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Electronic Supplementary Information

Rationally designed particle-in-aperture hybrid arrays as large-scale, highly reproducible SERS substrates

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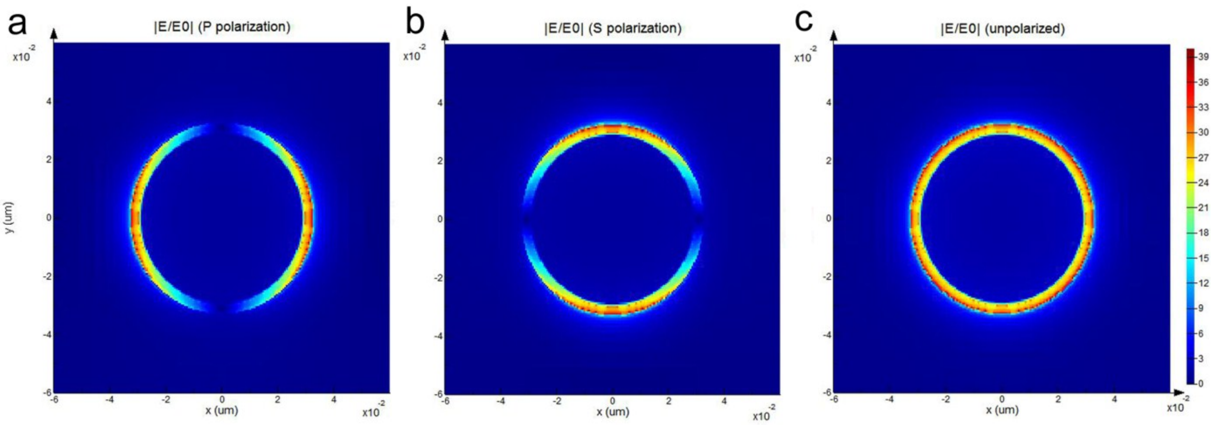

Fig. S1 Calculated near-field electric field profiles of the 28-nm-Ag PIA architecture illuminated by (a) p-polarized, (b) s-polarized and (c) unpolarized light.

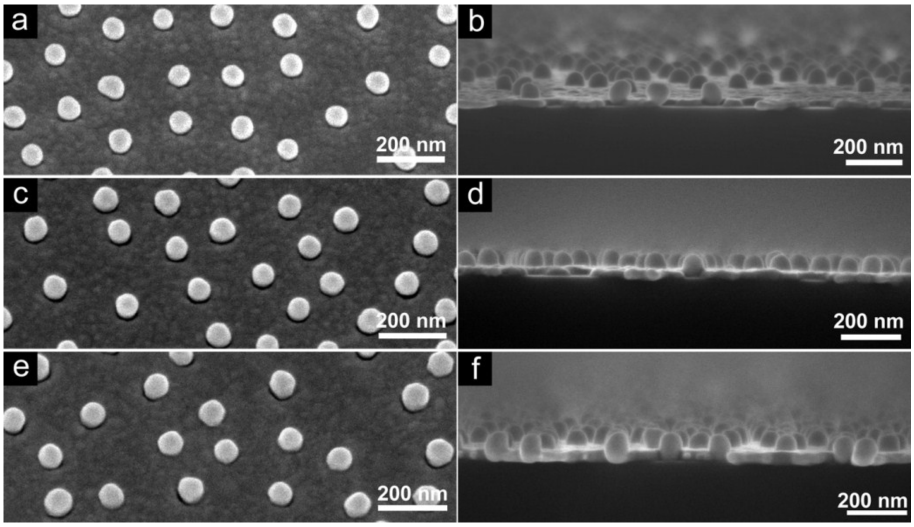

Fig. S2 Oblique-view (left column) and side-view (right column) SEM images of PIA arrays with different Ag thicknesses: (a, b) 15 nm, (c, d) 28 nm, and (e, f) 40 nm.

