

## Sombrero-Shaped Plasmonic Nanoparticles with Molecular-Level Sensitivity and Multifunctionality

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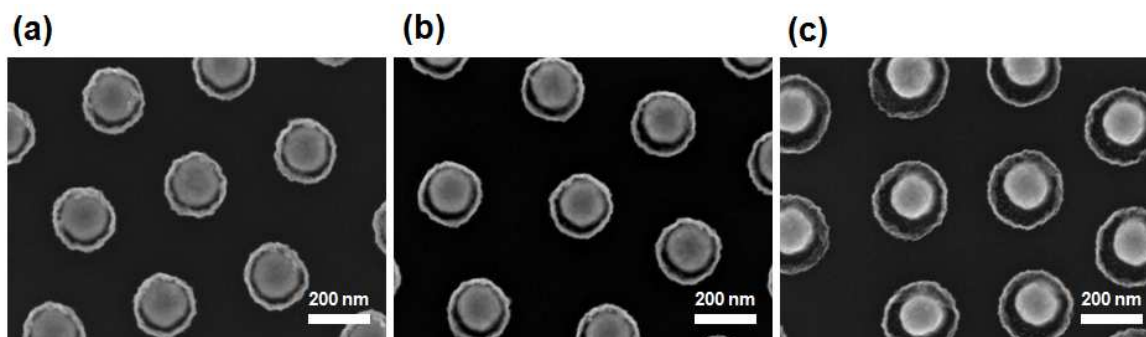
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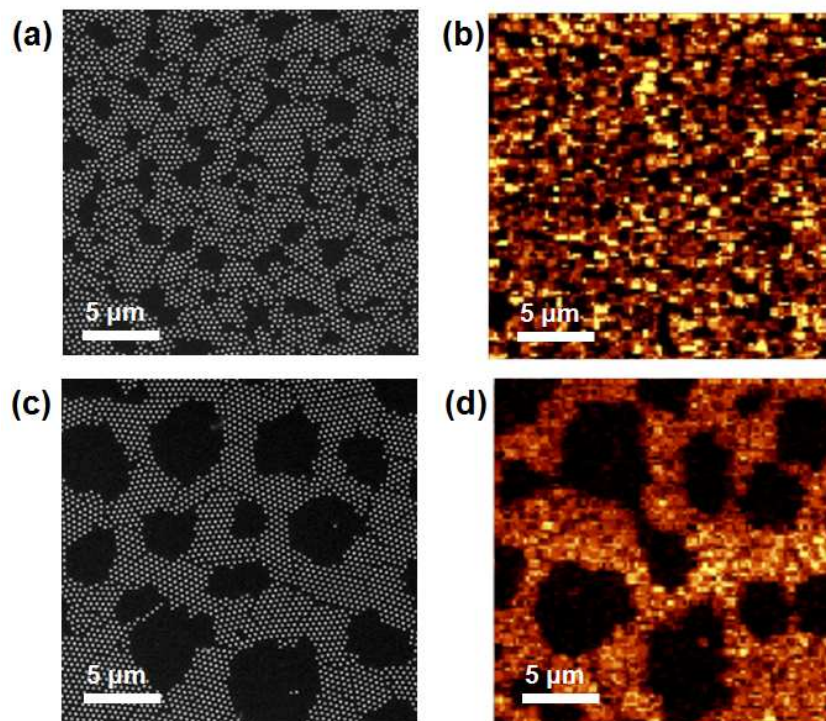
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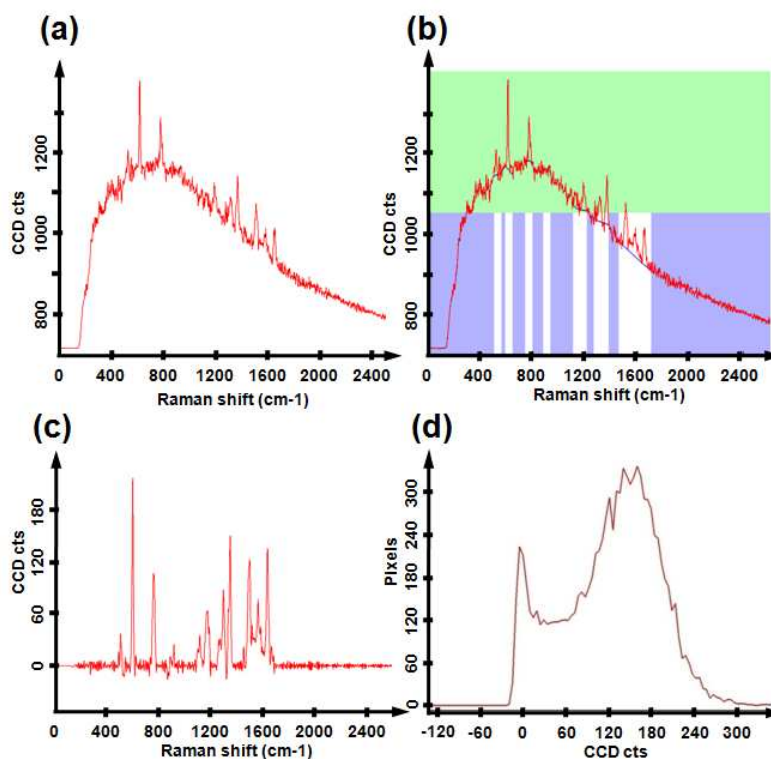
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**Figure S1.** SEM images of Raman sombrero nanoparticle arrays generated using different development times for the PMGI undercut layer. The samples were immersed in a commercial wet-chemical developer (LDD-26W, Shipley) for (a) 3 sec, (b) 5 sec, and (c) 10 sec to form undercut profiles in the PMGI resist.



