Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Hierarchical Silver Mesoparticles with Tunable Surface Topographies for Highly Sensitive Surface-enhanced Raman Spectroscopy

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1. Experimental conditions for samples S1 to S6.

Table S1 Synthesis conditions of samples S1 to S6.

Sample	C_{AgNO3}	$C_{L\text{-}AA}$	R_r	t
S1	1 mM	0.5 mM	130 rpm	20 min
S2	1 mM	10 mM	130 rpm	20 min
S3	0.5 mM	10 mM	150 rpm	15 min
S4	0.5 mM	10 mM	130 rpm	10 min
S5	1 mM	20 mM	130 rpm	20 min
S6	0.5 mM	50 mM	200 rpm	10 min

Note: C_{AgNO3}: concentration of $AgNO_3$, $C_{L\text{-}AA}$： concentration of L-AA, R_r: rotation rate of magnetic bar, t: reaction time.

The pH values of the reaction solutions for the synthesis of typical samples S1, S3, S4, and S6:

Before adding L-AA, the pH values for the $AgNO_3$ solutions are 5.83, 4.62, 5.03 and 5.24 for synthesis of samples S1, S3, S4, and S6, separately. After adding the L-AA solution, the pH values of the reaction solutions are 2.78, 2.68, 2.66 and 2.35 for synthesis of samples S1, S3, S4, and S6, separately.

2. Supported images

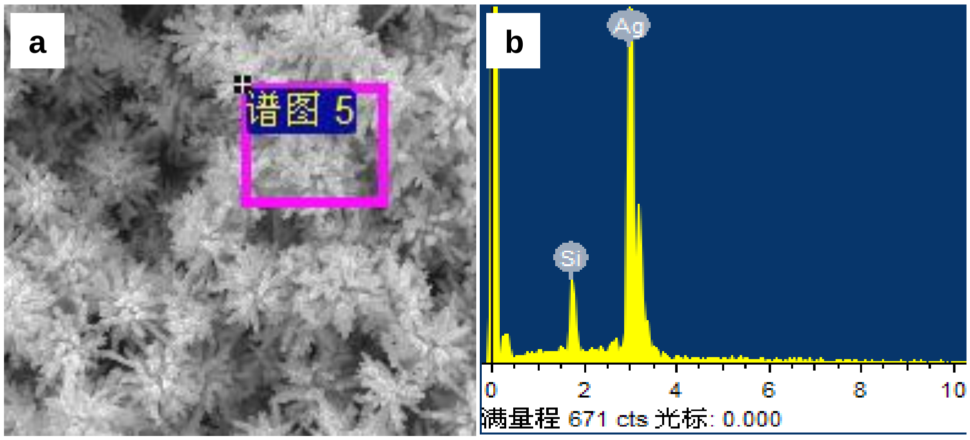

Fig. S1 (a) SEM image produced 0.5 mM $AgNO_3$ and 50 mM L-AA reacted at room temperature with a 200 rpm rotating magnetic bar. t=10 min (b) the EDS spectrum obtained from the circled area in (a).

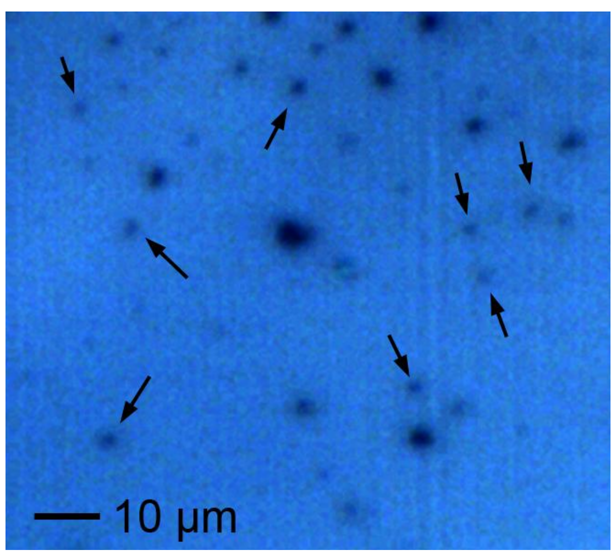

Fig. S2 Optical microscopy image of Ag mesoparticles supported on Si substrate for single-particle SERS measurement. The arrows indicate the separated “single-particle”.