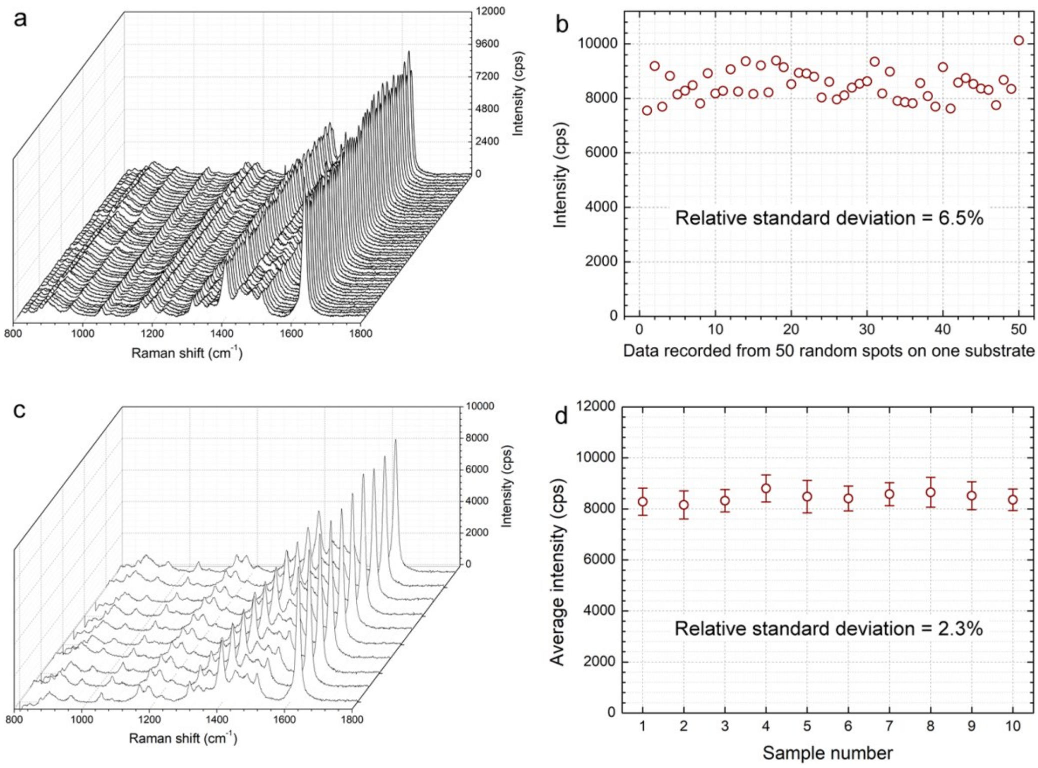

Fig. S3 (a) SERS spectra collected from 50 random spots on the 28-nm-Ag PIA substrate. (b) Intensity variation of the ring stretching mode at 1625 cm^{-1}. (c) Average SERS spectra recorded from 10 28-nm-Ag PIA substrates. Each line is the average result of SERS spectra recorded from 20 random spots throughout the whole substrate. (d) Substrate-to-substrate intensity variation of the ring stretching mode at 1625 cm^{-1}.

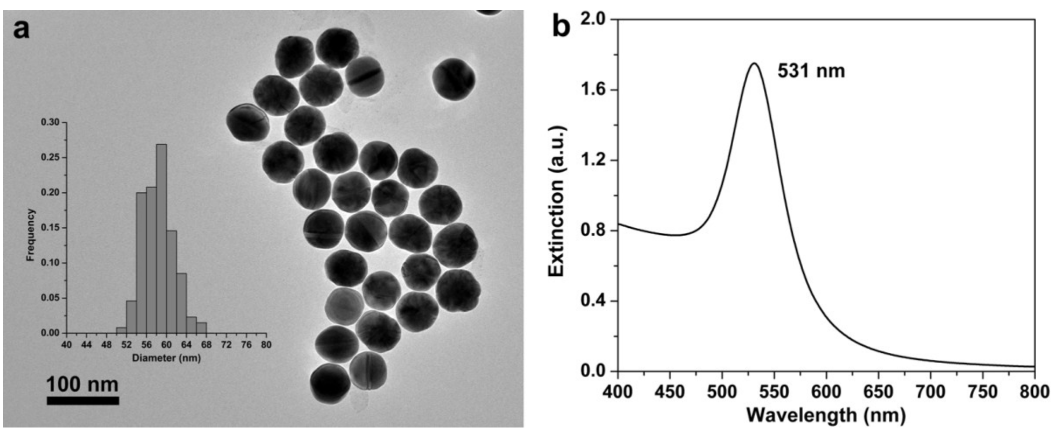

Fig. S4 (a) TEM image of the Au nanospheres with a mean diameter of 58 nm. Inset is the frequency histogram of diameter distribution, which is based on the data of more than 100 nanospheres. (b) UV-Vis extinction spectrum of the 58 nm Au nanosphere colloid.

