

## Electronic Supplementary Information

### **Porous Gold Nanodisks with Multiple Internal Hot Spots**

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#### **- Estimation of the ‘averaged’ SERS signal from a R6G molecule**

We assume the R6G solution was dried uniformly over the whole sample surface, due to the low surface tension (~23 dyne/cm) and rapid evaporation of methanol on a hot plate (90 °C). Total number of R6G in a 10 μl droplet of 0.1 mM is  $(0.1 \times 10^{-3}) \times (6.02 \times 10^{23}) \times (10 \times 10^{-6}) = 6.02 \times 10^{14}$ . Cross-sectional area ratio between Au nanodisk and the whole sample (1 cm square) is about  $(\pi \times 100^2 \text{ nm}^2)/(1 \text{ cm}^2) = 3.14 \times 10^{-10}$ . So, the average number of R6G staying on a single Ag nanoparticle cluster is approximately  $\sim 1.9 \times 10^5$ . Because the calculated confocal spot (diameter of ~250 nm) is larger than the lateral size of Au nanodisk (diameter of ~200 nm), we can assume that the measured SERS signal for each pixel in the intensity map (Fig.3h) was typically generated by a single nanodisk.

From the saturated SERS intensity (~1400 CCD cts), which was measured 0.1-mM-R6G treated Au nanodisk in Fig. 3h, and the number of R6G molecules ( $\sim 1.9 \times 10^5$ ), the SERS intensity is about  $7.4 \times 10^{-3}$  CCD cts/molecule. CCD cts represents charge-coupled device counts.

#### **- Estimation of the ‘averaged’ SERS enhancement factor**

Due to the fluorescence background of R6G at its resonance condition, it is difficult to measure the Raman intensity from a molecular R6G solution sample. So, enhancement factors are estimated from the relative intensity of fluorescence and SERS [reference S1,2]. The fluorescence signal of R6G was measured from 10 μl of  $10^{-5}$  M water solution. From the fluorescence intensity ( $\sim 1.9 \times 10^5$  CCD cts) and the number of R6G molecules ( $\sim 2.2 \times 10^3$ ) in the sampled volume, the fluorescence intensity is estimated about 84.5 CCD cts/molecule. The experimental procedure for the estimation of fluorescence intensity has been reported in detail in our previous papers [reference S3].

Therefore the experimentally estimated ‘averaged’ SERS enhancement factor is about  $\sim 5.5 \times 10^2$ , considering the relative ratio of the cross section of Raman scattering ( $4.1 \times 10^{-23} \text{ cm}^2$ ) and fluorescence ( $2.6 \times 10^{-16} \text{ cm}^2$ ) of R6G [reference S4,5]. The enhancement factor (EF) was calculated using the following equation.

$$EF = \frac{(SERS \text{ intensity}) / (\text{Molecules on a Au nanodisk})}{(\text{Fluorescence intensity}) / (\text{Molecules in solution})} \times \frac{(\text{Cross section of fluorescence})}{(\text{Cross section of Raman scattering})}$$

### - Estimation of the ‘maximum’ SERS enhancement factor

As compared to the saturated intensity from the 0.1-mM-R6G treated sample, ~10 % of SERS intensity was measured from the 1-nM-R6G treated sample for the case of the most porous nanodisk (Fig.3j). Therefore the experimentally estimated ‘maximum’ SERS EF is  $(\sim 5.5 \times 10^2) \times (0.1) \times (0.1 \text{ mM} / 1 \text{ nM}) = \sim 5.5 \times 10^6$ .