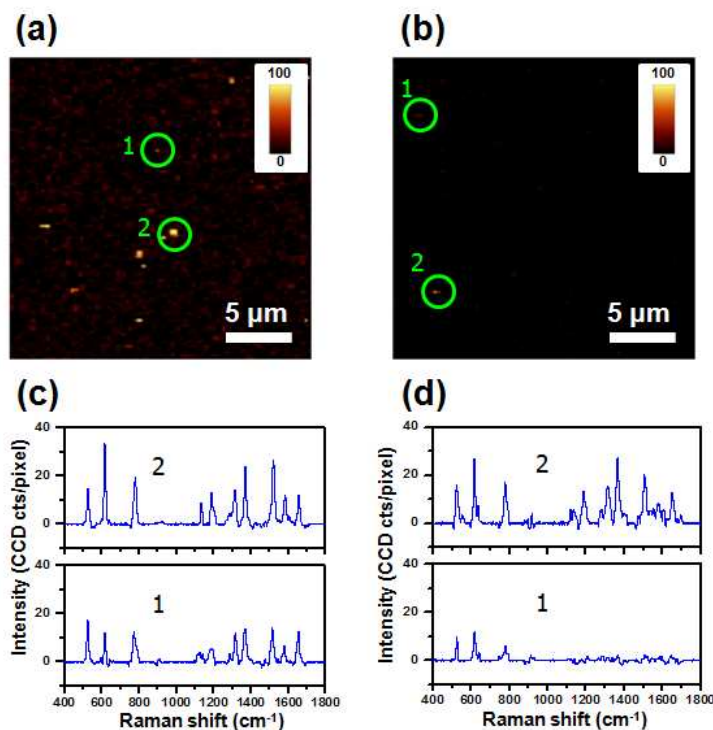
**Figure S2.** (a,c) SEM images of Raman sombrero nanoparticles and (b,d) SERS maps with the same magnification. The nanoparticle arrays analyzed in this study have two typical morphologies of (a) arrays with frequent small voids and (c) arrays with sparse large voids. The image pairs, (a,b) and (c,d), were not obtained from exactly the same areas.



**Figure S3.** For plotting the graph in Fig 3(f), we used the built-in software of the confocal Raman system (alpha500, WITec). Background extraction from whole SERS maps and calculation of signal intensity histograms were carried out by the software. (a) As-obtained spectrum of R6G. (b) Calculated background level was depicted as a blue colored line fitted by the average value of neighboring 5 pixels at every position, after masking several SERS peaks. (c) Background subtracted SERS spectrum of R6G. (d) Intensity histogram of the  $615\text{ cm}^{-1}$  peak. To calculate the average and standard deviation of signal intensity, the 1000 brightest pixels were selected from the intensity histogram to exclude signals from vacant Si regions and their boundaries.