Calculation of Enhancement Factors

The enhancement factors (EFs) in this work were calculated based on the following equation:

$$EF = \frac{I_{SERS}}{I_{bulk}} \times \frac{N_{bulk}}{N_{SERS}} \tag{S1}$$

where I_{SERS} and I_{bulk} are the intensities of characteristic vibrational bands in SERS and normal Raman spectra (see Fig. S5), respectively; N_{bulk} and N_{SERS} are the number of detected molecules in the laser spot volume in normal and SERS measurements, respectively. N_{bulk} can be estimated as follows:

$$N_{bulk} = \frac{\rho A h}{M} N_A \times 90\% \tag{S2}$$

where ρ is the density of MB powder (1.14 g/cm^3), A is the area of laser spot (0.79 μm^2), h is the penetration depth of the focused laser (ca. 15 μm), M is the molar mass of MB (373.9 g/mol), and N_A is the Avogadro constant.

As for the bare Au nanosphere array, its N_{SERS_NS} can be calculated according to the following equation:

$$N_{SERS\_NS} = \frac{N_d A A_{NS}}{\sigma} \tag{S3}$$

where N_d is the number density of Au nanospheres (2.38×10^{13} m^{-2}), A_{NS} is the surface area of a single Au nanosphere (ca. 1.06×10^4 nm^2), and σ is the area occupied by one MB molecule (0.8 nm^2)[1].

As for the flat Ag film, its N_{SERS_Ag} can be calculated according to the equation below:

$$N_{SERS} = \frac{A}{\sigma} \tag{S4}$$

For the PIA array, we ingore the enhancement contributions from the molecules on the top surface of the perforated Ag film and the upper hemispheres. Thus the number of the molecules inside the nanoring cavities (N_{SERS_PIA}) can be estimated as follows:

$$N_{SERS\_PH} = \frac{A N_d \left[\sqrt{d^2 + (R - r)^2} (R + r) + \frac{A_{NS}}{2} \right]}{\sigma} \tag{S5}$$

where d is the thickness of the Ag coating, R is the radius of the top circular face of the inverted truncated nanohole and r is the radius of the bottom face. By substituting equation S2, S3, S4, and S5 into equation S1, respectively, we have the EFs of the Au nanosphere array (EF_{NS}), the flat Ag film (EF_{Ag}), and the PIA hybrid array (EF_{PIA}):

$$EF_{NS} = 5.6 \times 10^4 \frac{I_{SERS}}{I_{bulk}} = 2.6 \times 10^3$$

$$EF_{Ag} = 2.3 \times 10^4 \frac{I_{SERS}}{I_{bulk}} = 40.9$$

$$EF_{PIA} = 8.6 \times 10^4 \frac{I_{SERS}}{I_{bulk}} = 4.5 \times 10^6$$

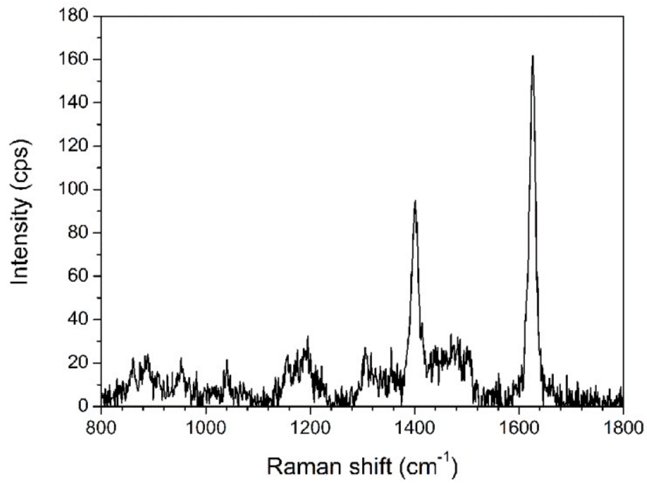

Fig. S5 Average normal Raman spectrum of MB powder.