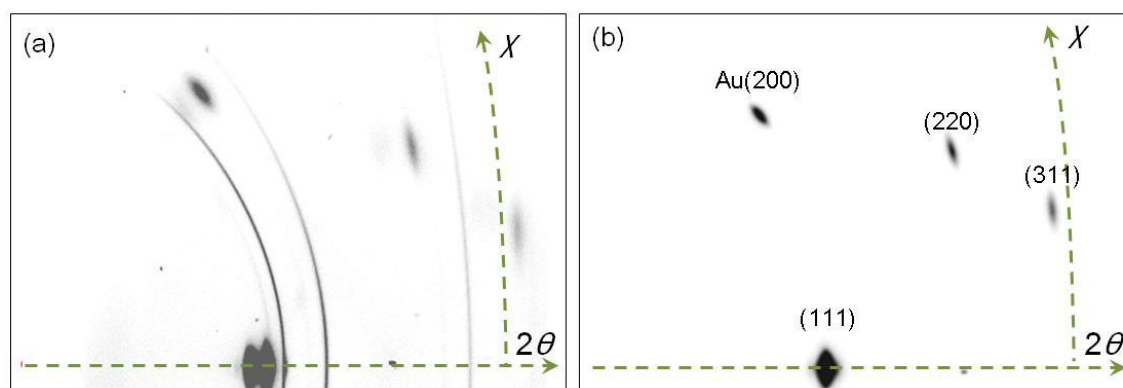
The maximum  $|E/E_0|^4$  values calculated by FDTD simulation (Fig. 4a) is  $\sim 1.0 \times 10^6$ , which is underestimated than the experimentally obtained value. However, it is reasonable to consider the simplified smooth sidewall in the simulation and the chemical enhancements [reference S6].

**Table S1.** Sputtering conditions for synthesizing AuCu alloys

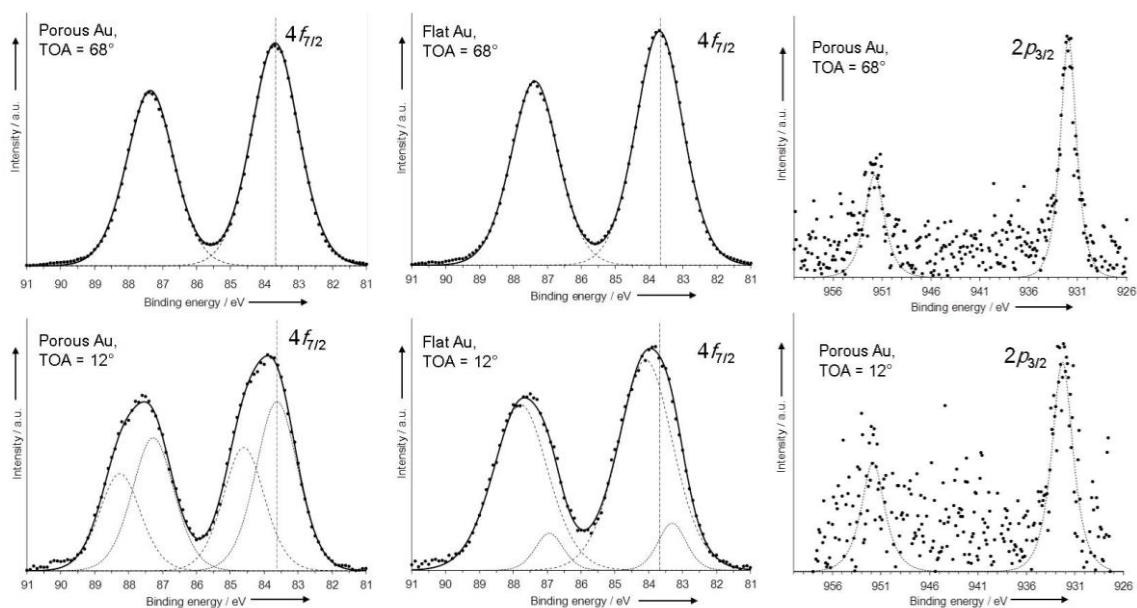
	Figure no.	Patterning	DC power /W (Au/Cu)	Ar pressure /Pa	Thickness /nm	Adhesion layer thickness /nm (Au/Ti)
(a) Net-like 2D layer*	2	No	100/200	0.3	80	5/5
(b) Highly porous disk	3d	Yes	100/200	0.3	120**	5/2
(c) Porous disk	3c	Yes	100/200	1.5	120**	5/2
(d) Less porous disk	3b	Yes	100/200	1.5	80**	5/2

\*Si wafer covered with 200-nm SiO<sub>2</sub> was used for substrate, and the oxide was removed by 1 M NaOH solution for the TEM observation.