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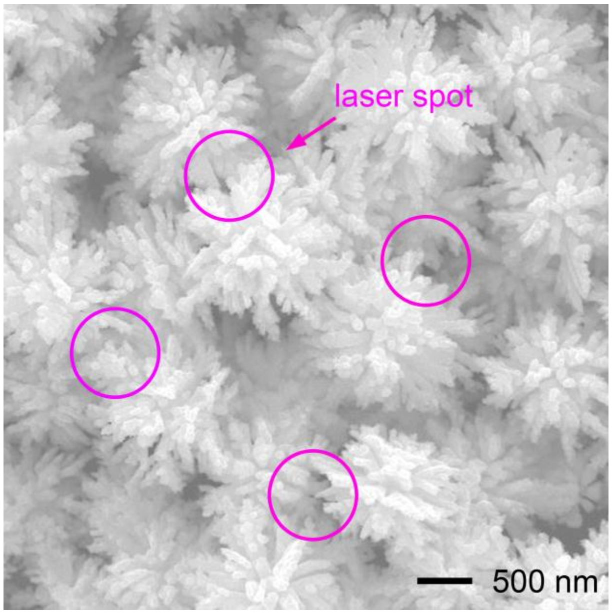


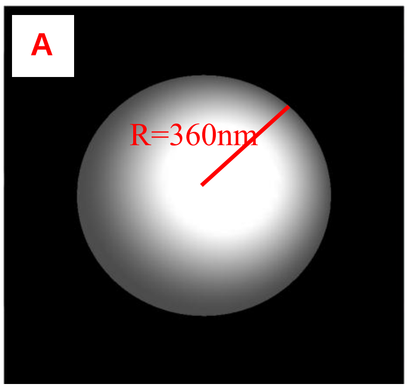
Fig. S3 Schematic illustration of the illuminated area by the laser spot in the particle aggregated film during the SERS measurement.

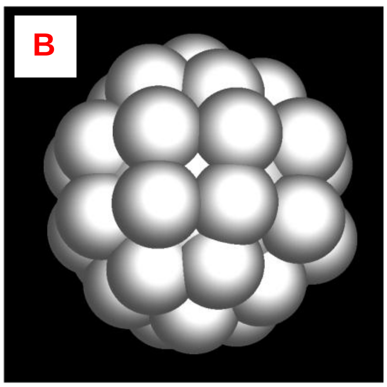
3. FDTD simulation

According to the Ag mesostructure obtained from experiment synthesized, five simplified simulation models with different surface morphology were constructed to obtain the local electric field distribution. The information of this model lists as following. The light used in the FDTD toward backward z axis and the polarization direction towards x axis. n=1, dx=dy=dz=4nm

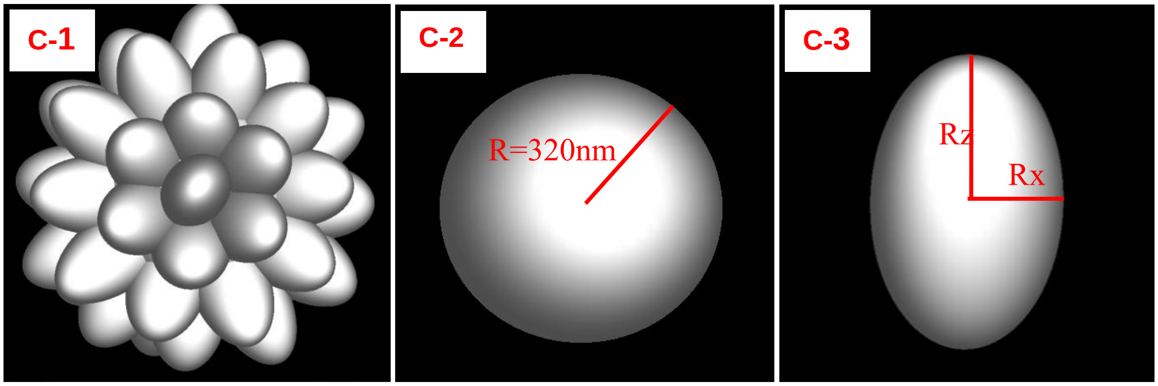
A: This simplified simulation was constructed using a sphere with smooth surface. R=360nm

