Electronic Supplementary Information (ESI)

Holey Au-Ag Alloy Nanoplates with Built-in Hotspots for Surface-Enhanced Raman Scattering

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1. Additional Experimental Details

1.1 Synthesis of Au-Ag nanoframes by galvanic replacement between Ag nanoplates and $HAuCl_4$: In a typical synthesis, Ag nanoplates were centrifuged from 20mL of the as-synthesized solution (Preparation, see Experimental Section) and redispersed in 3 mL of H_2O. Then, 2.0 mL of $HAuCl_4$ (0.1 mM) was introduced by using a syringe pump at a rate of 5 mL/h with vigorous stirring. The Au-Ag nanoframes were collected by centrifugation and washed with H_2O. An intermediate was obtained by changing the amount of $HAuCl_4$ (0.1 mM) to be 1.0 mL in a typical experiment.

1.2 Synthesis of Ag@Au core/shell nanoplates: In a typical synthesis (see our earlier report: *Adv. Funct. Mater.*, 2015, **25**, 5435), Ag nanoplates were centrifuged from 40 mL of their stock solution and redispersed in 2 mL of H_2O. A solution (pH ~12) was prepared by mixing 2.55 mL of H_2O, 1 mL of polyvinylpyrrolidone (PVP, 5 wt%, Mw 40 000), 200 μL of L-ascorbic acid (0.5 M), 200 μL of NaOH (0.5 M), 50 μL of Na_2SO_3 (0.1 M), and 4 mL of the growth solution of Au (see Experimental Section) in a glass vial, which was then merged with the solution of the Ag nanoplates to initiate the seeded growth. The reaction was then allowed to proceed undisturbed at 30 °C for 12 h. Finally, Ag@Au core/shell nanoplates were collected by centrifugation and washed with H_2O.

1.3 SERS analysis in oxidative solutions: Holey Au-Ag nanoplates was incubated with an aqueous solution containing CV (10^{-6} M) and H_2O_2 (0.2 M) for 2 h. Raman spectra were then recorded from the suspension with a 633 nm He–Ne laser line at room temperature. For all measurements, laser power was 3 mW, and the signal acquisition time was fixed to be 30 s.

1.4 Characterizations: TEM was performed with a Hitachi HT-7700 electron microscope equipped with a tungsten filament, operating at 120 kV. HRTEM and STEM were performed on a Philips Tecnai F20 FEG-TEM, operating at 200 kV. UV–vis spectra were measured on an Ocean Optics HR2000+ES spectrophotometer. Elemental analysis was conducted by inductively coupled plasma mass spectrometry (ICP-MS) with an Agilent 7500CE. Raman spectra were collected using a LabRAM HR800 confocal Raman spectrophotometer equipped with a 633 nm He-Ne laser.

2. Calculation of the enhancement factor (EF) of the holey Au-Ag alloy nanoplates from Figure 5e.

The enhancement factor of the holey Au-Ag alloy nanoplates was estimated using the following equation:

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

where $I_{surface}$ and $N_{surface}$ are the Raman intensity and numbers of CV (10^{-7} M) molecules absorbed on the holey Au-Ag alloy nanoplates on a silicon substrate. $I_{solution}$ and $N_{solution}$ are the Raman intensity probed from a CV (10^{-3} M) liquid in a capillary and numbers of CV molecules in the focus of the laser beam.

The Raman intensity $I_{surface}$ was 2000 counts at the peak of 1618 cm^{-1} (laser power density: 51.67 kW·cm^{-2}). $I_{solution}$ was measured to be 2500 counts (laser power density: 39.8 kW·cm^{-2}), which is equivalent to 3246 counts under laser irradiation at 51.7 kW·cm^{-2}. Acquisition times were fixed to be 10 s for all measurements.