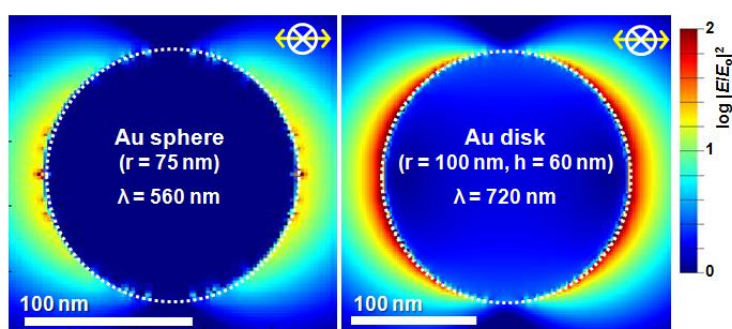
\*\*The thickness was calculated from the sputtering rates of a pure Au film and a pure Cu film deposited on a flat substrate.



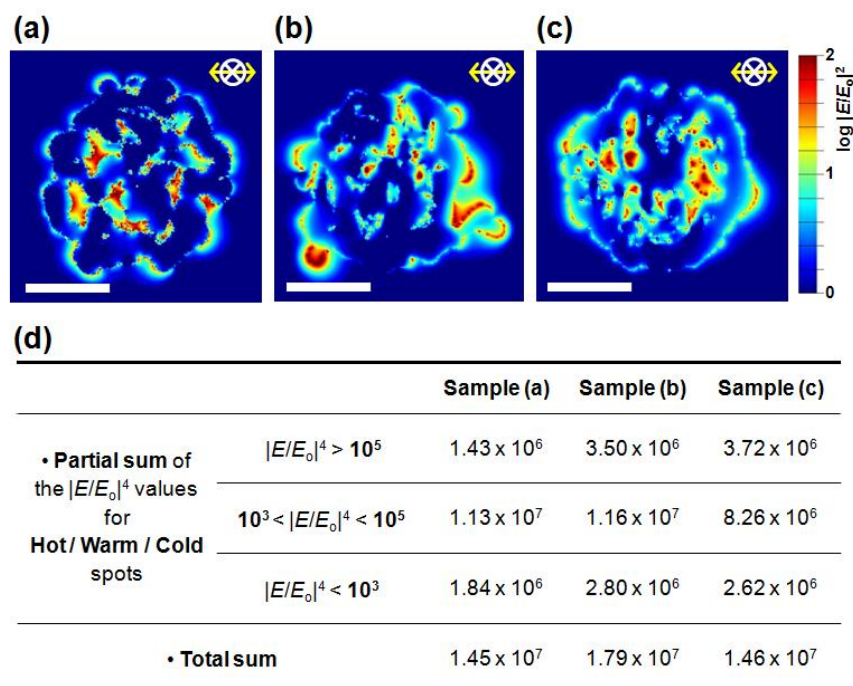
**Figure S1.** XRD data collected on an imaging plate: (a) as-deposited AuCu alloy film and (b) dealloyed film. The powder-like arcs in (a) are assigned to polycrystalline Cu phases.



