Supporting Information

Guided formation of sub-5 nm interstitial gap between plasmonic nanodisks

Jin Gyeong Son[a,b], Sang Woo Han[a], Jung-Sub Wi[b,*], Tae Geol Lee[b,*]

[a]*Department of Chemistry, Korea Advanced Institute of Technology, Daejeon, 305-070, Korea*

[b]*Center for Nano-Bio Measurement, Korea Research Institute of Standards and Science, Daejeon, 305-340, Korea*

***To whom all correspondence should be addressed.**

Tel: +82-42-868-5691
E-mail : jungsub.wi@kriss.re.kr

Tel: +82-42-868-5129; Fax: +82-42-868-5032
E-mail : tglee@kriss.re.kr

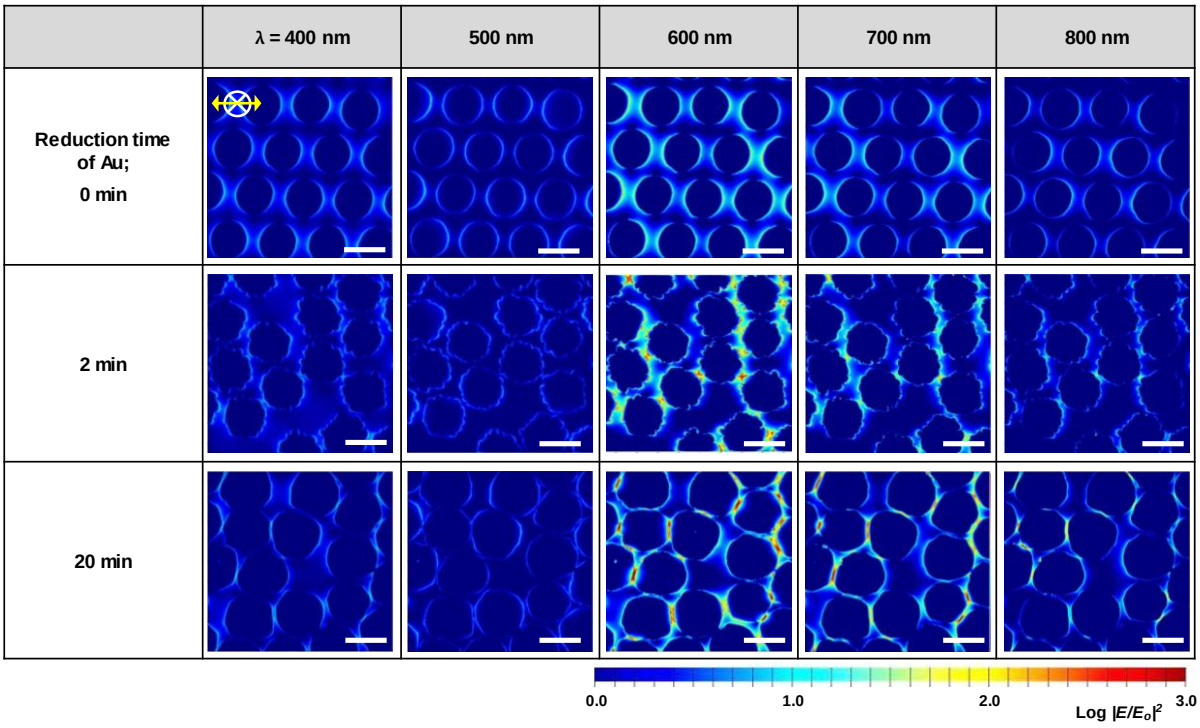

Fig S1. Squared magnitude of the local electrical field amplitude around three different Au nanodisks in Fig.1(a-c). Wavelengths of incident light are noted in the table. The incident direction of light and its polarization angle are indicated by the white and yellow arrows, respectively. All the scale bars are 200 nm.

`

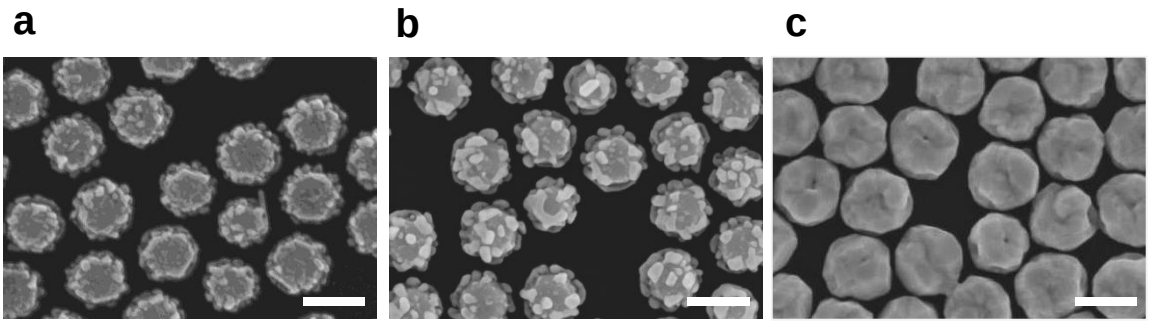

Fig S2. SEM images Au nanodisks with chemically developed Au islands. Au reduction time is (a) 2 min, (b) 5 min, and (c) 20 min. All the scale bars are 200 nm.

