Supporting Information

Magnetic Field Induced Aggregation of Nanoparticles for Sensitive Molecular Detection

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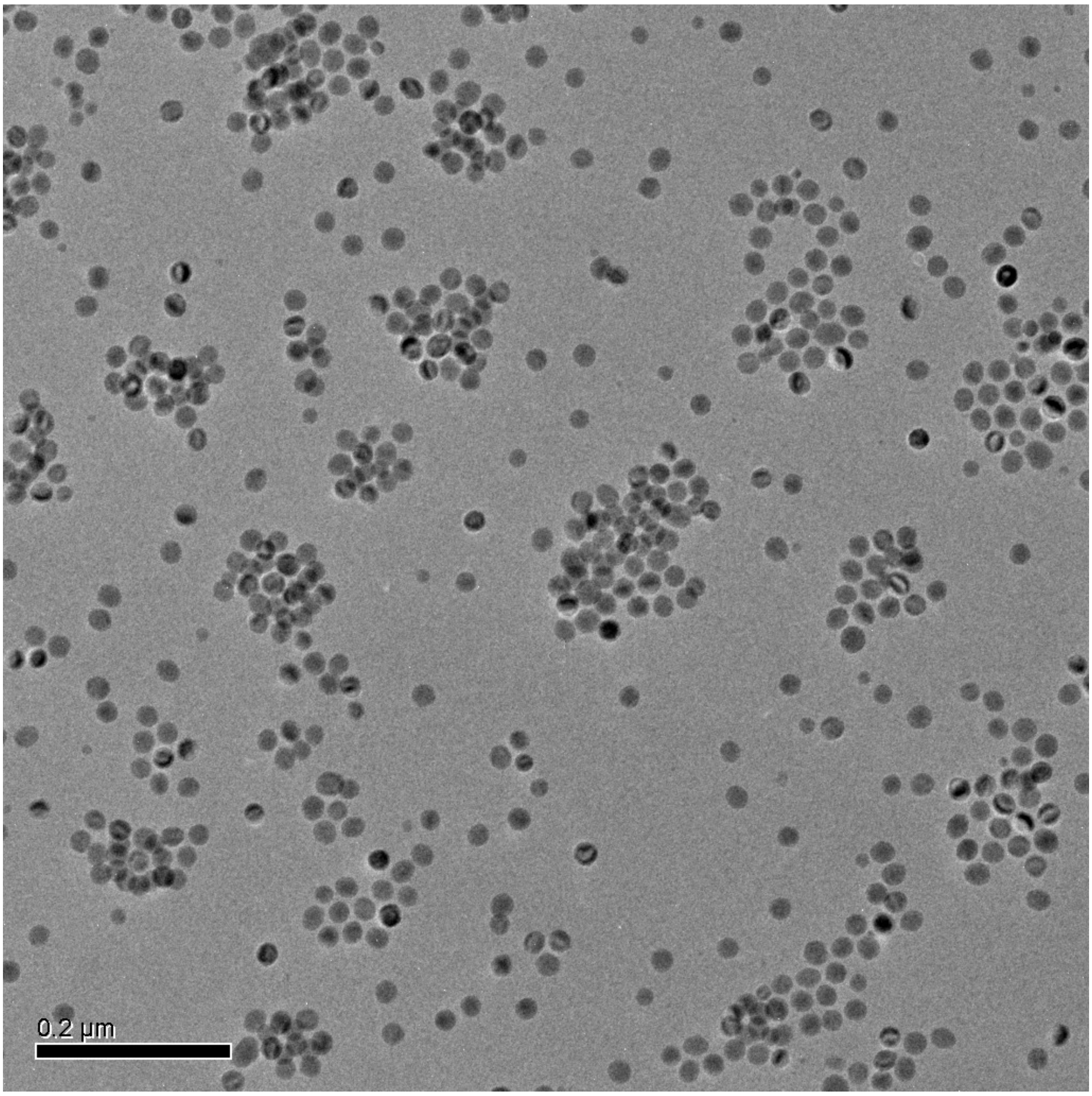
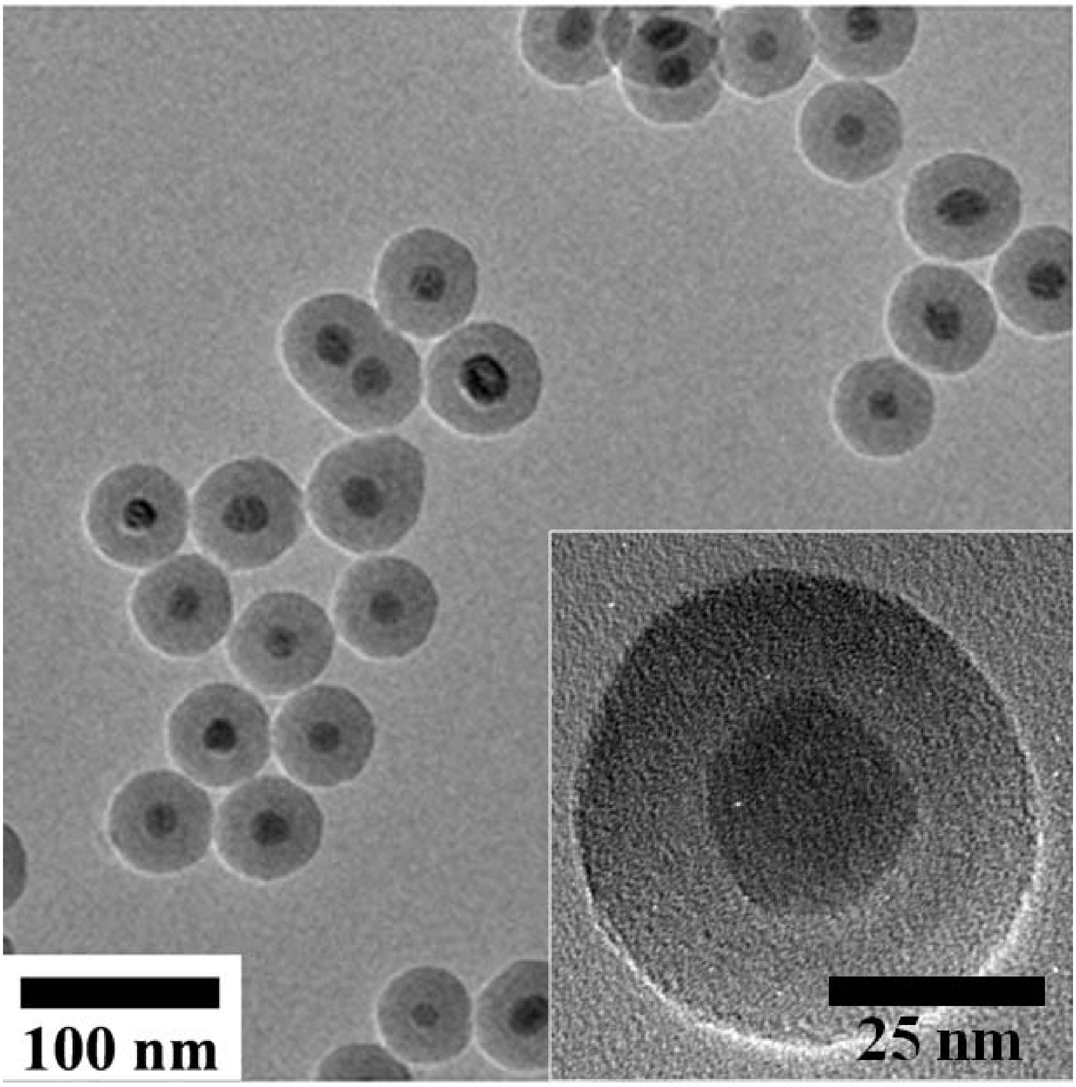
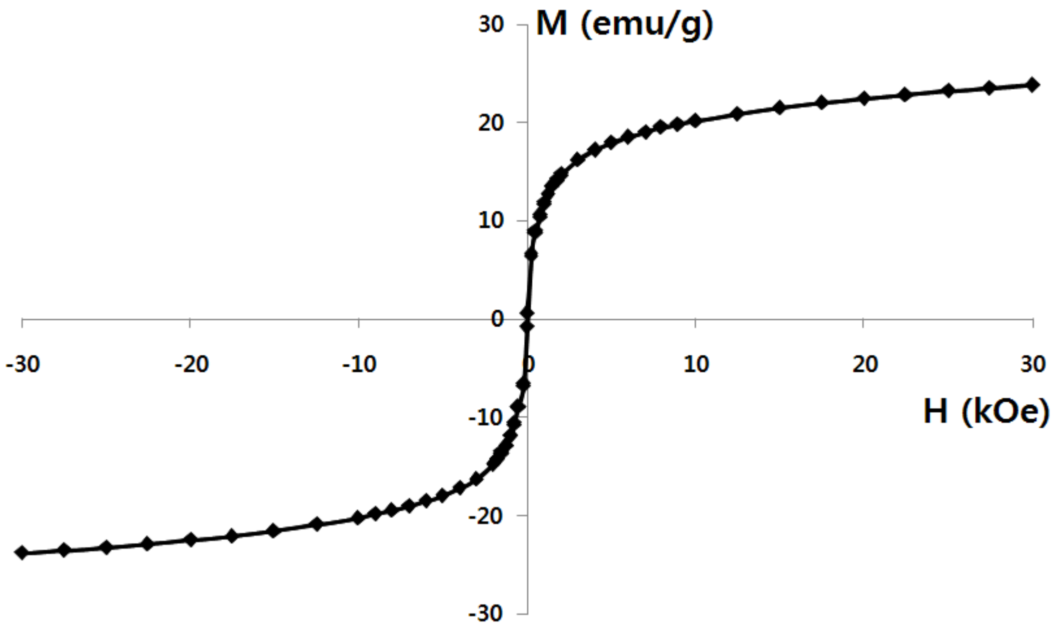


