# Supplementary Information: 3-Dimensional Plasmonic Substrates Based on Chicken Eggshell Bio-Templates for SERS Based Bio-Sensing

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### I. Finite difference time domain (FDTD) method.

FDTD method solves Faraday's law and Ampere's law, Equations 1 and 2, in differential form over a grid-based domain (where field components are defined only at the grid points) using Taylor expansions for the derivatives.

$$\frac{\varepsilon\,\partial \mathrm{E}}{\partial t} = \nabla \times \mathrm{H} - \mathrm{J} \qquad (1)$$

$$\frac{\varepsilon\,\partial \mathrm{H}}{\partial t} = \nabla \times \mathrm{E} \qquad (2)$$

The most popular discretization is based on Yee's algorithm and computes the E (electric field) and H (magnetic field) components at half grid points relative to each other and central spatial and leapfrog time differences are used for the derivatives [1]. A simple version of this can be generated for a 2D system in which the electric field only has x and y components, and the magnetic field has a z component. If the time step is denoted by τ, then the following equations are used:

$$\mathrm{E_x}^{n+1/2} = \mathrm{E_x}^{n-1/2} + \frac{\tau}{\varepsilon}\left(\frac{\partial \mathrm{H_z}^{n}}{\partial y} - \mathrm{J_x}^{n}\right) \qquad (3)$$

$$\mathrm{E_y}^{n+1/2} = \mathrm{E_y}^{n-1/2} + \frac{\tau}{\varepsilon}\left(\frac{\partial \mathrm{H_z}^{n}}{\partial x} - \mathrm{J_y}^{n}\right) \qquad (4)$$

$$\mathrm{H_z}^{n+1} = \mathrm{H_z}^{n} + \frac{\tau}{\mu}\left(\frac{\partial \mathrm{E_y}^{n+1/2}}{\partial x} - \frac{\partial \mathrm{E_x}^{n+1/2}}{\partial y}\right) \qquad (5)$$

### II. FDTD simulation setup.

The FDTD simulation domain was 1.6μm× 1.6 μm× 1.6 μm and 6μm× 6 μm× 6 μm for OS and SM, respectively. Perfectly matched layers (PMLs) were used on all the boundaries. However, anti-symmetric and symmetric boundary conditions were used for x-min and y-min for OS simulation. The effect of staircase approximation was addressed by reducing the mesh size around the features to 2 nm× 2 nm× 2 nm. The simulations were performed on a computer with 8-core calculation nodes, each carrying 4 GB memory. Gold dielectric constants were obtained from the literature [2].

### III. Calculated electric field (E-field) distributions.

Figure S1 presents the calculated E-field distributions for the representative OS and SM architectures. Figure S1a depicts 4 Au nanospheres (100 nm diameter) touching each other with an in-between empty space of dimension 100 nm (along the E-field direction). Figure S1b shows the characteristic SM architecture, where a 0.8 μm diameter Au disk (corresponds to knobs) is sitting on an infinite Au fiber of diameter 1.5 μm.

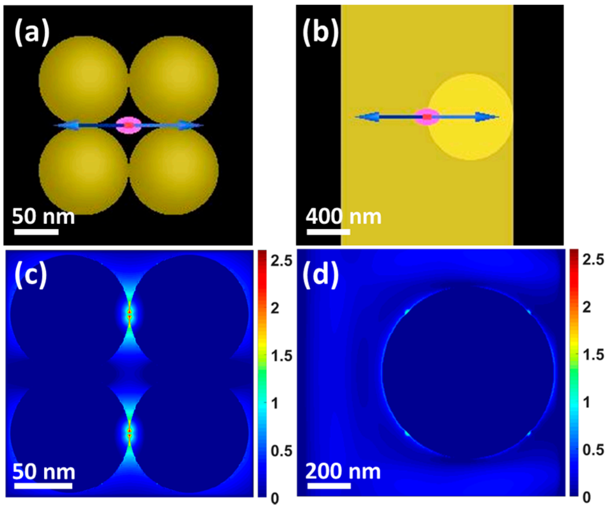


**Figure S1.** Representative (**a**) OS and (**b**) SM architectures. Calculated E-field distribution for (**c**) OS and (**d**) SM architectures. The incident wavelength is 785 nm.

As shown in Figure S1c and S1d, the E-field enhancement is larger for the aggregated nanospheres than that for the disk/fiber architecture. This qualitatively defends the better SERS performance of OS/IS region than the SM.

**IV. Calculation of SERS enhancement factor (EF).**

SERS EF is estimated according to the references 3 and 4 by comparing the 1575 $cm^{-1}$ peak in the SERS spectrum to the 1585 $cm^{-1}$ peak in normal Raman spectrum of the benzenethiol (BT) [3,4]. The EF can be written as

$$EF = \left(\frac{I_{SERS}}{I_{normal}}\right) \times \left(\frac{C_{normal}}{C_{SERS}}\right) \quad (6)$$

Here, $I_{SERS}$ and $I_{normal}$ represent the normalized (to power and integration time) count rates of the SERS and normal Raman signal, respectively. To obtain $I_{normal}$, BT is drop-casted on bare OS, IS, and SM regions without any Au coating. $C_{SERS}$ and $C_{normal}$ are the concentrations of the BT molecules in the SERS and normal Raman measurements. Table S1 enlists the calculated EF values for OS, IS, and SM regions.

**Table S1.** Calculation of SERS EF for egg OS, IS, and SM regions.

| Region | $C_{normal}$ (M) | Sample Power (mW) | Integration Time (s) | $I_{normal}$ (photons $s^{-1}$ $mW^{-1}$) | EF |
|---|---|---|---|---|---|
| OS | $4\times10^{-2}$ | 50 | 30 | 90 | $2.6\times10^{6}$ |
| IS | $4\times10^{-2}$ | 50 | 30 | 86 | $1.8\times10^{6}$ |
| SM | $4\times10^{-1}$ | 15 | 30 | 1040 | $1.5\times10^{5}$ |

## References

1. Yee, K. Numerical solution of initial boundary value problems involving maxwell's equations in isotropic media. *IEEE Trans. Antennas* **1966**, *14*, 302–307.
2. Johnson, P.B.; Christy, R.-W. Optical constants of the noble metals. *Phys. Rev. B* **1972**, *6*, 4370.
3. Chen, J.; Su, H.; You, X.; Gao, J.; Lau, W.M.; Zhang, D. 3D $TiO_2$ submicrostructures decorated by silver nanoparticles as SERS substrate for organic pollutants detection and degradation. *Mater. Res. Bull.* **2014**, *49*, 560–565.
4. Lin, P.Y.; Hsieh, C.W.; Tsai, P.C.; Hsieh, S. Porosity-controlled eggshell membrane as 3D SERS-active substrate. *ChemPhysChem* **2014**, *15*, 1577–1580.