Supporting Information for

Microspheres on Silver Film over Nanoparticle Arrays as Optoplasmonic Hybrid Materials for SERS

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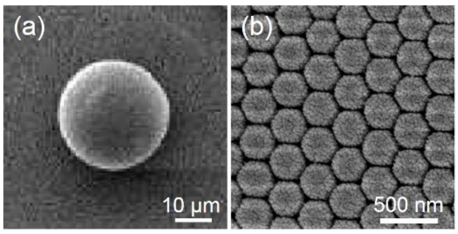

Figure S1. SEM images of (a) a 30-μm-diameter PS microsphere and (b) a 300 nm MFON coated with a 3-nm-thick SiO_2 film.

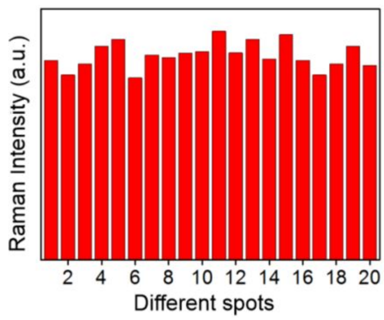

Figure S2. Raman mapping measurements of MB (corresponding intensity at 1618 cm^{-1}) on a 300 nm MFON substrate.

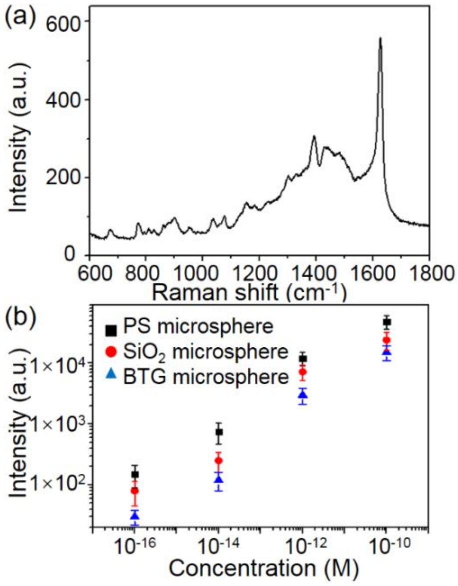

Figure S3. (a) Raman spectra of MB (1×10^{-10} M) on an OHM consisted of a 30-μm-diameter PS microsphere on top of a SiO_2 substrate deposited with a 50-nm-thick Ag film. (b) Intensity variation of prominent peak, 1618 cm^{-1} of MB as a function of concentration on OHMs consisted of different microspheres on top of the 300 nm MFON coated with a 3-nm-thick SiO_2.

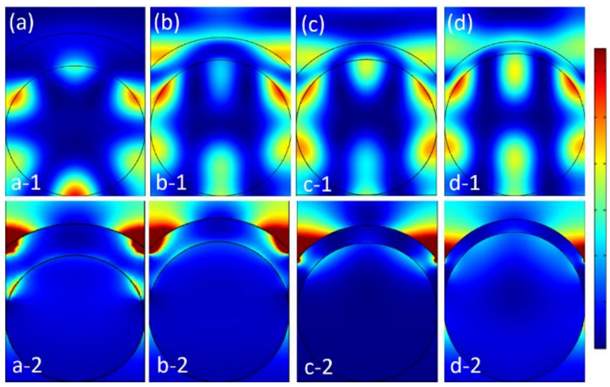

Figure S4. Electric field intensity distributions in the X-Z plane of the MFONs with different nanoparticle diameters at the wavelengths of the peaks in the absorption curves. (a) 250 nm, (b) 300 nm, (c) 400 nm, and (d) 580 nm.

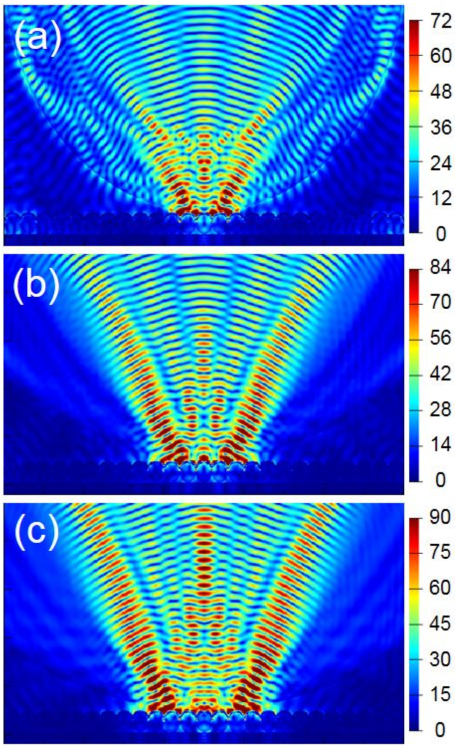

Figure S5. Electric field intensity distributions in the X-Z plane at 532 nm of PS microspheres with different diameters on top of the 300 nm MFON coated with a 3-nm-thick SiO_2 film. (a) 10 μm, (b) 15 μm, and (c) 20 μm.