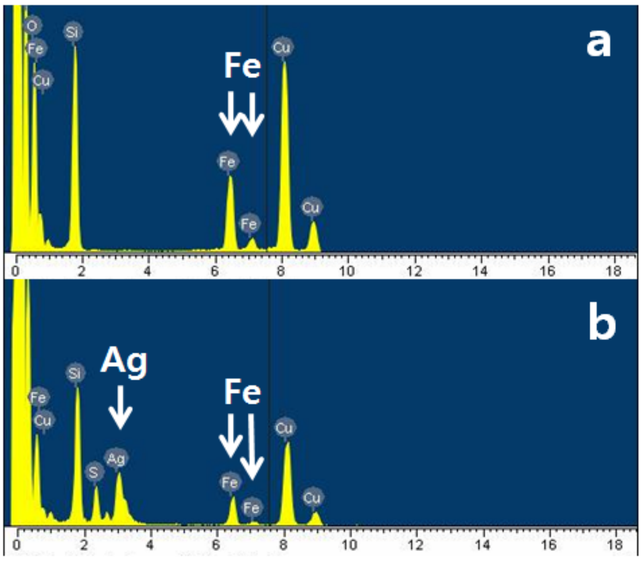
Supporting Figure 1. TEM image of 18 nm magnetite NPs used as cores for M-SERS dots.



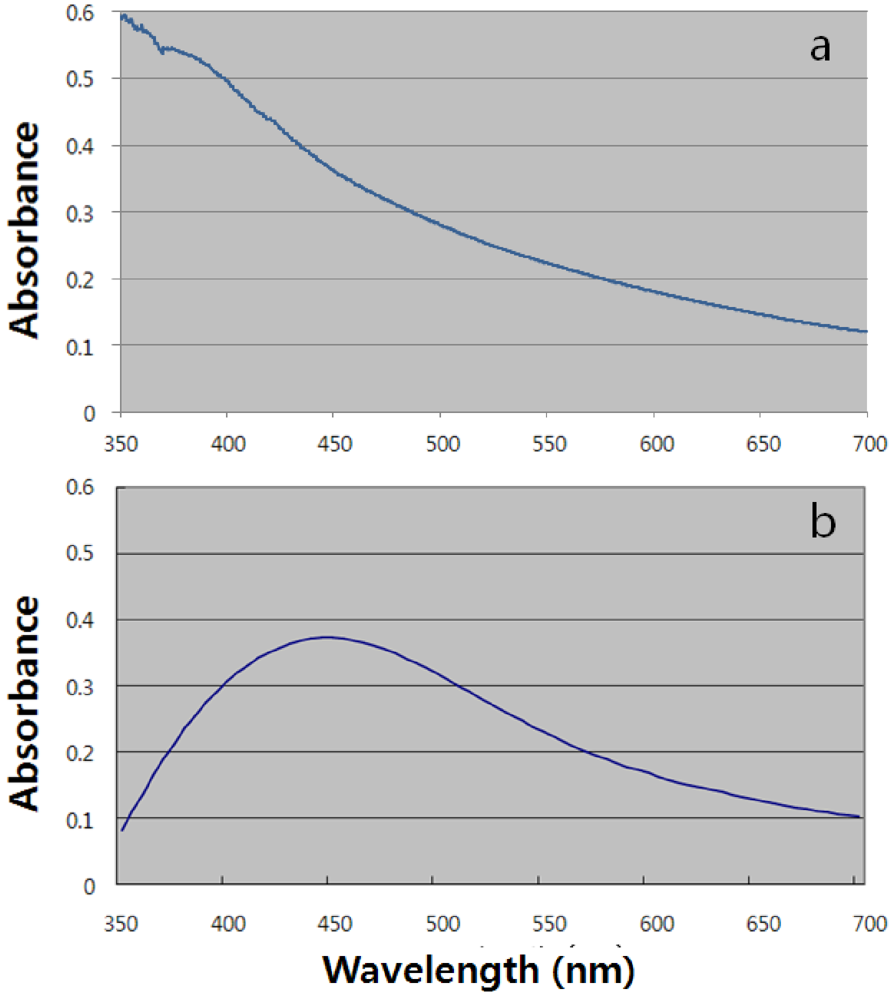
Supporting Figure 2. TEM image of 50 nm silica coated magnetite NPs (M-dot)



