Supporting Information

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A Hierarchically Ordered Array of Silver-Nanorod Bundles for Surface-Enhanced Raman Scattering Detection of Phenolic Pollutants

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This Supporting Information includes:

Part S1. Experimental Section

Part S2. Enhancement Factor Calculation

Part S3. Figure S1-S14, and Table 1

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Part S1. Experimental Section

**Fabrication of Binary Templates.** The through-pore anodic aluminum oxide (AAO) templates were prepared via two-step anodization of pure aluminum foil in 0.3 M oxalic acid under 50 \( V_{\text{dc}} \) at 8 °C.\[^{[S1]}\] Uniform monolayer colloidal crystal composed of polystyrene (PS) spheres (2 µm in diameter) was deposited on a glass slide by an interface self-assembly method and then transferred onto an AAO template by the floating method (Figure S1 and S2), as described in detail previously.\[^{[S2,S3]}\] After being dried at room temperature, the monolayer PS sphere-covered AAO template was held at 110 °C for 60 min to make the PS spheres intimate contact with the AAO template and block the AAO pores underneath the PS spheres. Then the monolayer PS spheres on the AAO template was etched by argon plasma using a plasma cleaner (PDC-32G, high power) for 30 min to obtain a non-close-packed monolayer PS spheres on AAO template.\[^{[S4]}\]

**Fabrication of Ordered Arrays of Ag-Nanorod Bundles.** A layer of Au (~200 nm in thickness) was sputtered on both the PS sphere surfaces and the AAO template surface that was not covered by the PS spheres to serve as the electrode for the further growth of the Ag-nanorod in the AAO pores. Then the Ag-nanorods were electrodeposited inside the Au layer-covered AAO pores at a constant current of 150 \( \mu \text{A} \) at 20 °C for 20 min. The electrolyte consisted of \( \text{AgNO}_3 \) (5 g L\(^{-1}\)), ethylene diamine tetraacetic acid (3 g L\(^{-1}\)), \( \text{Na}_2\text{SO}_3 \) (25 g L\(^{-1}\)), and \( \text{K}_2\text{HPO}_4 \) (10 g L\(^{-1}\)). Subsequently the monolayer PS spheres were removed in the \( \text{CH}_2\text{Cl}_2 \) solution, leading to exposure of the PS spheres-blocked AAO pores. A layer of Au (~200 nm in thickness) were sputtered on the AAO to cover the exposed empty pores, and then a layer of Cu (more than 100 \( \mu \text{m} \) in thickness) was electrodeposited on the Au layer to support the Ag-nanorods after dissolution of the AAO template. Afterwards, the Ag-nanorod array was exposed by etching the AAO template in the 3 M NaOH solution at room temperature for 1 h, washed with de-ionized (DI) water several times, and then stored in DI water before being transferred into the analyze solution for SERS sensing.
Characterization. The as-prepared Ag-nanorod bundle arrays were characterized by a field-emission SEM (SIRION 200) and an ultraviolet-visible-near-infrared spectrophotometer (Hitachi, U-4100). SERS measurements were conducted under a confocal microprobe Raman system (Renishaw, inVia) with an excitation wavelength of 632.8 nm. During SERS measurement, the laser light was vertically projected onto the samples with a resultant beam diameter of \( \sim 5 \, \mu m \). The blank hexagonal regions without the Ag-nanorods can be observed by the optical microscopy of the Raman spectrometer. To improve the signal reproducibility and uniformity, all the SERS spectra were taken from the spots whose centers were such blank regions. There were about 12 bundles of Ag-nanorods in the laser beam with a diameter of 5 \( \mu m \). For checking its signal uniformity, the ordered Ag-nanorod array was dipped into a 10 nM ethanol solution of 4-MBA for 12 h, then taken out and air-dried. To calculate the SERS enhancement factor, the ordered Ag-nanorod array was immersed into a 0.1 mM ethanol solution of 2-NT for 12 h, then taken out, rinsed with ethanol and air-dried. To evaluate the SERS sensitivity toward methyl parathion, 2,4-D, and their mixture in water, the ordered Ag-nanorod array substrates were dipped into a aqueous solution with different concentrations of methyl parathion, 2,4-D, and their mixture for 6 hours, respectively, then taken out and air-dried.

