Electronic Supplementary Information

Well-oriented epitaxial gold nanotriangles and bowties on MoS_2 for surface-enhanced Raman scattering

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1. The modulation of the substrate temperature and thermal deposition

During thermal evaporation, the MoS_2 samples were kept at a controlled temperature higher than room temperature. The temperature was controlled by a high-temperature ceramic heating micro-plate, which was operated by current heating. By changing the current, we can accurately tune the temperature gradually modulated within the range from room temperature to 580 °C. To make sure that the substrate temperature was stable, we waited 2h for temperature stabilization before gold

film deposition. After the temperature reached to the desired temperature, a thin layer of gold film was thermally evaporated onto the sample surface in a vacuum thermal evaporator at a deposition rate of 0.5 Å/s under a vacuum of ~ 10^{-4} Pa, which was then characterized by scanning electron microscopy (SEM), Raman and PL spectroscopy.

2. Sample preparation for TEM

The Au nanotriangles/MoS_2 sheets were cleaved from SiO_2/Si substrates by using a blade, and then dusted onto holey carbon TEM grids. Methanol was dropped onto the TEM grids to disperse the Au nanotriangles/cleaved MoS_2 sheets. The cleaved surfaces of MoS_2 should be roughly parallel to carbon films of the TEM grids. The TEM grids were dried naturally in air and loaded into a high-resolution transmission electron microscope (JEOL 2010F) for further characterization. The Au nanotriangles/MoS_2 sheets suspending over carbon holes were examined by HRTEM and selected area electron diffraction. The MoS_2 sheets were double-tilted to align the <001> direction parallel to the e-beam when HRTEM images were taken.

3. The distribution of edge lengths of Au nanotriangles

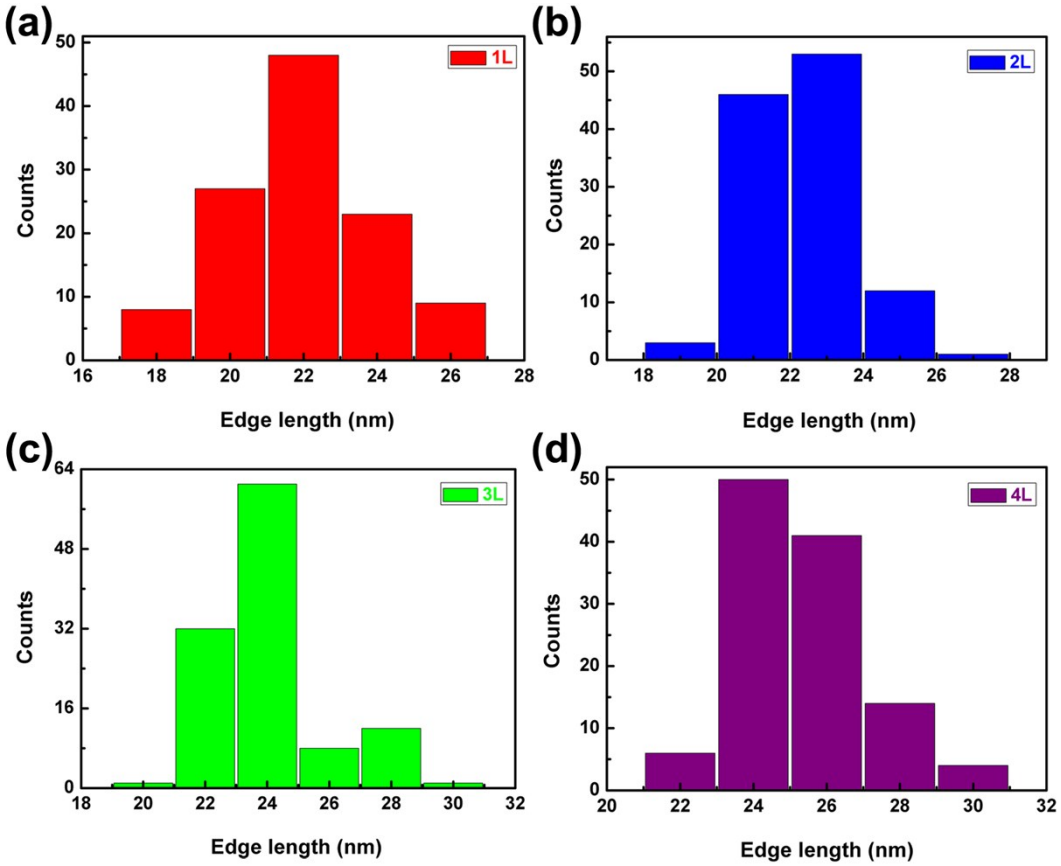

Fig.S1. The distribution of edge lengths of Au nanotrianles shown in Fig.2a and b.

