Supporting Information

for

Hierarchical Growth of Au Nanograss with Intense Built-In Hotspots for Plasmonic Applications

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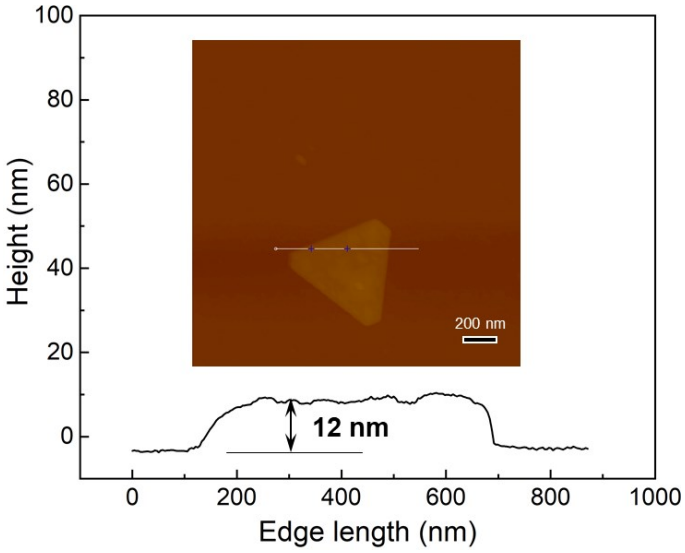

Fig. S1 A typical AFM image and the corresponding height profile for a pristine Au nanoplate. The surface roughness of the nanoplate can be attributed to the PVP (M.W., 40,000) coating.

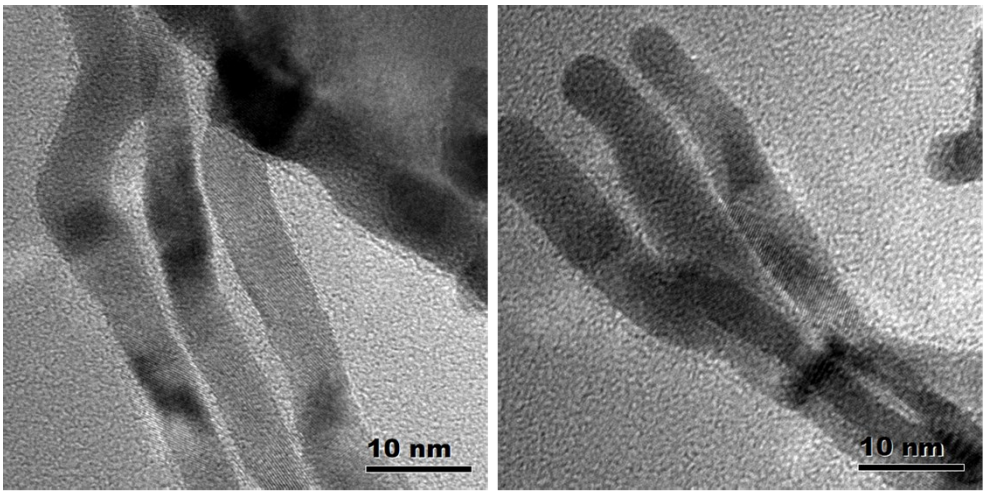

Fig. S2 Typical high-resolution TEM images of Au nanowires grown on the Au nanoplates that show the diameter of the nanowires.