### [Estimation of the number of R6G attached to a Raman sombrero nanoparticle]

We assume the R6G solution was dried uniformly over the whole sample surface, due to the low surface tension ( $22\sim 23\text{ dyne/cm}$ ) and rapid evaporation of methanol on a hot plate ( $90\text{ }^\circ\text{C}$ ). Total number of R6G in a  $2\text{ }\mu\text{l}$  droplet of  $1\text{ nM}$  is  $(1 \times 10^{-9}) \times (6.02 \times 10^{23}) \times (2 \times 10^{-6}) = \sim 1.20 \times 10^9$ . Cross-sectional area ratio between a single Raman sombrero nanoparticle and the whole sample ( $3\text{ mm square}$ ) is about  $(\pi \times 90^2\text{ nm}^2)/(3^2\text{ mm}^2) = \sim 2.83 \times 10^{-9}$ . So, the number of R6G staying on a single Raman sombrero nanoparticle is approximately  $\sim 3$ .



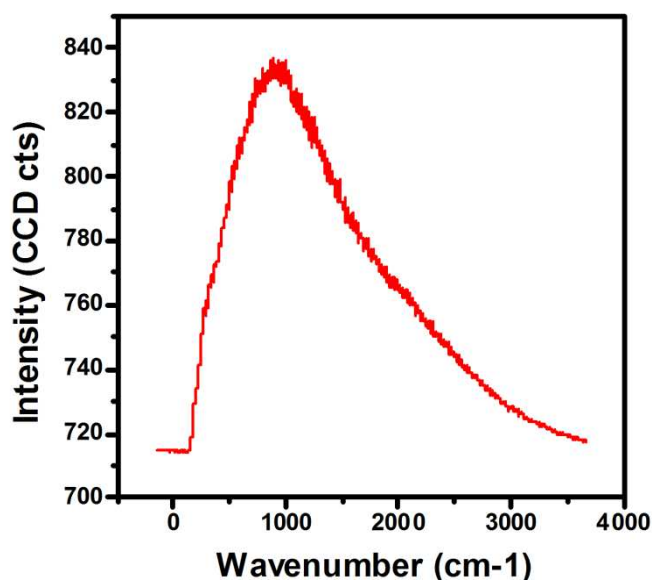
**Figure S4.** Two-dimensional intensity map of SERS signals, integrated between 590 and 640  $\text{cm}^{-1}$ , from the Ag Raman sombrero nanoparticle array with R6G concentrations of (a)  $10^{-10}$  M and (b)  $10^{-12}$  M. (c) and (d) show representative R6G Raman spectra from the two spots indicated in SERS maps of (a) and (b), respectively. Baseline signals are corrected.

#### [Estimation of the peak SERS enhancement factor]

Due to the huge 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 of the Raman sombrero nanoparticles are estimated from the relative intensity of fluorescence and SERS [reference S1,2]. The fluorescence signal of R6G was measured from 10  $\mu$ l of  $10^{-5}$  M water solution contained between two cover glasses. Because of the surface tension of the water, a thin uniform liquid layer between two cover glasses was generated without overflow. Assuming that the excitation volume is a cylinder, the diameter of the laser beam ( $d \approx 240$  nm) was calculated from the wavelength and numerical aperture of the objective lens, and the height ( $h \approx 8$   $\mu$ m) was referred from the resolution depth of confocal microscopy [reference S3]. From the fluorescence intensity ( $\sim 186000$  CCD cts), which was integrated from the peak shown in Fig. S5 by numerical software (OriginPro 7.5), and the