Supporting Figure 3. Field dependent magnetization of silica-coated magnetite NPs at 300 K.



Supporting Figure 4. EDX analysis. a) silica coated magnetite NPs, b) M-SERS dots.



Supporting figure 5. UV data (2.2 mg/mL). (a) silica-coated magnetic NPs, (b) Ag-M-Dots (blank : silica-coated magnetic NPs).

Supporting Info I. Calculation of SERS hot spot enhancement

(a) Increase of Raman signal at both aggregated and unaggregated Ag-M-dots was mostly affected by an increase of NP numbers in a certain cross sectioned Raman laser range and also by the hotspots of the adjoining NPs while other factors were ignored in this experiment. Because increase of the Raman signal is related to the number of NPs in the Raman laser range, the total increase of the Raman signal divided by the increase of NP numbers is equal to Raman signal enhancement by hotspot (HS), as stated below.

Therefore,

$$\textbf{HS (Raman signal enhancement by hot spot)} = \frac{I_a/I_u}{N_a/N_u}$$

$$= \mathbf{(85{,}000 / 80) / (324{\sim}1010 / 158)}$$

$$= \mathbf{166 \sim 518}$$

Where I_a represents the Raman signal intensity value of aggregated Ag-M-dots and I_u represents that of unaggregated Ag-M-dots.

In our experiment, a Raman labeled compound, benzenethiol, was introduced into the Ag-M-dots.

Measured values from experiments are as follows.

$\mathbf{I_a}$ = 8,500 (measured by 514 nm laser, 50×lens, **1/10 filter**), which equals **85,000** with full filter.

Here, we assumed that the full filter gives a 10 times larger Raman signal intensity than with the 1/10 filter.

$\mathbf{I_u}$ = **80** (measured by a 514 nm laser, 50×lens, full filter)

Thus, signal intensity for I_a was increased by a thousand fold over that of I_u.

N_a represents the number of NPs in aggregated Ag-M-dots and N_u represents the number of NPs in unaggregated Ag-M-dots in the same laser range.

Laser penetration depth was considered as follows. Ag-M-dots were composed of silver NPs, magnetite, and silica NPs. Among these, silica NPs are the most transparent. Therefore, laser penetration in Ag-M-dots might be less than that of the same size of pure silica NPs.

Therefore,

N_a (number of Ag-M-dots that affect SERS intensity in the aggregated form) will be between **N_a(M)** and **N_a(m)**.

Where **N_a(M)** comes from maximum laser penetration and **N_a(m)** comes from minimum laser penetration.

The laser cannot penetrate Ag-M-dots, and only NPs on the surface are affected; therefore, the laser beam cross sectioned area divided by the Ag-M-dot cross sectioned area will give **N_a(m)** as follows:

N_a(m) = Laser beam cross sectioned area / Ag-M-dot cross sectioned area

$= [\pi \times r_{\text{laser beam}}^2] / [\pi \times r_{\text{Ag-M-dot}}^2] =$ **324 units**

(In our experiment, a laser beam of cylindrical form has a 450×10^{-9} m radius and 5.9 μm height, and Ag-M-dots of the sphere form have a 25×10^{-9} m radius.)

N_a (M) was calculated as follows:

If laser signal intensities were not reduced when passed through Ag-M-dots, and if we assume that the aggregated Ag-M-dots formed FCC structure, **N_a**(M) will be the laser volume fraction of FCC (0.74)[S1] divided by the volume of Ag-M-dots.

Signal reduction by Ag-M-dot was considered as follows. Here we assumed that Raman laser power was decreased 14% per 23 nm penetration in the silica layer.[S2] From this, τ will be 152.5 nm, where $e^{-\frac{23}{\tau}} = 0.86$.