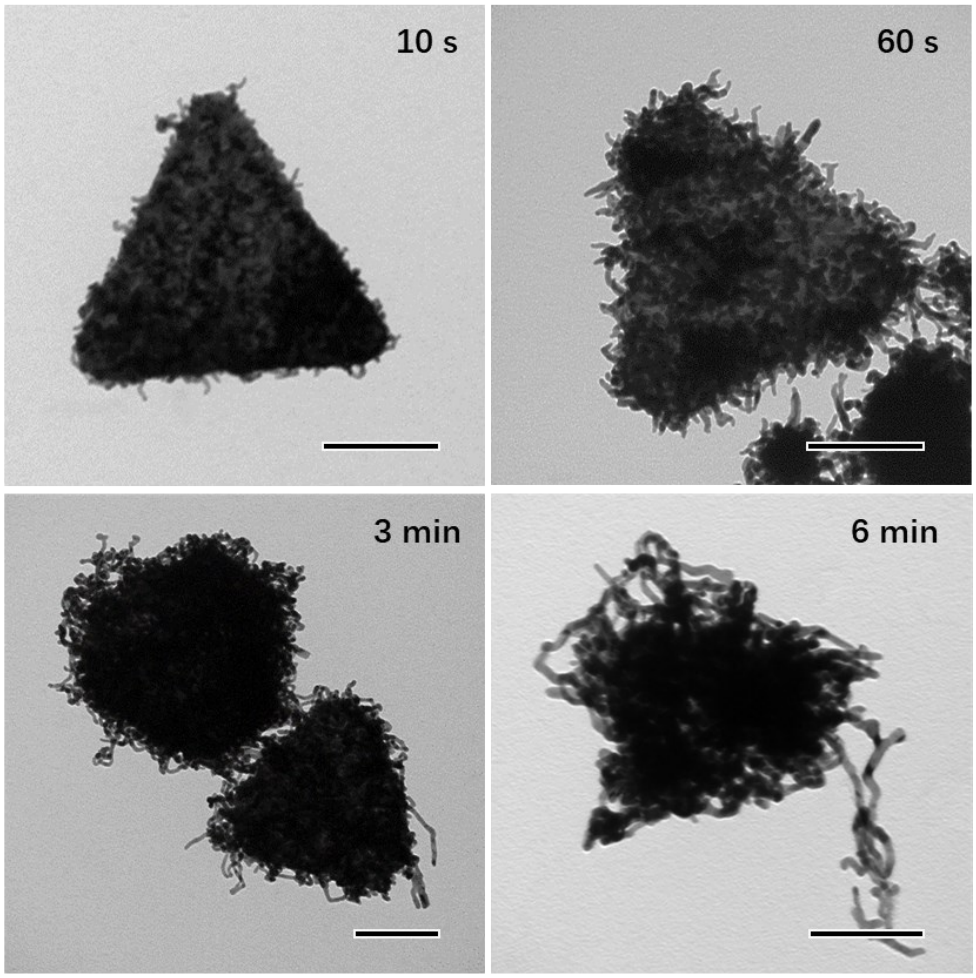

Fig. S3 Typical TEM images of the grown Au nanoplates obtained after growth in the presence of CTP for 10 s, 60 s, 3 min and 6 min, respectively. Scale bar: 100 nm.

Table S1. Summary of the diameter, length, density and inter-distance of the nanowires obtained under different reaction conditions. Due to the bending behavior, the length range of the nanowires were given. Assuming the long wires evolved from short ones, thereby their density and inter-distance remain constant. Each arrow of the data were obtained by investigating hundreds of nanowires.

Reaction condition	diameter / nm	Length / nm	Density / nm^{-2}	Distance / nm
0.5 mM of CTP, 10 s	5.1	7−12	185	8
0.5 mM of CTP, 60 s	6.1	20−25	185	8
0.5 mM of CTP, 3 min	6.2	40-60	185	8
0.5 mM of CTP, 6 min	6.4	105-150	185	8
0.15 mM of CTP, 3 min	13.9	30-50	330	4