$N_{solution}$ was estimated using the following equation:

$$N_{solution} = 6.02\times10^{23}\ mol^{-1}\times10^{-3}\ \mathrm{mol/L}\times\left[\pi\left(\frac{d}{2}\right)^2\times H\right] = 1.8\times10^{9}$$

where *d* is the diameter of the laser spot, $d = \frac{1.22\lambda}{0.25} = 3.1\ \mu m$; *H* is the effective depth of focus and can be estimated experimentally to be 400 μm.

$N_{surface}$ can be estimated as:

$$N_{surface} = D \times S_p \times N_l$$

where *D* is the density of the CV molecules absorbed on the silicon substrate and the holey Au-Ag alloy nanoplates, which is assumed to be a constant without preferential distribution. S_p is the effective surface area of a single holey Au-Ag alloy nanoplate, and can be estimated by a simplified model (edge length *l* = 45 nm; thickness = 6 nm; perimeter of the holes = 360 nm; area of the holes = 450 nm^2) to be 2586 nm^2. N_l is the number of the holey Au-Ag alloy nanoplates in the laser spot.

The area of the laser spot $S_l = \pi\left(\frac{s}{2}\right)^2 = 5.8\times10^5\ nm^2$, where *s* is the diameter of the laser spot, $s = \frac{1.22\lambda}{0.9} = 858\ nm$.

Thus,

$$N_l = \frac{S_l}{\frac{\sqrt{3}}{4}l^2} = 662$$

In the experiment, 25 μL of an aqueous CV solution (10^{-7} M) was dried onto the substrate and dipped 3 times in water to remove weakly absorbed molecules. About ~6.8 % of the CV molecules remained after dipping, as estimated experimentally (This value is assumed to be independent of the CV concentration, and was determined by UV-vis spectroscopy with CV of a high concentration).

Thus,

$$\mathrm{N_{CV}} = 25\times10^{-6}\mathrm{L}\times10^{-7}\mathrm{mol/L}\times6.02\times10^{23}mol^{-1}\times6.8\% = 1.0\times10^{11}$$

Assume the holey Au-Ag alloy nanoplates covered all surface area of the substrate,

Thus, N_p (the number of the holey Au-Ag alloy nanoplates on the substrate) can be estimated to be:

$$N_p = \frac{S_{Si}}{\frac{\sqrt{3}}{4}l^2} = 7.3\times10^{10}$$

where $\mathrm{S_{Si}}$ is the surface area of the 8 mm × 8 mm substrate ($6.4\times10^{13}\ nm^2$).

Thus, D can be estimated by the following equation:

$$\mathrm{D} = \frac{\mathrm{N_{CV}}}{\mathrm{S_{Si}} + N_p \times 360 \times 6} = 4.5\times10^{-4}\ nm^{-2}$$

Therefore,

$$N_{surface} = \mathrm{D}\times S_p \times N_l = 770$$

$$\mathrm{EF} = \left(\frac{I_{surface}}{N_{surface}}\right) / \left(\frac{I_{solution}}{N_{solution}}\right) \approx 1.4\times10^{6}$$