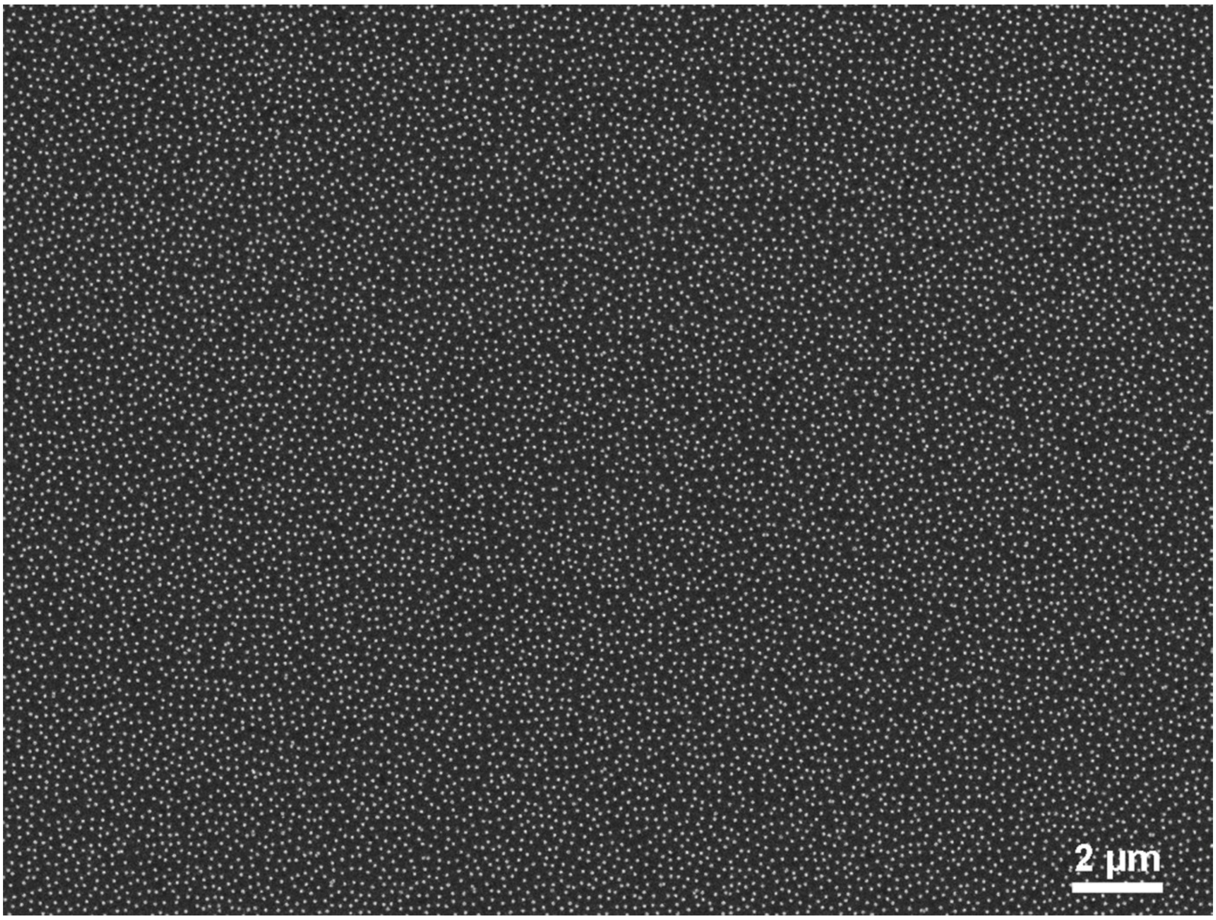

Fig. S6 Large-area SEM image of the PIA array.

References

[1] G. Laurent, N. Félidj, J. Aubard and G. Lévi, *Phys. Rev., B,* 2005, **71**, 045430.