B: The model was construed with a large sphere in the centre and some small sphere in the surface. The radiuses respectively are 300nm and 120nm. (R=300nm, r=120nm)

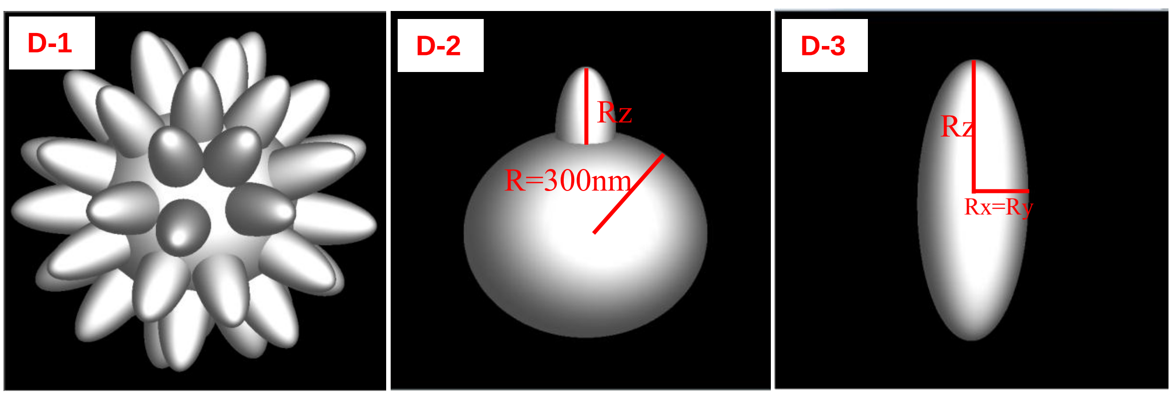




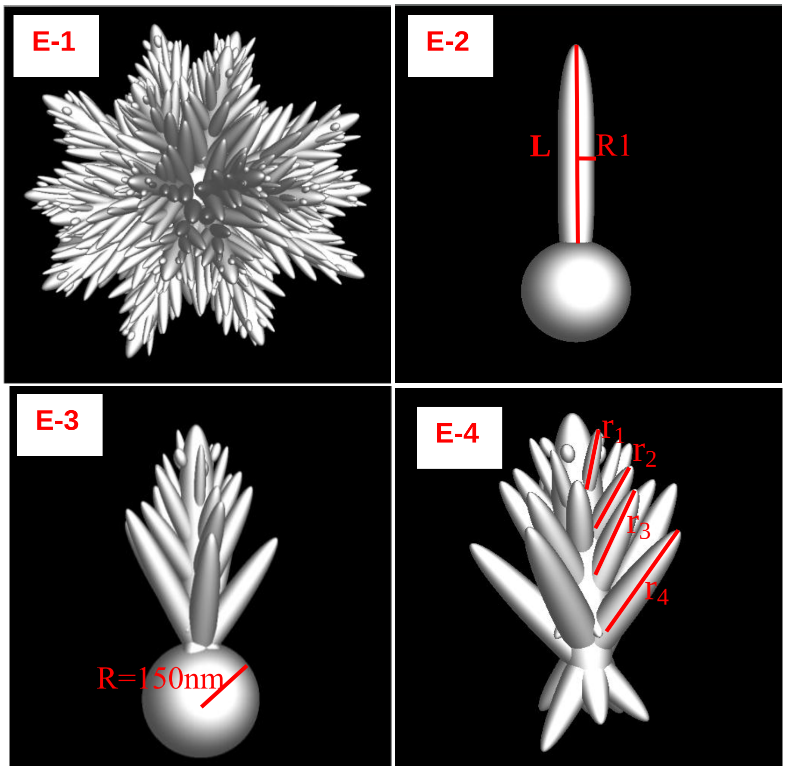
C: Model C has a sphere in the centre (C-2) and some ellipses as the petals in the surface (C-3). The centers of these ellipses distract in the surface of the sphere and the length of petals was from 170nm to 220nm. Some parameters lists as following: R=320nm, Rx=90nm, Ry=110nm, Rz =[170nm, 220nm].