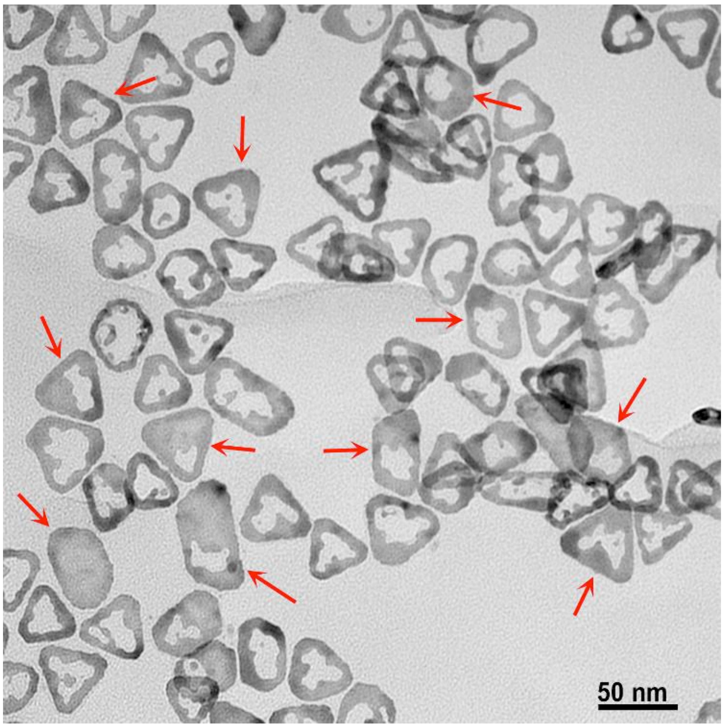

Figure S1. TEM image of hollow Au-Ag alloy nanoplates synthesized by galvanic replacement of Ag nanoplates with $HAuCl_4$ in the absence of PVP. Arrows indicate the nanostructures at different stages of the galvanic replacement.

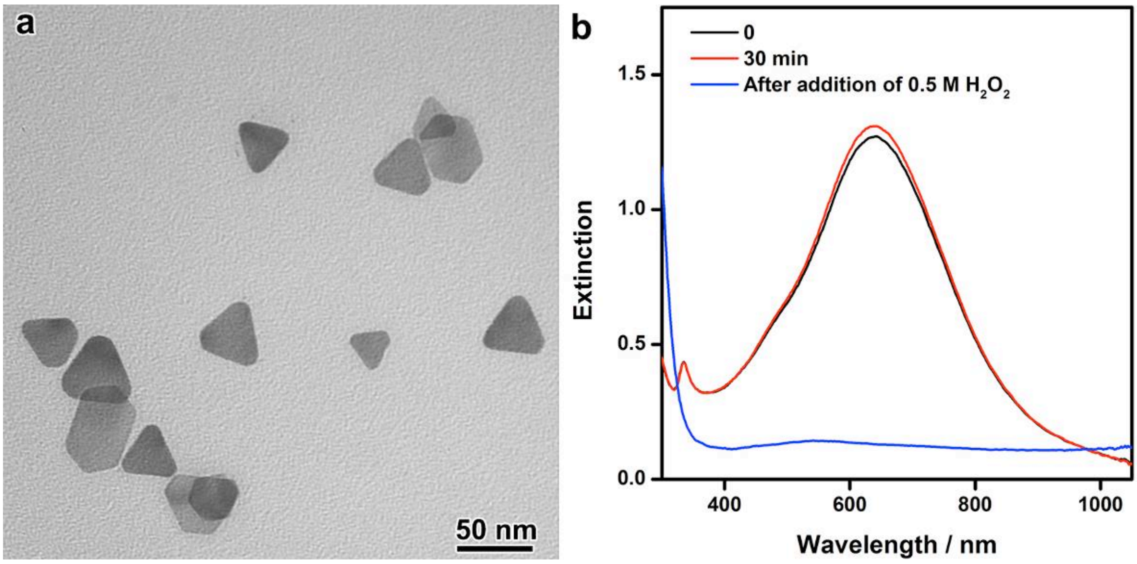

Figure S2. (a) TEM image of the Ag nanoplates after treatment with $Na_3Au(SO_3)_2$ at pH 11. (b) UV-vis spectra of the Ag nanoplates (0 min), the Ag nanoplates after treatment with the sulfite-coordinated gold precursor for 30 min, and the nanoplates after further treatment with 0.5 M H_2O_2.