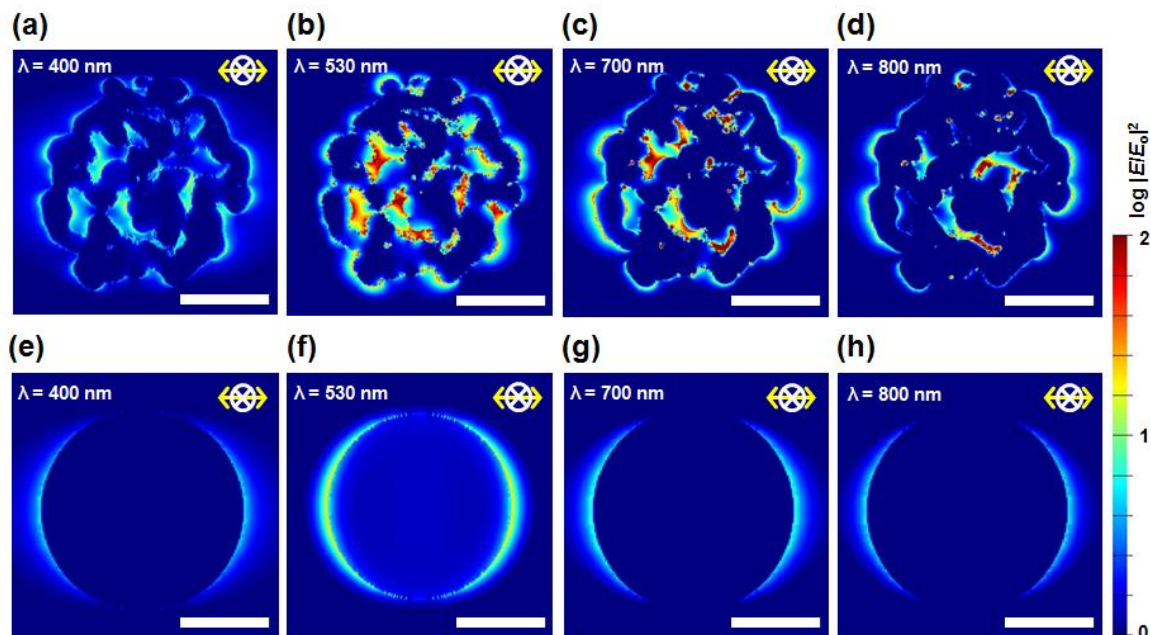
**Figure S2.** Angle-resolved X-ray photoelectron spectra of Au  $4f_{7/2}$  and Cu  $2p_{3/2}$  for porous Au shown in Figure 1. The Au spectra were compared with those of a flat 200-nm-thick Au layer deposited by evaporation on a Si substrate with a 20-nm Ti adhesion layer. The takeoff angles were  $68^\circ$  and  $12^\circ$ . The background was subtracted using the Shirley method. The Au  $4f$  data show that Au had a less-screened core level state in the vicinity of the surface ( $4f_{7/2}$  peak located around 84.0 eV) and a more-screened state in the bulk ( $4f_{7/2}$  peak located around 83.6 eV). That is, the electronic states of porous Au appear to be the same as that of non-porous one Au. The composition of porous Au was  $\text{Au}_{95}\text{Cu}_5$  at  $12^\circ$  and  $\text{Au}_{97}\text{Cu}_3$  at  $68^\circ$ . The small satellites of Cu  $2p$  shown between the two peaks can be assigned to shake-up peaks.<sup>1,2</sup>



**Figure S3.** Squared magnitudes of the local electric field amplitude of (left) Au nanosphere and (right) Au nanodisk in Air. For a fair comparison, both nanostructures have almost the same volume and the field amplitudes were monitored from their resonant wavelengths. The direction, polarization angle, and wavelengths of incident light are described as insets.



**Figure S4.** (a-c) Squared magnitudes of the local electric field amplitudes of three different porous Au nanodisks on Si substrate. The wavelength of the incident light is 530 nm, and its direction and polarization angle are described as insets. All scale bars are 100 nm. (d) Table for the comparison of pixel-weighted sum of  $|E/E_0|^4$  values from three nanodisks of Fig. S4(a-c). The partial sum of  $|E/E_0|^4$  values was calculated for hot ( $|E/E_0|^4 > 10^5$ ), warm ( $10^3 < |E/E_0|^4 < 10^5$ ), and cold ( $|E/E_0|^4 < 10^3$ ) spots.



**Figure S5.** Squared magnitudes of the local electric field amplitude of (a-d) the nanoporous Au nanodisk and (e-h) the solid Au disk on Si substrate. The direction, polarization angle, and wavelengths of incident light are described as insets. All scale bars are 100 nm.

### References for Supplementary Information

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- S5. M. Suzuki et al., J. Phys. Chem. B **108**, 11660 (2004).
- S6. K. L. Wustholz et al., J. Am. Chem. Soc. **132**, 10903 (2010).