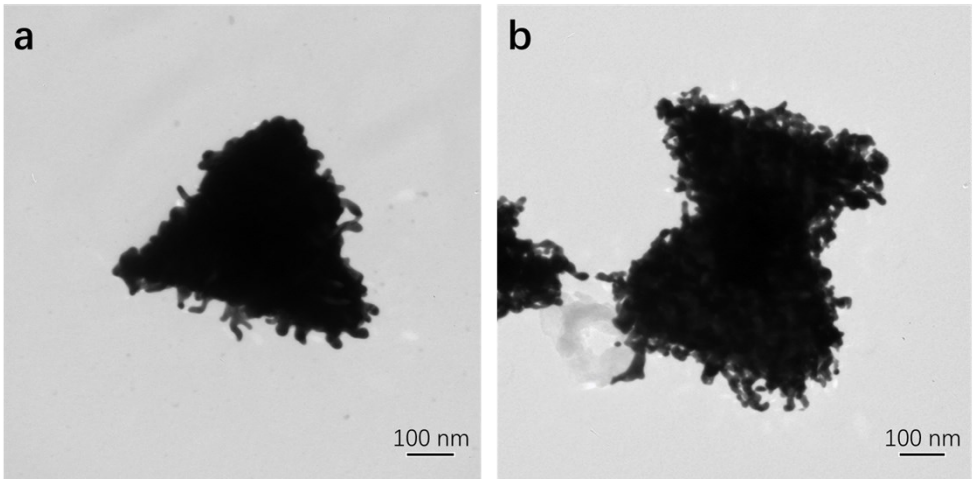

Fig. S4. Typical TEM images of the grown Au nanoplates obtained after growth in the presence of CTP at concentration of 0.05 M (a) and 0.15 M (b), respectively.

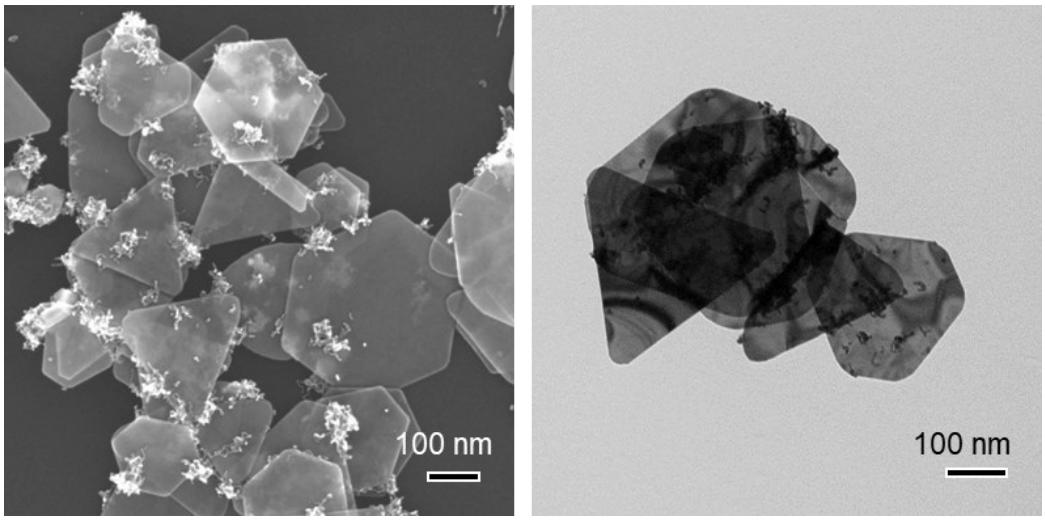

Fig. S5 Typical SEM (left) and TEM (right) images of the grown Au nanoplates obtained after incubation of the plate seeds with CTP (0.5 mM) for 3 h prior to growth, respectively.