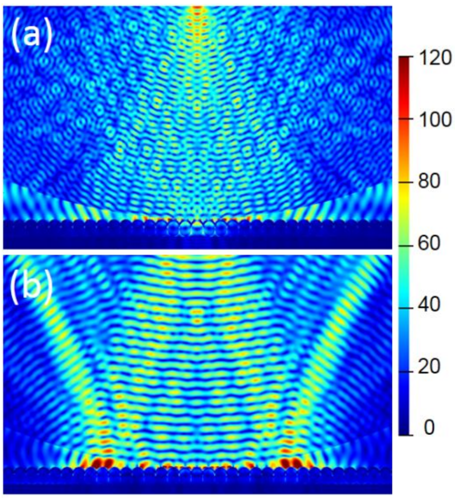

Figure S6. Electric field intensity distributions in the X-Z plane at 532 nm of a 30-μm-diameter (a) $BaTiO_3$ and (b) SiO_2 microsphere on top of the 300 nm MFON coated with a 3-nm-thick SiO_2 film.

1. Probe Molecule Selection

MB is chosen as analyte to study the Raman activities because of its low fluorescence quantum yield.[1] And it forms a well-defined monolayer on the silver surface with a characteristic molecular footprint, which is critical for the estimation of the total number of molecules being probed during SERS measurements, and therefore a precise estimation of enhancement factor is possible.

2. SERS Enhancement Factor Calculations

The SERS enhancement factor (EF) was calculated by comparing the SERS signal of MB adsorbed on a MFON and that of MB on a SiO_2 substrate. Samples for SERS measurements were prepared by drop-coating the MB (10 μL, 10^{-10} mol/L) ethanol solution onto MFONs with different nanoparticle diameters, and then the substrates were dried in room temperature. After the solvent evaporated (0.5 hours later), the solution formed a circular layer with a diameter of ~6.0 mm. The average surface coverage calculated is 2.13×10^{9} molecules/cm^2. Thus, the average occupied area per MB molecule is supposed to be about 4.69×10^{-10} cm^2, which is obviously larger than the maximum surface area per MB (about 1.35×10^{-14} cm^2). So, we can infer that the deposited MB film is a monolayer. The sample for the standard Raman measurement was prepared by dropping the MB (10 μL, 10^{-4} mol/L) ethanol solution onto a SiO_2 glass slide. The solution formed a circular layer with a diameter of ~5.0 mm.

To determine the EF of the MFONs, the SERS EF value of MB was calculated by the following expression [2]:

$$\mathrm{EF} = \frac{I_{SERS} / N_{SERS}}{I_{REF} / N_{REF}} = \frac{I_{SERS}}{I_{REF}} \times \frac{N_{REF}}{N_{SERS}} \tag{1}$$

where the N_{REF} and N_{SERS} denote the number of probe molecules which contribute to the standard and SERS signals, while the I_{REF} and I_{SERS} denote the corresponding standard Raman and SERS intensities, respectively. In the experiment, because the MB adsorbed onto the sliver is a monolayer, the EF can be written in the following form.

$$\mathrm{EF} = \frac{I_{SERS}}{A \times \frac{M_{SERS}}{S_{SERS}}} \times \frac{A \times \frac{M_{REF}}{S_{REF}}}{I_{REF}} = \frac{I_{SERS} \times S_{SERS} \times M_{REF}}{I_{REF} \times S_{REF} \times M_{SERS}} \tag{2}$$

where the M_{SERS} and M_{REF} are the number of MB molecules dropped onto a MFON and a standard SiO_2 glass slide, respectively. The S_{SERS} and S_{REF} are the geometrical areas of the MB coated films, and A is the recorded area of a laser spot. Since SERS and Raman spectra are obtained under the same excitation angle, the laser spot area of the standard Raman can be ignored. The representative band at 1618 cm^{-1} is selected to calculate the EF. We calculated the

EF by using the equation (2) in the Supporting Information. The calculated EFs are 6.84×10^{6}, 3.74×10^{7}, 2.38×10^{7}, and 4.78×10^{6} when the nanoparticle diameters are 200, 300, 400, and 580 nm, respectively.

References

[1] Atherton, S. J.; Harriman, A. J. Am. Chem. Soc. 1993, **115**, 1816-1822.

[2] R. Gupta, and W. A. Weimer, Chem. Phys. Lett. 2003, **374**, 302.