D: The model was constructed with a sphere in the centre and some ellipses as the stabs in the surface (D-2, D-3). The length of the stabs was from 180nm to 230nm. Some parameters lists as following: R=300nm Rx=Ry=75nm, Rz=L=[180nm, 230nm] .



E: The model was constructed with a sphere in the centre and some ellipses with different length and thickness in the surface (E-2, E-3). Some parameters lists as following: R=150nm, R_1=50nm, r_0=15nm, r=25nm, r_1=100nm, r_2=150nm, r_3=200nm, r_4=300nm. Where R and R1 are the radius of the sphere in the centre and the main branch, L is the length of the main branch, r_1 to r_4 are the length of the subordinate branches and r, r_0, $2\times r_0$, $2.5\times r_0$ are the radius of the subordinate branches.



4. Calculation of SERS enhancement factor

The computational formula of the CV (crystal violet) molecule SERS enhancement factor is:

$$EF = \frac{I_{surface} / N_{surface}}{I_{solution} / N_{solution}} = \frac{I_{surface}}{N_{surface}} \times \frac{N_{solution}}{I_{solution}} \quad (1)$$

In this formula, $I_{solution}$ and $N_{solution}$ are respectively the signal intensity and the number of CV molecule about 10^{-4} mol/L CV aqueous solution. Then, $I_{surface}$ and $N_{surface}$ are respectively the signal and the intensity of CV molecule on the surface of single silver particle.

1) Firstly, the calculation of $I_{solution}$ and $N_{solution}$

In our previous reports, we use a low-magnification Raman objective (×10) to probe about 400 μm^3 the CV aqueous solution.[1-2] The Raman intensity was probed without use of the D2 attenuation piece with 5.5 mW laser power and the signal collection time was 20 s. The obtained Raman spectrum of CV solution is shown in Fig. S4.

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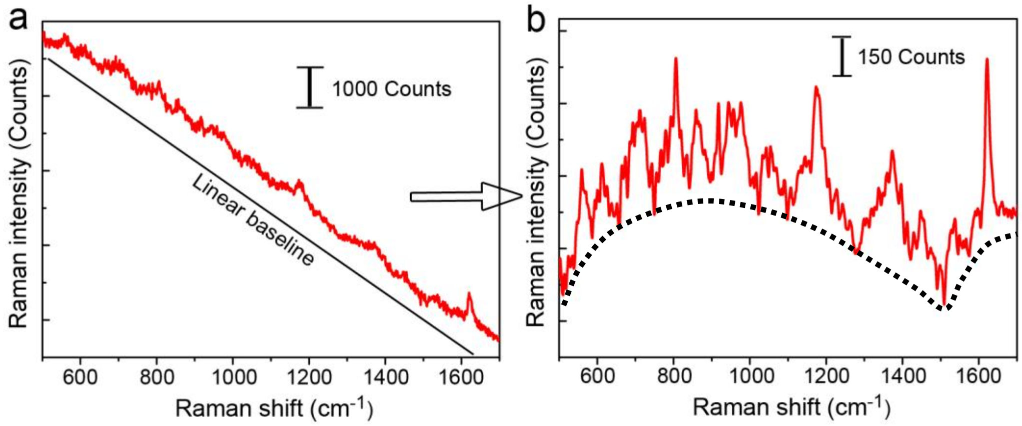

Fig. S4 (a) Raman spectrum of 10^{-4} mol/L CV aqueous solution. (b) Raman spectrum after subtracting a linear baseline. The dotted curve indicates the fluorescent baseline formed by CV molecules which are excited under 633 nm laser.