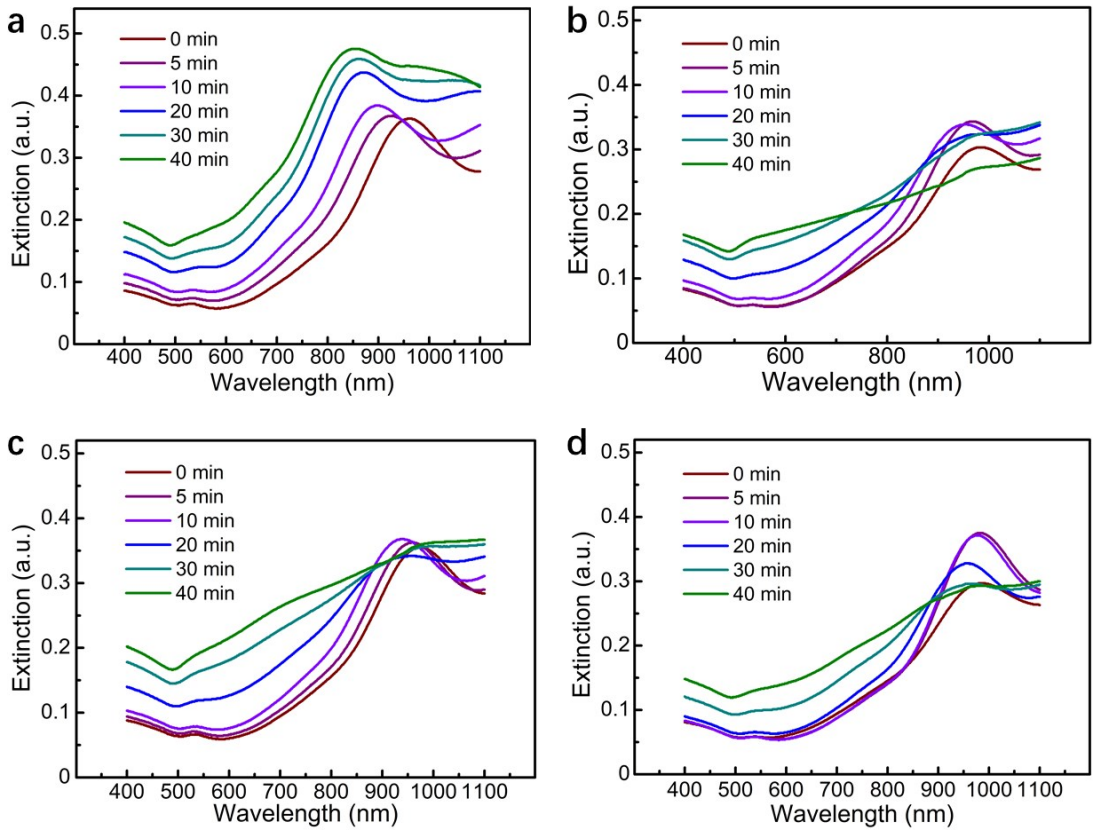

Fig. S6 Evolution of the extinction spectra during the solution-phase synthesis of the Au nanograss in the presence of CTP at different final concentrations: 0.44 (a), 2.66 (b), 4.4 (c) and 31 μM. The $HAuCl_4$ precursor solution (1.0 mM) was injected to a seed solution prepared by mixing 150 μL of colloidal Au nanoplate (~0.01 nM), 100 μL of AA (0.04 M) and 870 μL of CTP.