4. The gap distribution of gold bowties on MoS_2

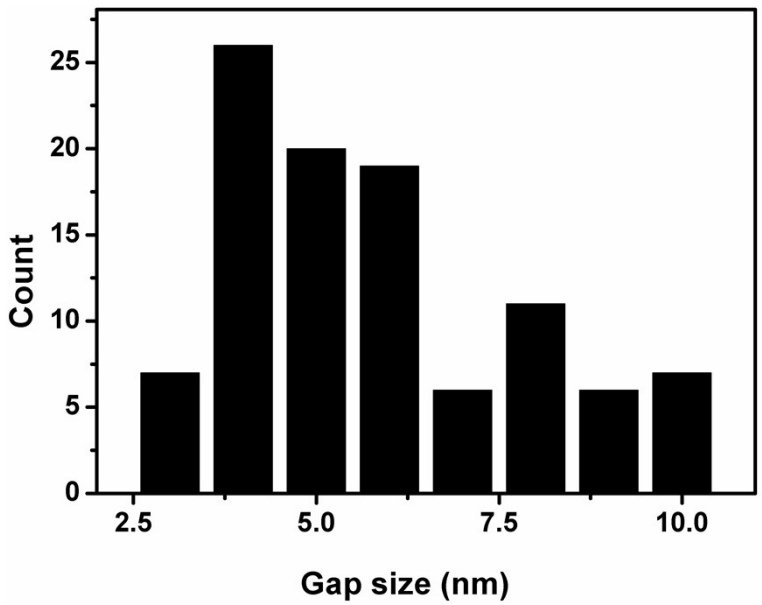

Fig.S2. The distribution of edge lengths of Au nanotrianles shown in Fig.2a and b.

5. The calculation method

We performed numerical simulations using Finite Difference Time Domain (FDTD) method to demonstrate the optical response of the well-oriented ultrathin gold nanotriangles. The influence of MoS_2 layer on the nanotriangles was neglected due to its atomically thin feature. In the simulation, glass (SiO_2, index=1.45) was used as the substrate, and gold was chosen as the material for nanotriangles, with permittivity described using Drude model by fitting the experimental data from the literature.[1]