The number of the probed CV molecule and the SERS intensity at 1172 cm^{-1} were:

$$N_{\text{solution}} = 6.02\times10^{23}\times10^{-4}\,mol\,/\,L\times400\,\mu m^{3} = 2.408\times10^{7} \tag{2}$$

the Raman intensity at 1172 cm^{-1} was:

$$I_{\text{solution}} = 397\,/\,(5.5\,/\,0.034) \approx 2.45\,(\text{counts}) \tag{3}$$

where, 5.5 (mW) and 0.034 (mW) is the laser power probing on the solution and on the surface of silver mesoparticle. So, we can get:

$$\frac{N_{\text{solution}}}{I_{\text{solution}}} = \frac{2.408\times10^{7}}{2.45} = 9.8286\times10^{6} \tag{4}$$

2) Secondly, the calculation of I_{surface} and N_{surface}

Through the observation to the SERS spectrum of single silver particle, the signal intensity at 1172 cm^{-1} can be estimated. We did some approximate treatment to calculate the number of CV molecules probed on a single silver mesoparticle.

$$N_{\text{surface}} = \rho_{\text{CV}}\times S_{\text{probe}} \tag{5}$$

$$S_{\text{probe}} = \pi\times(425nm)^{2} \tag{6}$$

$$\rho_{\text{CV}} = \frac{N_{\text{CV}}}{S_{\text{total}}} \tag{7}$$

$$S_{\text{total}} = S_{\text{si}} + S_{\text{particles}} = S_{\text{si}} + N_{\text{silver}}\times S_{\text{silver}} \tag{8}$$

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Where ρ_{CV} is the density of CV molecule on the silver particles substrate, S_{probe} is the surface area probed by laser whose spot diameter is 850 nm, N_{CV} is the number of CV molecule we used and S_{total} is the total area of SERS substrate which incorporate the area of silicon wafer (S_{si}) and the area of all the silver mesoparticle ($S_{\mathrm{particles}}$). Since we used 100 μL, 10^{-7} mol/L CV molecule to drop on the 0.7 cm × 0.7 cm silicon wafer substrate and depending on Wang's report that through one rinse to the substrate, about 10% of CV molecules were retained,[3-5] the number of CV molecule we used can be calculated as this follow:

$$N_{\mathrm{CV}} = 6.02\times10^{23}\times100\mu L\times10^{-7}\,mol/L\times10\% = 6.02\times10^{11} \tag{9}$$

Assuming that silver mesoparticles are covered on 40% surface area of the substrate, the number of the silver mesoparticles (N_{silver}) on the substrate can be estimated as:

$$N_{\mathrm{silver}} = 40\%\times S_{\mathrm{si}}/(\pi r^2) \tag{10}$$

Where r is the average radius of the silver mesosoparticles. We suppose 80% surface area of the sphere in the centre of silver particle is covered by stab, the number of the stab can be estimated as:

$$N_{\mathrm{stab}} = 80\%\times S_{\mathrm{sphere}}/(\pi R_{\mathrm{x}}^{\,2}) \tag{11}$$

$$S_{\mathrm{silver}} = 20\%\times S_{\mathrm{sphere}} + N_{\mathrm{stab}}\times S_{\mathrm{stab}} \tag{12}$$