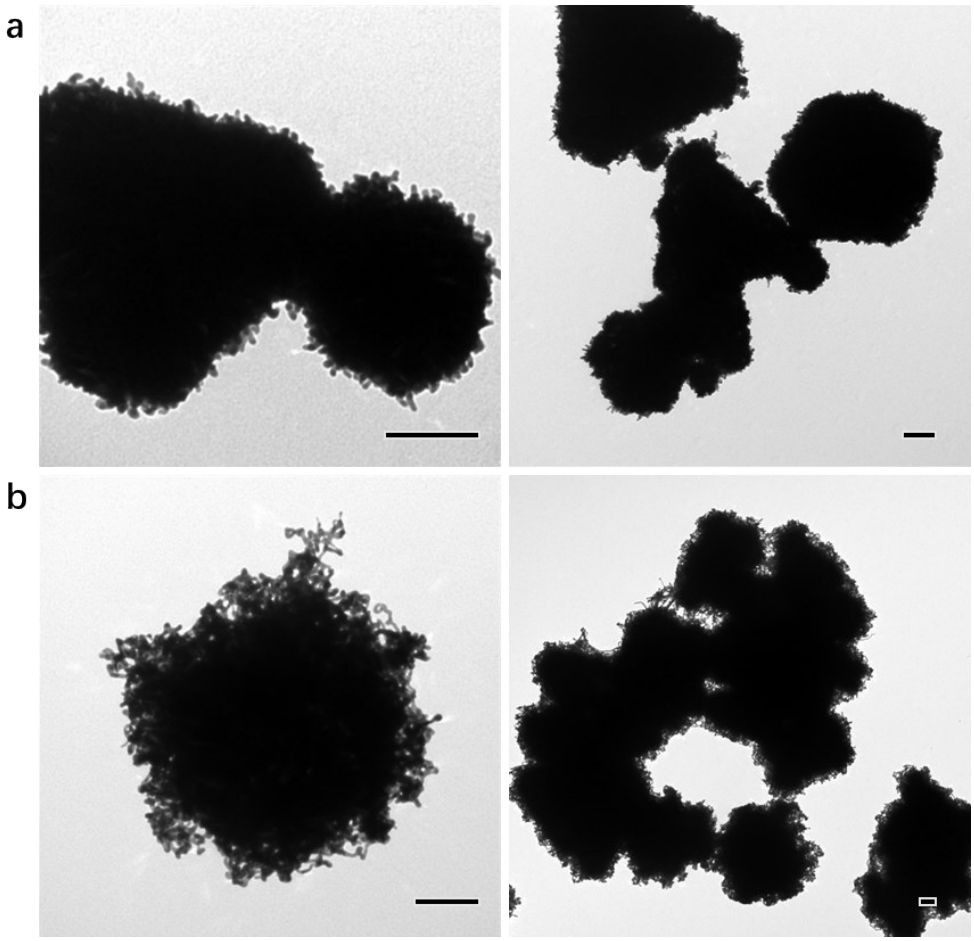

Fig. S7 CTP-modulated growth of nanograsss on Au nanoplates, which relavent to Fig. 4d in the main text. Growth of Au nanograss on an island-deposited Au nanoplate for 10 s (a) and 3 min (b). All scale bars are 100 nm.

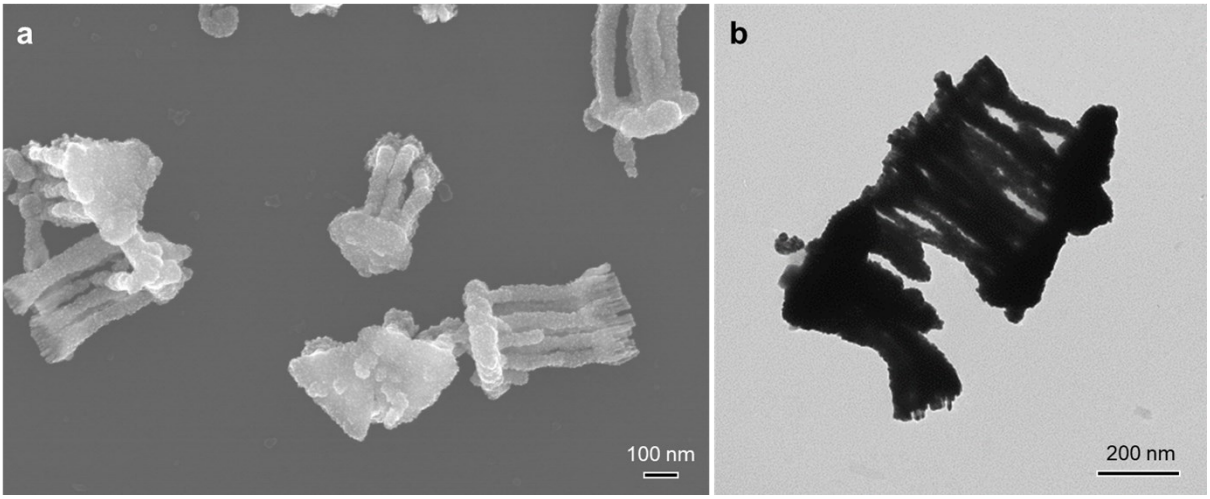

Fig. S8 Typical large-scale SEM (a) and TEM (b) images of the Au nanotubes-on-plate nanostructures, which are relavent to Fig. 4d in the main text.