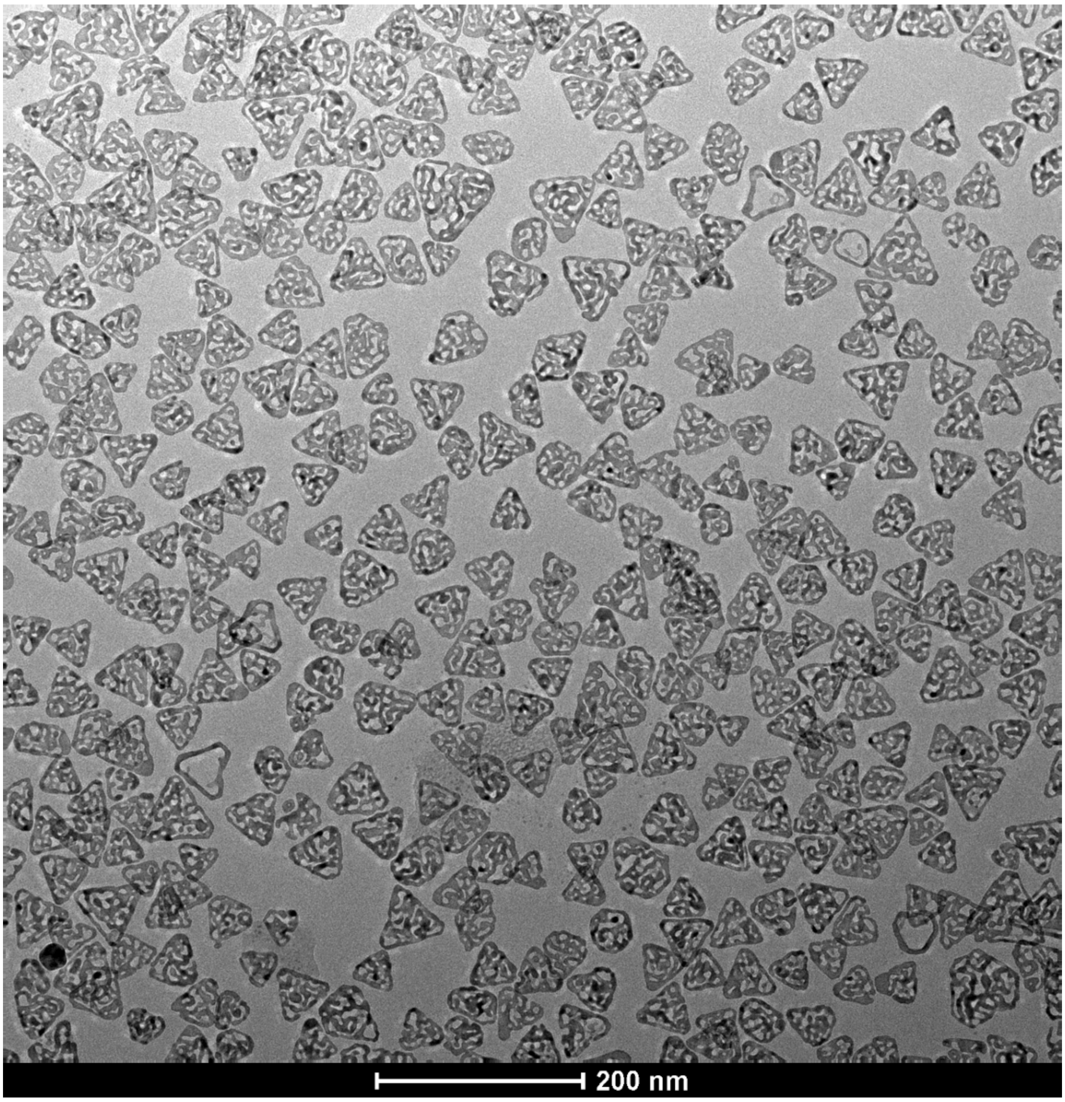

Figure S3. A low-magnification TEM image of the holey Au-Ag nanoplates.