FDTD simulations. FDTD simulations were conducted using the commercially available Optiwave software. The simulation cell was constructed with a grid size of 1 nm. A monochromatic light source of 633 nm was used to match the laser used in experiments. The dielectric constant of silver was taken from Palik. The EM field enhancement was calculated by \( (E/E_0)^2 \) with only the peak value used.
Part S2. Enhancement Factor Calculation

The EF of the Ag-nanorod bundle array was determined by computing the ratio of SERS to normal Raman scattering (NRS) of 2-NT using the following expression

$$\text{EF} = \frac{I_{\text{SERS}}/N_{\text{SERS}}}{I_{\text{NRS}}/N_{\text{NRS}}}$$

where $I_{\text{SERS}}$ and $I_{\text{NRS}}$ correspond to the integrated SERS and NRS intensities, respectively, normalized for acquisition time and laser power. $I_{\text{NRS}}$ was determined to be 296 cts mW$^{-1}$ s$^{-1}$ (Curve I in Figure S13). $N_{\text{SERS}}$ and $N_{\text{NRS}}$ are the number of molecules probed in the SERS and NRS measurements. $N_{\text{SERS}}$ is established by the surface area ($S$) illuminated by the laser beam and the packing density ($D$) of 2-NT molecules on the surface of substrate. The $D$ of 2-NT was reported to be 2.4×10$^{14}$ molecule/cm$^2$. The average number of Ag-nanorod bundles illuminated by a laser beam (with a diameter ~5 µm) is estimated to be 12. Each bundle is made up of ~37 nanorods. The average surface of a nanorod (with an average diameter of 65 nm and an average length of 800 nm) is $800 \times 65\pi + 0.25 \times 65^2 \pi$ (nm$^2$) = 1.67×10$^5$ (nm$^2$) = 1.67×10$^{-9}$ (cm$^2$). So $S = 12 \times 37 \times (1.67 \times 10^{-9})$ cm$^2$ = 7.41×10$^{-7}$ cm$^2$, and thus $N_{\text{SERS}} = S \times D = 1.78 \times 10^8$. $N_{\text{NRS}}$ is the number of 2-NT molecules in a cylinder with a diameter of 5 µm (i.e. the diameter of the laser beam) and a height of 26 µm (i.e. the laser confocal depth). $N_{\text{NRS}} = 1.22 \text{g/cm}^3 \times \pi \times (2.5 \times 10^{-4} \text{cm})^2 \times (26 \times 10^{-4} \text{cm}) \times (6.02 \times 10^{23})/160 \text{g} = 2.4 \times 10^{12}$. $I_{\text{SERS}}$ is 3.086×10$^6$ cts mW$^{-1}$ s$^{-1}$ (Curve II in Figure S13). So $\text{EF} = (I_{\text{SERS}}/N_{\text{SERS}})/(I_{\text{NRS}}/N_{\text{NRS}}) = 3.086 \times 10^6/(1.78 \times 10^8 \times 2.4 \times 10^{12}/296 = 1.4 \times 10^8$. 

$I_{\text{NRS}}$ was determined to be 296 cts mW$^{-1}$ s$^{-1}$ (Curve I in Figure S13).
Part S3. Figure S1-S14, and Table S1

Figure S1. The photograph of a bare AAO template (left) and an AAO template covered by the PS sphere monolayer (right).

Figure S2. A SEM image of ordered close-packed PS sphere monolayer on AAO template surface.
**Figure S3.** (a,b) SEM images of ordered non-close-packed PS sphere monolayer on AAO template surface.

**Figure S4.** Photograph of an AAO template with Ag-nanorods electrodeposited in its nanopores.
Figure S5. (a,b) SEM images of an AAO template after electrodeposition of the Ag-nanorods and removal of the PS sphere monolayer.

Figure S6. SEM images of vertically distributed Ag-nanorods (a) before and (b) after etching AAO membrane, demonstrating that the Ag-nanorod length is ~800 nm.
Figure S7. (a-c) The measured distances of gaps between the neighboring Ag-nanorods, and (d) the gap distance distribution.

Figure S8. The optical absorption spectrum of an Ag-nanorod bundle array.
Figure S9. A SEM image of Ag nanoparticles trapped in the gaps between the neighboring Ag-nanorods.

Figure S10. SERS peak (615 cm$^{-1}$) intensity of R6G on the Ag-nanorod bundle array plotted as a function of time during evaporation of water. The wet Ag-nanorod array was transferred into a R6G solution (1 µM) for 1 h, and rinsed with pure water for several times; then a single 2-µL droplet of pure water was dropped on it for SERS measurement during water evaporation.
**Figure S11.** FDTD simulated EM field enhancement. Both (a) double Ag-nanorods and (b) a bundle of 37 Ag-nanorods were investigated with the gap size varied as 0 nm, 1 nm, 2 nm, 5 nm, 10 nm, 20 nm, 50 nm, and 73 nm. (c) A gap size of 2 nm was found to give the highest peak EM field enhancement for both simulation scenarios.

**Figure S12.** A SEM image of the Ag-nanorod bundles fabricated using only the AAO template.
Figure S13. (Curve I) normal Raman spectrum of 2-NT film and (Curve II) SERS spectrum of 2-NT adsorbed on the ordered array of Ag-nanorod bundles.

Figure S14. SERS spectrum of 1 µM PCB-3.

Table S1. The average 1585 cm⁻¹ peak intensities of 4-MBA SERS spectra collected from 5 substrates of different batches.

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Part S4. References