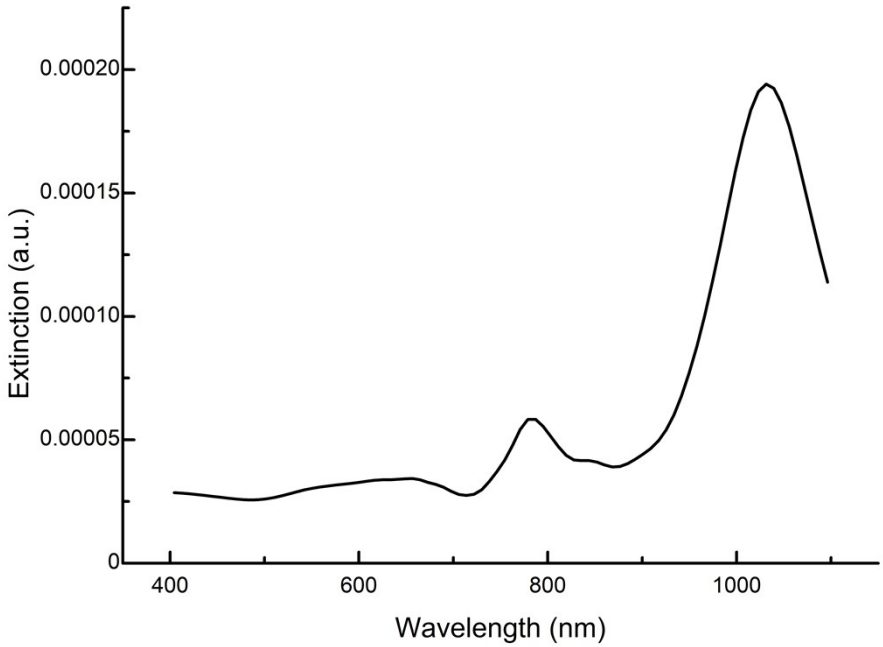

Fig. S9 Simulated extinction spectrum of the model Au nanograss.

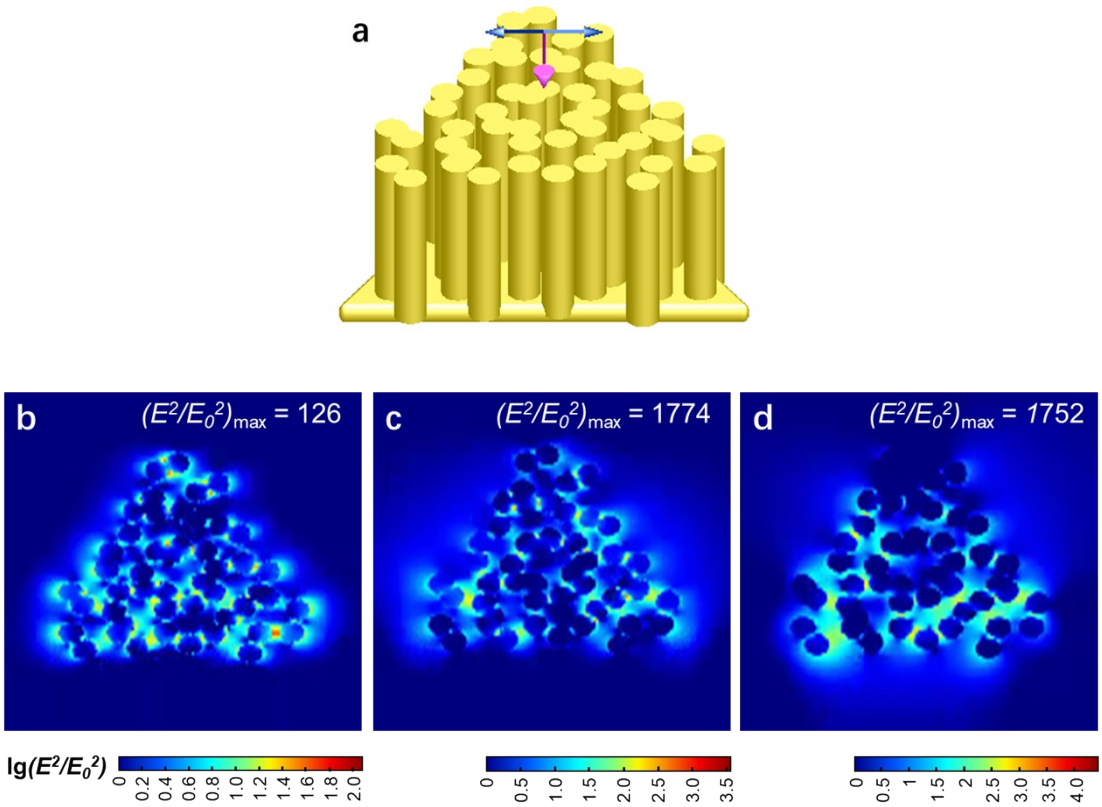

Fig. S10 Theoretical calculations of the electromagnetic field distributions of the array of straight Au nanowires. (a) Schematic illustration for the models of the straight Au nanowire array used in the FDTD simulations. (b−d) Simulated near-field electromagnetic filed distributions of the straight Au nanowire array obtained under irradiation by an incident plane wave at wavelengths of 535 nm (b), 633 nm (c) and 787 nm (d), respectively.