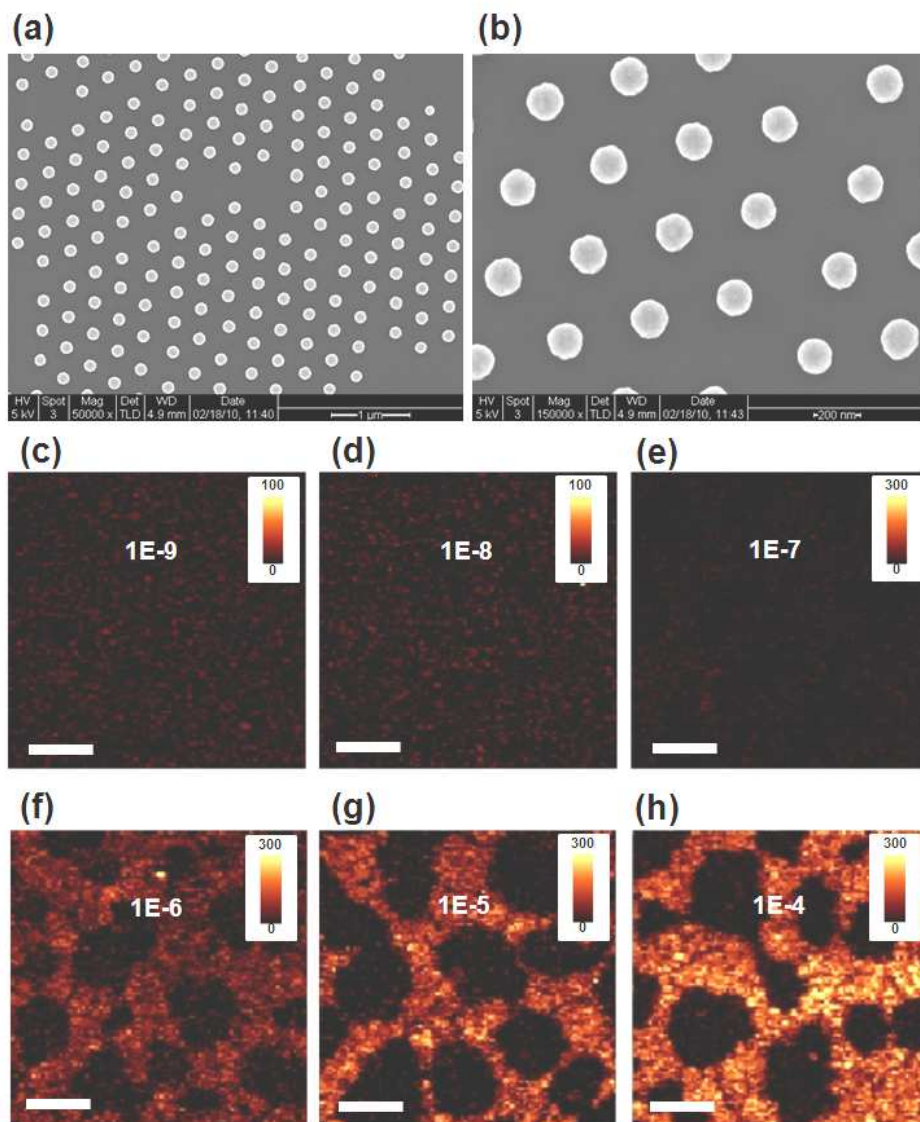
number of R6G molecules ( $\sim 2.2 \times 10^3$ ) in the calculated excitation volume, the fluorescence intensity is about 84.5 CCD cts/molecule. Raman signal from 3 molecules on Raman sombrero nanoparticles is about  $\sim 390$  (CCD cts), which was integrated from the  $615 \text{ cm}^{-1}$  peak in Figure 3(e). Therefore the estimated SERS enhancement factor is about  $1.0 \times 10^7$ , 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.