Where R_{x} is the cross section radius of the stab. When we calculate the silver particle, the stab can be estimated as rotational ellipsoid, so its geometric equation and surface area formula are:

$$\frac{x^2}{a^2}+\frac{y^2}{a^2}+\frac{z^2}{c^2}=1 \tag{13}$$

$$S_{\mathrm{ellipsoid}} = 2\pi ac\left[\frac{a}{c}+\frac{c}{\sqrt{c^2-a^2}}\right]\sin^{-1}\left(\frac{\sqrt{c^2-a^2}}{c}\right) = 2\pi ac\left[\frac{a}{c}+\frac{1}{\sqrt{1-\frac{a^2}{c^2}}}\right]\sin^{-1}\left(\sqrt{1-\frac{a^2}{c^2}}\right) \tag{14}$$

$$S_{\mathrm{stab}} = S_{\mathrm{ellipsoid}}/2 \tag{15}$$

In conclusion, the formula of N_{surface} is:

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$$N_{\text{surface}} = \rho_{\text{CV}} \times S_{\text{probe}} = \frac{N_{\text{CV}}}{S_{\text{total}}} \times \pi \times (425nm)^2 = \frac{N_{\text{CV}}}{S_{\text{si}} + N_{\text{silver}} \times S_{\text{silver}}} \times \pi \times (425nm)^2$$

$$= \frac{N_{\text{CV}} \times \pi \times (425nm)^2}{S_{\text{si}} + \left[\frac{40\% \times S_{\text{si}}}{\pi r^2}\right] \times \left[20\% \times S_{\text{sphere}} + \frac{80\% \times S_{\text{sphere}}}{\pi R_{\text{x}}{}^2} \times S_{\text{stab}}\right]}$$

$$= \frac{6.02 \times 10^{11} \times \pi \times (425nm)^2}{S_{\text{si}} + \left[\frac{40\% \times 4.9 \times 10^{-5}}{\pi r^2}\right] \times \left[20\% \times 4 \times \pi \times R^2 + \frac{80\% \times 4 \times \pi \times R^2}{\pi R_{\text{x}}{}^2} \times S_{\text{stab}}\right]}$$

$$= \frac{6.02 \times 10^{11} \times \pi \times (425nm)^2}{4.9 \times 10^{-5} + \left[\frac{40\% \times 4.9 \times 10^{-5}}{\pi r^2}\right] \times \left[20\% \times 4 \times \pi \times R^2 + 80\% \times 4 \times \frac{R^2}{R_{\text{x}}{}^2} \times S_{\text{stab}}\right]}$$

$$= \frac{0.34143}{4.9 \times 10^{-5} + \left[\frac{0.6242 \times 10^{-5}}{r^2}\right] \times \left[2.512 \times R^2 + 3.2 \times \frac{R^2}{R_{\text{x}}{}^2} \times S_{\text{stab}}\right]} \quad (16)$$

$$EF = \frac{I_{\text{surface}}}{N_{\text{surface}}} \times 9.8286 \times 10^6 \quad (17)$$

5. Enhancement factor of four different silver particles

S1: I_{surface} =704 (counts), $R = r = 360nm$

Because some spheres exist in the surface of silver particle, assuming that the surface area of the particle is three -fold of the area of sphere, i.e. $S_{\text{silver}} = 2.5 \times S_{\text{sphere}}$, then

$$N_{\text{surface}} = \frac{0.34143}{4.9 \times 10^{-5} + \left[\frac{1.96 \times 10^{-5}}{\pi \times r^2}\right] \times 2.5 \times 4 \times \pi \times R^2} = \frac{0.34143}{4.9 \times 10^{-5} + 1.96 \times 10^{-5} \times 2.5 \times 4} = 1.3936 \times 10^3$$

$$EF = \frac{704}{1.3936 \times 10^3} \times 9.8286 \times 10^6 = 4.97 \times 10^6$$

S3: $I_{\text{surface}} = 3.094 \times 10^3$, R=320nm, Rx=90nm, Ry=110nm, Rz=200nm, r=500nm

When we calculate the area of the petal (S_{stab}), we simplified it as a rotational ellipsoid (a=100nm, c=200nm) to calculate as the formula (14) and (15).