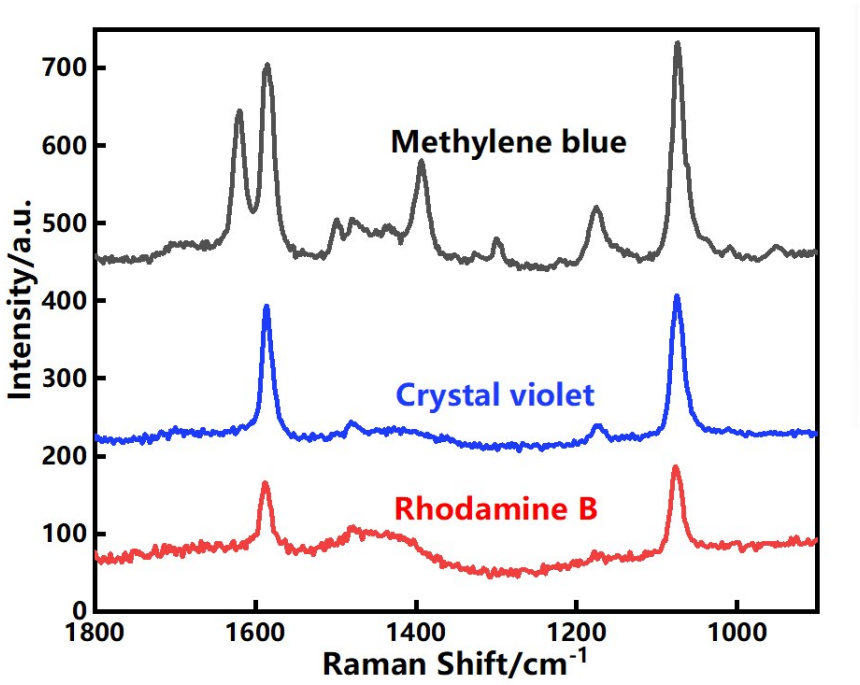

Fig. S11 SERS spectra of methylene blue, crystal violet and rhodamine B adsorbed onto the Au nanograss (~1.0 pM) in solution. The concentration of each Raman analyte was set to 1.0 × 10^{-6} M.

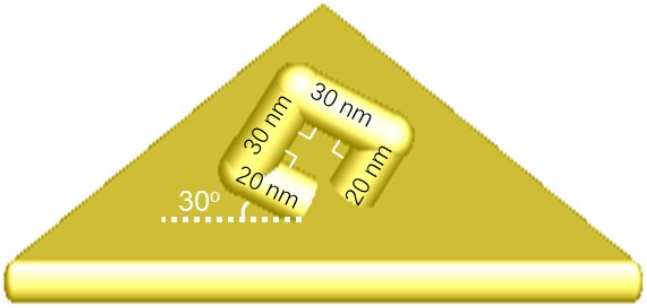

Fig. S12 The schematic design of a single bent Au nanowire on a Au nanoplate used in the FDTD simulations. The Au nanowire consists of four straight segments that are connected to the neighboring one(s) with a sphere. Each bent nanowire is of 100 nm in total length with a diameter of 15 nm, and consists of four coplanar straight nanowire segments that are of 20 nm, 30 nm, 30 nm, and 20 nm in length, respectively. The plane is vertical to the plate. In a single nanowire, each of the straight segment is connected to the neighboring one(s) at a right angle with a sphere (15 nm in size) as the junction, while the segment that contacts with the plate has an angle of 30° to the plate. The inter-distance between two bent nanowires in each group is set at 15 nm.