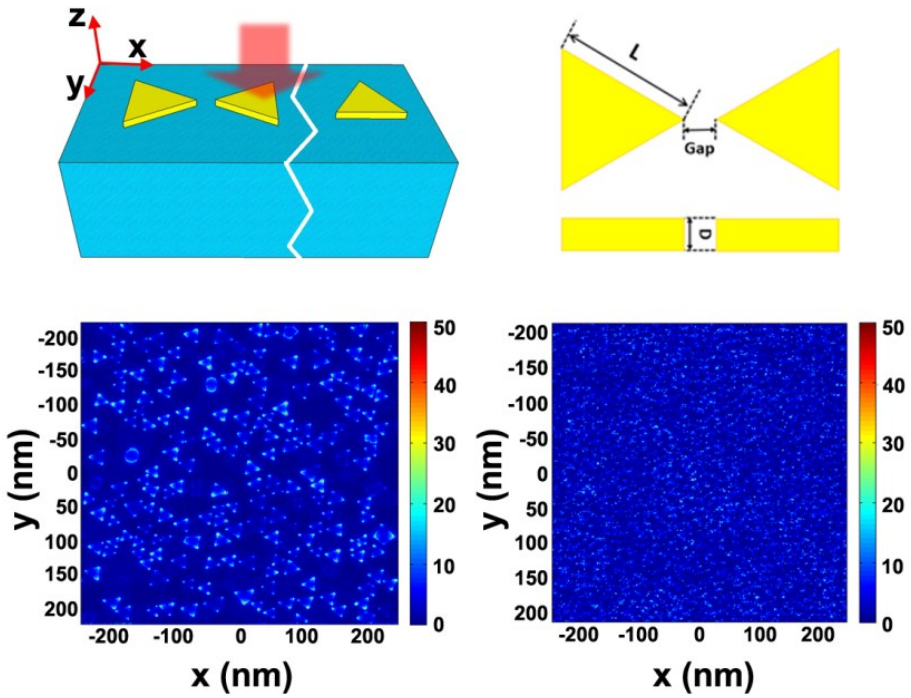

Fig. S3. Schematic (a) and front/side (b) views of the nanotriangles. The edge length (*L*), spacing gap, and thickness (*D*) of the simulated gold nanotriangles are 20, 3, 2 nm, respectively. Field distributions for well-oriented gold nanotriangles (c) and gold coarse film (d), respectively.

Figure S1a and b are the schematic and front/side views of the nanotriangles we used here for simulation, respectively. The incident light impinges on the triangular structure normally polarized

along *x* direction. Field distributions shown in the main text are extracted from 0.2 nm below the bottom surface of triangular structures. The images of Figure S1c and d are obtained by importing SEM photos directly into the FDTD software. Although the intensity of the triangles is much lower than the random distributed islands in the coarse film, the E_{max} for triangle is about 2 times higher (145/78) than coarse film, which is consistent with our experimental Raman measurement. We calculated the average Raman enhancement factor using equation $EF = \frac{1}{a}\int E^4 da$, and found EF for triangles is only about 6 (30224/5209) times higher than the film, far from the experimental result (about 40). We think this difference can be attributed to two aspects: (i) SEM photos are deformed after imported to our simulation software. (ii) Quantum effect is not taken into consideration, thus leading to over estimation for the EF of the coarse film, as islands separation in the film could be sub-nanometer. In subnanometer regime, quantum effect limits the field enhancement strongly.[2]

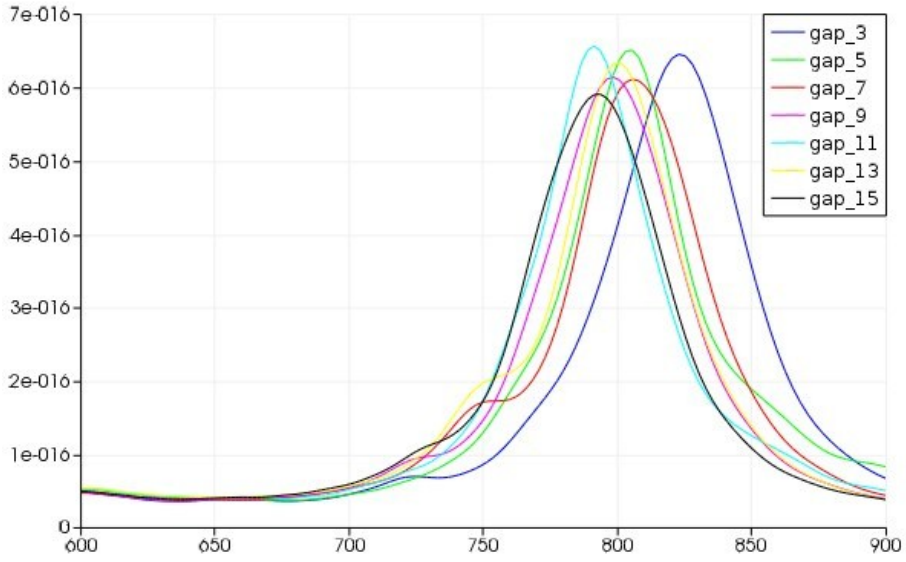

Fig. S4. The calculated extinction spectra of the gold bowtie structures as a function of the spacing gap. It is seen that these bowtie structures all show significant plasmon resonances near 785 nm, and the resonant peak is much closer to 785 nm as the spacing gap increases. Here the nanotriangle has

an edge length of 20 nm and thickness of 2 nm.

(1) Johnson, P. B.; Christy, R. W. *Phys. Rev. B* **1972**, *6*, 4370.

(2) Ciracì1, C.; Hill, R. T.; Mock, J. J.; Urzhumov, Y.; Fernández-Domínguez, A. I.; Maier, S. A.; Pendry, J. B.; Chilkoti, A.; Smith, D. R. Science 2012, 337, 1072.