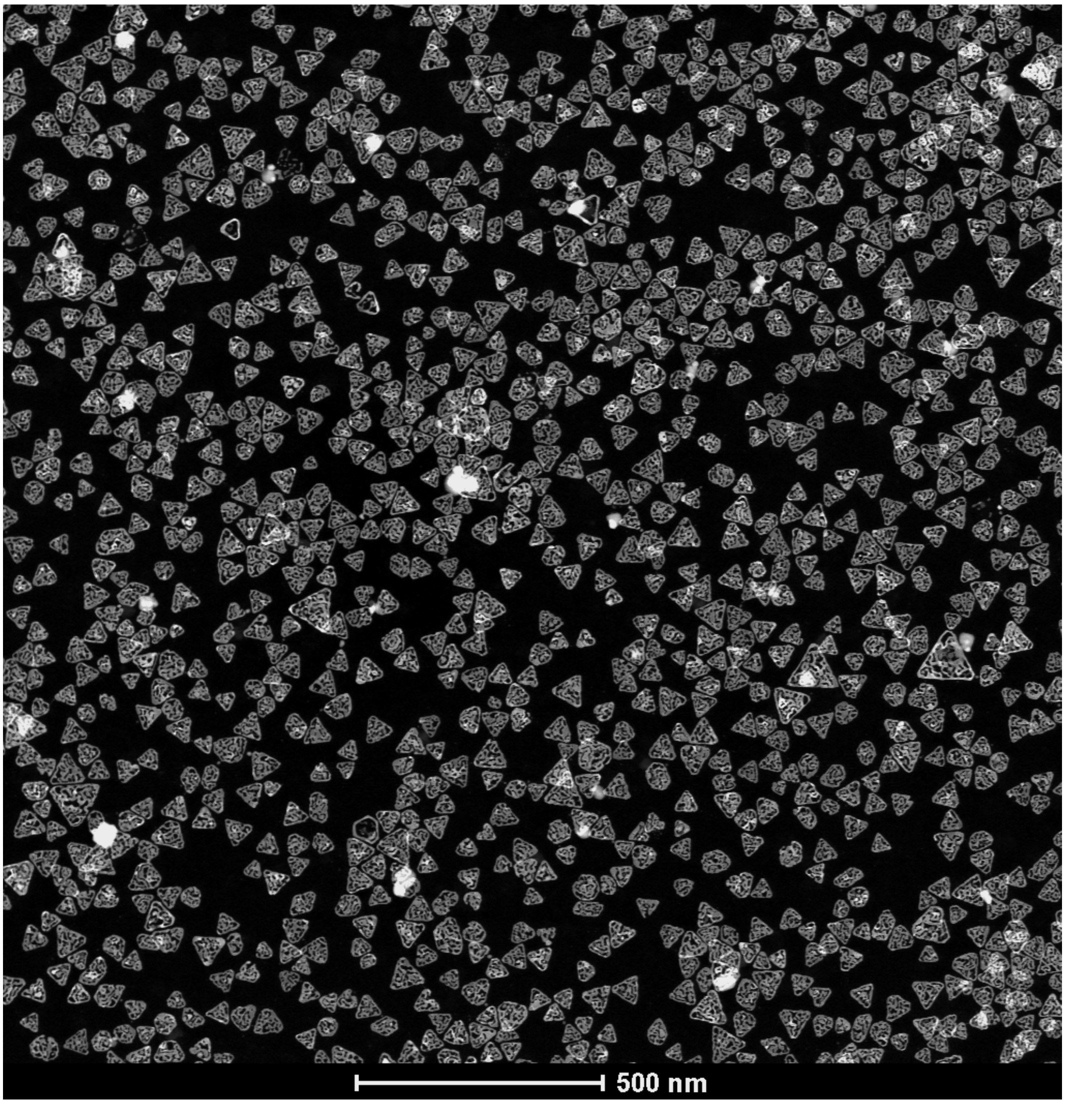

Figure S4. A low-magnification HAADF-STEM image of the holey Au-Ag nanoplates.