Calculation of the Raman enhancement factors

The enhancement factors for the nanostructures investigated in this study were estimated using the following equation

$$EF = \left(\frac{I_{surface}}{N_{surface}}\right) / \left(\frac{I_{solution}}{N_{solution}}\right)$$

where $I_{surface}$ and $I_{solution}$ are the Raman intensities of ABT at band 1574 cm^{-1} observed from a single Au nanoplate and a bulk solution (1.0×10^{-3} M), respectively, which were measured under identical conditions. Besides, $N_{surface}$ and $N_{solution}$ are the numbers of ABT molecules on the single Au nanoplate and from the bulk solution. As an example, we show the calculation procedure for the EF of the Au nanograsses.

The calculation of $N_{solution}$ can be approximately expressed as:

$$N_{solution} = 6.02 \times 10^{23}\ mol^{-1} \times 1.0\times10^{-3}\ mol/L \times \left[\pi\left(\frac{d}{2}\right)^2 \times H\right] = 1.7\times10^{8}$$

where $d \approx 1$ μm is the diameter of the laser spot under the Raman measurement condition. The value of effective depth H was determined to be 350 μm by referring a previous method (K. Liu, *et al.*, *Nano Lett* **2016**, *16*, 3675).

A droplet (10 μL) of islands-on-plate nanostructure (thickness ~12 nm, edge length ~200 nm and assuming all plates are triangular) with a known concentration (0.035 pM) was dropped on a silicon wafer (5 × 5 mm). As a result, we have the number of nanoplate

$$N_p = 6.02 \times 10^{23}\ mol^{-1} \times 3.5 \times 10^{-14}\ mol/L \times 10^{-5}\ L = 2.1\times10^{5}$$

According to our previous calculations, the effective surface area of a single island-on-plate grown for 30 min on the Si wafer is approximately $S_p = 5.3\times10^4$ nm^2. Also, there is $S_p = 1.7\times10^4$ nm^2 for the pristine nanoplate (G. Wang, *et al.*, *Chem* **2017**, *3*, 678).

Then, 10 μL of ABT solution (1.0×10^{-6} M) was dried under lucifugal condition. Thereby, the number of ABT molecule adsorbed on the entire Si wafter is

$$N = 6.02 \times 10^{23}\ \text{mol}^{-1} \times 10^{-5}\ \text{L} \times 1.0\times10^{-6}\ \text{mol/L} = 6.02\times10^{12}$$

Then, the initial average density could be estimated as

$$D = \frac{N}{N_p \times S_p + S_{rest-si}} = 0.24\ \text{nm}^{-2}$$

where $S_{rest\text{-}si}$ is the rest (bare) area on the Si water to Au nanoplate deposition. After washing for 3 times, the adsorbed ABT molecules on the Au nanoplates were partially removed. By means of UV-Vis spectral analysis, we determined that 49% of the adsorbed ABT remained on the surface during each washing process. This value was experimentally determined for Au nanoplates in solution, and was applied to each washing step for all the Au nanostructures tested. Subsequently,

$$N_{surface} = D \times S_p \times (49\%)^3 = 1496$$

Eventually, there is

$$EF = \left(\frac{I_{surface}}{N_{surface}}\right) / \left(\frac{I_{solution}}{N_{solution}}\right) = 4.0 \times 10^6$$

For the pristine plate, the adsorbed molecule numbers are estimated to be 480. Since the SERS signal was collected from about 6 particles, and the EF value was estimated to be 4.2×10^4 in average.

To calculate the average number of ABT adsorbed on each wires-on-plate nanostructure, firstly the number of wires-on-plate was estimated. By means of SEM observation, we noted that about one third of the area of the Si wafer was occupied by the adsorbed Au nanoplates. After deposition of nanowires on the Au nanoplates and the subsequent desorption by sonication, around 30% of the grown Au nanoplates. Thereby, the number of the Au nanograsses could be

calculated. Next, ABT was mixed with the Au nanograsses for adsorption purpose. After centrifugation, the UV-Vis absorbance of the resultant supernatant was analyzed and compared to that for the islands-on-plate nanostructure. It was deduced that the adsorption capability of the Au nanograss was ~1.2 times that of the islands-on-plate nanostructure. Therefore, ~1796 ABT molecules per Au nanograss were estimated. Based on the same EF computing method, an EF of 2.9×10^7 was earned by using the above formula.