$$S_{\text{stab}} \approx 1.0882 \times 10^{-13}$$

$$N_{\text{stab}} = \frac{80\% \times 4 \times \pi \times R^2}{\pi \times Rx \times Ry} \approx 34$$

$$N_{\text{silver}} = \frac{40\% \times S_{\text{Si}}}{\pi r^2} = \frac{0.6242 \times 10^{-5}}{25 \times 10^{-14}} = 2.4968 \times 10^7$$

$$N_{\text{surface}} = 2.31 \times 10^3$$

$$EF = \frac{3.094 \times 10^3}{2.31 \times 10^3} \times 9.8286 \times 10^6 = 1.32 \times 10^7$$

S4: $I_{\text{surface}} = 3.76 \times 10^3$, $R = 300nm$, $R_x = R_y = 75nm$, $R_z = 220nm$, $r = 500nm$

$$S_{\text{stab}} = 8.8993 \times 10^{-14}$$

$$N_{\text{stab}} = \frac{80\% \times 4 \times \pi \times R^2}{\pi \times Rx^2} \approx 52$$

$$N_{\text{silver}} = \frac{40\% \times S_{\text{Si}}}{\pi r^2} = \frac{0.6242 \times 10^{-5}}{25 \times 10^{-14}} = 2.4968 \times 10^7$$

$$N_{\text{surface}} = 2.0062 \times 10^3$$

$$EF = \frac{3.76 \times 10^3}{2.0062 \times 10^3} \times 9.8286 \times 10^6 = 1.84 \times 10^7$$

S6: $I_{\text{surface}} = 7.505 \times 10^3$, $R = 150nm$, $R\text{x} = 50nm$, $L = 500nm$, r=750nm

We estimate some main branch as the FDTD simulation model and some subordinate branch as rotational ellipsoid. Where S_{main} is the main branch which covers the surface area of a cylinder (S_{cylinder}) and half of a rotational ellipsoid (S_{tip}) and S_{stab} is the total surface area of these subordinate branch which contains five kind of stab (named $S_{\text{stab\_1}}$, $S_{\text{stab\_2}}$, $S_{\text{stab\_3}}$, $S_{\text{stab\_4}}$, $S_{\text{stab\_5}}$). The number of these stab respectively are 10, 10,8, 7 and 7. $S_1 \sim S_5$ was calculated as the formula (14) and (15).

$$S_{\text{main}} = S_{\text{cylinder}} + S_{\text{tip}} = 2\pi RL + 6.5605 \times 10^{-14} = 1.7551 \times 10^{-13}$$

$$S_{\text{stab\_1}} = 10 \times S_1 = 1.5399 \times 10^{-14}$$

$$S_{\text{stab\_2}} = 10 \times S_2 = 7.7688 \times 10^{-14}$$

$$S_{\text{stab\_3}} = 8 \times S_3 = 1.5610 \times 10^{-13}$$

$$S_{\text{stab\_4}} = 7 \times S_4 = 2.1753 \times 10^{-13}$$

$$S_{\text{stab\_5}} = 7 \times S_5 = 3.8932 \times 10^{-13}$$

$$S_{\text{stab}} = S_{\text{main}} + S_{\text{stab\_1}} + S_{\text{stab\_2}} + S_{\text{stab\_3}} + S_{\text{stab\_4}} + S_{\text{stab\_5}} = 1.0315 \times 10^{-12}$$

$$N_{\text{stab}} = \frac{80\% \times 4 \times \pi \times R^2}{\pi \times Rx^2} \approx 29$$

$$N_{\text{silver}} = \frac{40\% \times S_{\text{Si}}}{\pi r^2} = \frac{0.6242 \times 10^{-5}}{(7.5)^2 \times 10^{-14}} = 1.1097 \times 10^7$$

$$N_{\text{surface}} = 8.9479 \times 10^2$$

$$EF = \frac{7.505 \times 10^3}{8.9479 \times 10^2} \times 9.8286 \times 10^6 = 8.24 \times 10^7$$

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