Supplementary Information

Flexible plasmonic nanocavity: a universal platform for the identification of molecular orientations

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I: Fabrication of the AuNPs nanoarrays with anodic aluminum oxide (AAO) membranes.

The AAO was anodized on aluminum foils with a film thickness of 300 nm and pore width of 35 nm, as shown in Figure S1(a). The AAO with designed parameters were produced by Shenzhen Topmembranes Technology. The produced samples were placed in 5 wt % phosphoric acid at a constant temperature of 30 °C for 27 minutes to broaden the AAO pores. Then the AAO was spin-coated with a polymethyl methacrylate (PMMA) layer, and baked at 120 °C for 10 minutes to ensure that PMMA filled the pores. Then, the aluminum foil was removed from the AAO membrane in 100 g/L CuCl₂ solution. The membrane was subsequently transferred to 5 wt % phosphoric acid at 30 °C for 35 min to remove the AAO barrier layer. The membrane was transferred into acetone to remove the PMMA, and then transferred onto silicon or quartz substrates. The AAO features a pore diameter of ~75 nm and a thickness of about 270 nm as shown in Figure S1(b). Then 40 nm thick gold was deposited on the samples at 0.5 Å s⁻¹ under the vacuum of 4×10^{-4} pa to fabricate the Au plasmonic nanoarrays. Afterwards, the AAO template was peeled off from the substrate with tape, leaving patterned AuNPs on the substrate.



Figure S1. SEM images of the AAO before (a) and after (b) pore broadening, respectively.



Figure S2 (a) Statistics of the diameter of the AuNPs in the SEM image from Figure 1(b) in the main text. (b) XRD spectra of AuNPs on quartz.



II: Simulations of the EM fields in the nanocavities.

Figure S3 (a). Calculated EM fields around the nanocavity with different overlap ratio n and polarization angle θ . (b) The intensity ratio between the field components at x and y axes as a function of the polarization angle. The data were extracted from the calculated results in the cavities in Figure S3(a).



Figure S4. Calculated EM field distribution in the around the nanocavity with a gap distance of 5 nm in the case of n = 1/3 and $\theta = 0^{\circ}$. It is observed that the gap mode squeezes all the optical fields perpendicularly along the y axis with field vector spinning around the propagation axis, and the results remain the same when θ was modulated from 0° to 90°. In contrast, the cavity modes can be quite different in momentum in our experiments when the gap distance is reduced to 1 nm.

III: Fabrication of the molybdenum disulfide nanocavity

Continuous MoS₂ layers were employed for the polarization-dependent studies. The XPS characterization of the MoS₂ layers was displayed in Figure S5. The Au nanoparticles (AuNPs) arrays were fabricated by employing AAO membranes as masks on quartz substrates in E-beam evaporation. The sample with a centimeter-scale is shown in Figure S6a. The MoS₂ layer was transferred onto one of the AuNPs nanoarray membrane, as illustrated in Figure S6b. Afterwards, PMMA was spin-coated on the two samples in (a) and (b), and baked in the air. The membranes were peeled off from the quartz substrates in an alkaline solution, and flexible membranes were obtained (Figure S6c). These two samples were adhered together by Van de Walls force and then dried, which have been described in the manuscript. Finally, the AuNP-MoS₂-AuNP sandwich plasmonic nanocavity was obtained (Figure S6d).



Figure S5. The XPS spectra of S and Mo of the MoS₂, respectively.



Figure S6. A set of photography illustrating the processes in preparing the MoS₂ sandwiched plasmonic nanocavities. (a) Prepared AuNPs sample on a quartz substrate. (b) Another AuNPs sample with a transferred MoS₂ layer on top. (c) Flexible plasmonic membranes peeled off from the quartz substrate in (a) and (b). (d) Fabricated MoS₂ sandwiched flexible plasmonic nanocavity sample on silicon wafer. The diameter of the quartz substrate is 15 mm.

IV. The Raman spectra and vibrational assignment of Rhodamine 6G.



Figure S7. The Raman spectra of Rhodamine 6G on Au at different concentrations. The spectra have been normalized by the mode intensities at 1649 cm⁻¹. The marked mode at 234 cm⁻¹ suggests that a chemical bond between the metal and the nitrogen atom with free electron pairs.

SERS (cm ⁻¹)	Assignment
611	C-C ring in-plane bending in xanthene/phenyl rings
774	C-H out-of-plane bending
1127	CH in-plane bending in xanthene/phenyl rings
1184	C-H in-plane bending in xanthene ring
1310	hybrid mode (xanthene/phenyl rings and $\rm NHC_2H_5$ group)
1362	C-C stretching in xanthene ring
1508	C-C stretching in xanthene ring
1573	C-C stretching in phenyl ring
1649	C-C stretching in xanthene ring

Table S1. Spectral data and vibrational assignment of R6G.

*The SERS data were extracted from our experimental data from the plasmonic sandwich nanocavities. The data is consistent with the normal Raman spectra of bare R6G molecules from previous publications.^{1, 2}

V. Calculation of the enhancement factor of the plasmonic sandwich nanocavities.

The enhancement factor (EF) for SERS is defined by:

$$EF = (I_{\text{SERS}}/N_{\text{SERS}})/(I_{\text{Ref}}/N_{\text{Ref}})$$

where I_{SERS} and I_{Ref} are the intensities of the selected Raman peak of SERS and normal Raman spectra, respectively. N_{SERS} and N_{Ref} are the number of molecules in the laser spot area during Raman measurements.

The Raman signal of R6G (10^{-2} M) is used as a non-SERS reference. The calculated enhancement factor of the plasmonic sandwich nanocavities is about 10^6 when the polarization angle is 80° . Considering that the laser spot of the Raman confocal microscopy was about 1 μ m and the effective projected area of the laser spot was significantly reduced, we can roughly come to the agreement that the final EF of the cavity should be on the order of 10^7 .

REFERENCE

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