Calculation of the SERS enhancement factors (EFs)

In order to obtain the experimental value for enhancement factor (EF), we compared the SERS intensity of the 4-aminobenzenethiol (4-ABT) molecules on the 20-min-enlarged Au nanodisk to the Raman intensity of the 4-ABT powder. The powder was well packed to form a pellet. The EF for 4-ABT is calculated according to the following equation,[1]

$$EF = \frac{I_{SERS} N_{Raman}}{I_{Raman} N_{SERS}}$$

where I_{SERS} and I_{Raman} are the vibration intensities in the SERS and Raman spectra of 4-ABT, as shown in Figure S2, respectively. N_{SERS} and N_{Raman} are the numbers of 4-ABT molecules that contribute to the Raman intensity and SERS on the enlarged Au nanodisks, respectively. The calculated laser spot size is 858 nm. The Raman system has general optic system; the focal volume was followed axial minimum of 3D diffraction pattern. To define the focal volume of the 4-ABT powder, the height (h) was calculated by following equation[2],

$$\mathrm{h} = \frac{2\lambda\eta_D}{(NA)^2}$$

where η_D is the refractive index of 4-ABT (~ 1.6),[3] and NA is the numerical aperture of the objective lens (100×, NA = 0.9). The calculated height is 2.5 μm. For the calculation of molecular number in Raman sample, the density of 4-ABT (d = 1.18g/cm^3) and its molecular weight (125.19 g/mol) were used.[4] Under the focal volume, illumination region by the laser light is equal to $N_{raman} = (V \times d)/(M.W. \times AN)$ where V is focal volume, d is the density of 4-ABT, M.W. is the molecular weight and AN is Avogadro's number 6.022 x 10^{23}. The calculated N_{Raman} is 1.96 x 10 ^{9}. In the calculation of EFs, we assume that 4-ABT molecules were adsorbed as a monolayer and fully covered and the 4-ABT size estimated 0.2 nm^2.[5] The calculated N_{SERS} is 6.98 × 10 ^{5}. Using the above calculated value, enhancement factor of 20 min - enlarged Au nanodisks is 1.41 × 10 ^{5}.

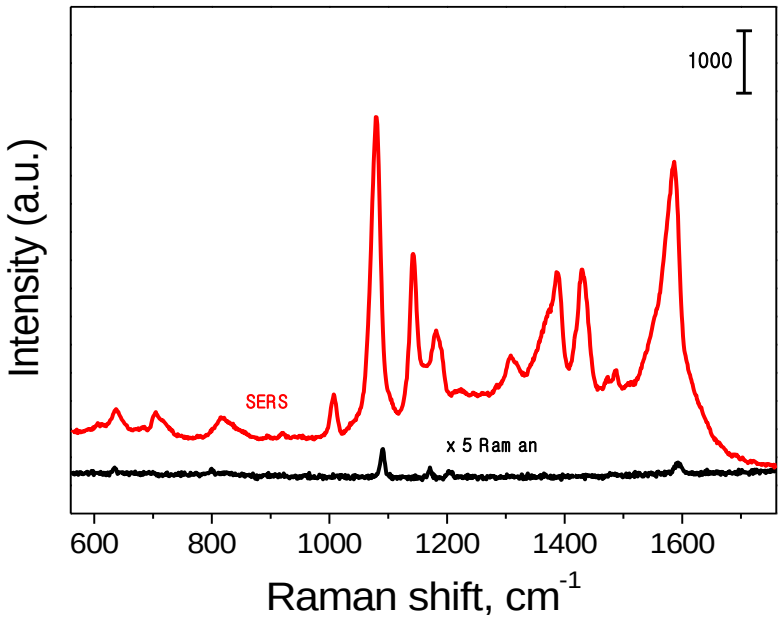

Fig S3. (a) Raman spectra of the solid 4-ABT (black line), and (b) SERS spectra of 4-ABT molecules on the enlarged Au nanodisks.

Reference

1. Y. Fang, N. H. Seong, D. D. Dlott, *Science*, 2008, **321**, 388–392
2. B. Pawley, *Handbook of Biological Confocal Microscopy*; Plenum Press: New York, 1995
3. R. Liu, B. Liu, G. Guan, C. Jiang, Z. Zhang, *Chem. Commun*. 2012, **48**, 9421–9423
4. A. Martin, J. J. Wang, D. Lacopino, *RSC Advnaces*, 2014, **4**, 20038-20043
5. A. Gole, S. R. Sainkar, M. Sastry, *Chem. Mater.* 2000, **12**, 1234