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

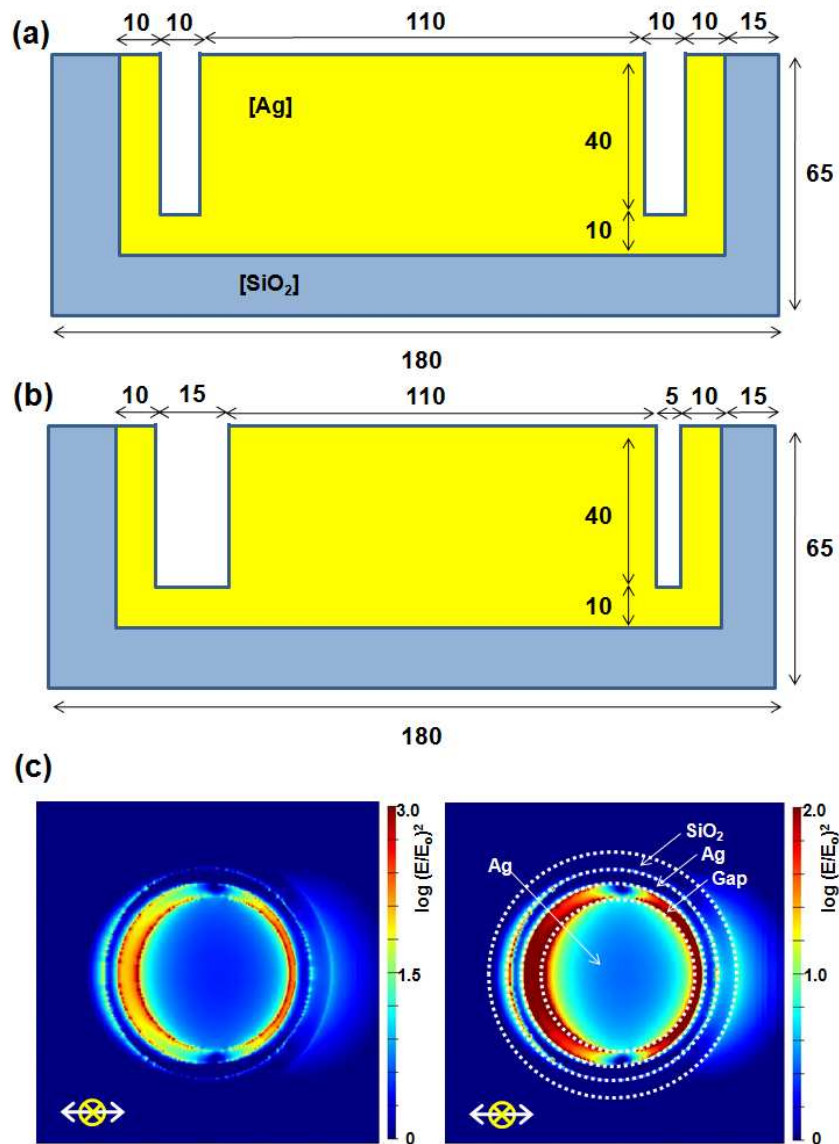


**Figure S5.** Fluorescence signal of R6G from the exact same laser configuration with the SERS measurement (532 nm laser, 1.4 mW, 100x objective lens, accumulation time of 0.036 sec).  $10 \mu\text{l}$  of  $10^{-5}$  M R6G water solution was contained between two 12 mm diameter cover glasses.





**Figure S6.** (a,b) Plan-view SEM images of Ag nano-disk array. (c-h) 2-dimensional intensity map of SERS signal, between 590 and 640  $\text{cm}^{-1}$ , from the Ag nano-disk array with different concentrations of Rhodamine 6G; (c)  $10^{-9}$  M, (d)  $10^{-8}$  M, (e)  $10^{-7}$  M, (f)  $10^{-6}$  M, (g)  $10^{-5}$  M, and (h)  $10^{-4}$  M. The scale bar in (c-f) is 5  $\mu\text{m}$ .



**Figure S7.** (a,b) Cross section and dimensions of Raman sombrero nanoparticle with (a) symmetric core and (b) asymmetric core. Units in the illustration are nm. The Ag nano-disk was drawn with 150 nm diameter and 50 nm height. The particles were placed in a uniform medium of air and illuminated from the top with a plane wave. (c) The plan-view of local electrical field amplitudes of Raman sombrero nanoparticles. The field contour is obtained from the top surface of nanoparticles, and is displayed with two color scales of [left]  $(E/E_0)^2 = 1 \sim 10^3$ , [right]  $(E/E_0)^2 = 1 \sim 10^2$ . The direction of incident light and its polarization are indicated as yellow and white colored arrows, respectively, at each inset.

## [Comparison of the averaged SERS enhancement factor and the averaged $(E/E_0)^4$ value ]

The saturated SERS intensity measured from the sombrero treated with a  $10^{-4} \sim 10^{-6}$  M of R6G solution is about  $\sim 3010$  (CCD cts), which was integrated from the  $615 \text{ cm}^{-1}$  peak in Figure 3(e). As compared to the 1 nM R6G treated sample where the peak SERS EF is  $1.0 \times 10^7$ , the number of R6G molecules and signal intensity are increased by  $10^3 - 10^5$  and 7.7 times, respectively. Therefore, the experimentally estimated area-weighted average SERS EF would be a  $(1.0 \times 10^7) \times (7.7) / (10^3 \sim 10^5) = \sim 10^3 - \sim 10^5$ . As shown in Fig. S7(c), most parts of the circular gap have the  $(E/E)^2$  value above 100, and the theoretical area-weighted average of  $(E/E_0)^4$  value of  $1.1 \times 10^4$  from a top surface of the sombrero is well matched with the averaged SERS EFs. For calculating the averaged  $(E/E_0)^4$ , the brightest 30000 pixels in the Fig. S7(c) were used. Because the size of each pixel is  $1 \text{ nm}^2$ , the corresponding area of 30000 pixels covers the top surface of the sombrero ( $\sim 25400 \text{ nm}^2$ ), including nearby area.

## [References for Supporting Information]

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