin-like Au-NPs@Ag-NHS nanodot arrays.

Via similar experimental methods in Part S3, 5 uL of 10^{-10} M R6G aqueous solution was dripped on the as-prepared urchin-like Au-NPs@Ag-NHS hybrid nanodot arrays substrate, and diffused into a circle area with a diameter of 5 mm. Then, the N_{SERS} was calculated to be 301. The normal and SERS Raman intensity of the R6G are shown in figure S7, in which we can get that the I_{SERS} and I_{Nor} are 3590 unites and 1740 unites, respectively. So, the EF is calculated to be 1.23×10^7.