Volume of Ag-M-dots affecting SERS signal intensity, $V_{\mathbf{reduce}}$, can be calculated using the laser beam cross sectioned area multiplied by $\int_0^\infty e^{-\frac{h}{\tau}} dh$.

Here we assumed that penetration depth is ∞, because the height of aggregated Ag-M-dots was calculated to approximately 440 μm (See Supporting Info I b), which was exceedingly thicker than 457 nm (95% SERS signal comes from ~457 nm ; See Supporting Info III).

Then, **N_a** (M) = $[V_{\mathbf{reduce}} / V_{\text{Ag-M-dot}}] \times R_{\text{Ag-M-dot}} \times 0.74$ (FCC packing volume fraction)

$= [V_{\mathbf{reduce}}(9.70\times10^{-20}\ \text{m}^3) / V_{\text{Ag-M-dot}}\ (6.55\times10^{-23}\ \text{m}^3/\text{unit})] \times R_{\text{Ag-M-dot}}\ (0.902) \times 0.74$

$= \mathbf{1.01\times10^{3}}$ **units**

Where, $V_{\mathbf{reduce}} = \pi r_{\text{laser beam}}^{2} \int_{0}^{\infty} e^{-\frac{h}{\tau}} dh$

$= \pi r_{\text{laser beam}}^{2} \tau$

$= 9.70\times10^{-20}\ m^{3}$

$V_{Ag\text{-}M\text{-}dot}$ (volume of Ag-M-dot)

$= 4/3\times\pi\times r_{Ag\text{-}M\text{-}dot}{}^{3}$

$= 6.55\times10^{-23}\ m^{3}$

$R_{Ag\text{-}M\text{-}dot}$ is the SERS signal reduction rate of a Ag-M-dot.

For simple calculation of $R_{Ag\text{-}M\text{-}dot}$, we assume that the laser penetration rate in spherical Ag-M-dots is the same as that of the cylindrical shape, with the same volume and diameter. Therefore, a cylinder of 25 nm radius and 33.3 nm (See Supporting Info Ic) height will possess the same volume as that of 25 nm spherical Ag-M-dots.

Then

$R_{Ag\text{-}M\text{-}dot}$ (SERS signal reduction rate of an Ag-M-dot)

= [Raman laser power at the top of the cylinder (1) + Raman laser power at the bottom of the cylinder ($0.86^{h/23}$)] / 2

= 0.902

Number of Ag-M-dots of unaggregated form in a Raman laser cross sectioned area; $\mathbf{N_u}$, was calculated from V_L (Raman laser volume) multiplied by n_u (number density of Ag-M-dots in unaggregated solution) (See Supporting Info 1c). Here, because 92% of Ag-M-dots were not overlapped in 97.4% probability (See Supporting Info 1d), overlapping of Ag-M-dots, which can reduce the SERS signal, was ignored.

$\mathbf{N_u}$ $= V_L$ (Raman laser volume)$\times n_u$

$= V_L\ (3.753\times10^{-18}\ m^{3})\times n_u\ (4.221\times10^{19}\ \text{unit}/m^{3})$

= **158.4 units**

Where, n_u is the number density of Ag-M-dots in unaggregated solution.

For these calculations, we assumed that

a, Raman signal intensity is proportional to the amount of silver NPs;

b, other factors, such as capillary, cannot affect SERS intensity, except for the amount of silver NPs and hot spots;

c, unaggregated Ag-M-dots have no hot spot in Ag-M-dots;

d, every Ag-M-dot has the same Raman intensity;

e, all Ag-M-dots are completely spherical in shape, with the same size (r=25 nm, contains magnetite of r = 9 nm);

f, aggregated Ag-M-dots are cylindrical in shape;

g, laser volume is cylindrical in shape.

(b) Height of aggregated Ag-M-dots was calculated as follows.

Dispersed Ag-M-dots were all in aggregated form. If we assume that a total volume of aggregated Ag-M-dots is equal to the total volume of unaggregated Ag-M-dots, the height of aggregated Ag-M-dots (H) multiplied by the total area of aggregated Ag-M-dots is equal to the total solution volume in a capillary multiplied by n_u (number density of Ag-M-dots in unaggregated solution) multiplied by the volume of Ag-M-dots, as stated below.

H (Height of aggregated Ag-M-dots) = Total solution volume in capillary$\times n_u \times V_{Ag\text{-}M\text{-}dot}$/(total area of aggregated Ag-M-dots)

$$= {[(1.5\times10^{-3}\mathrm{m})^2\times\pi\times(2.48\times10^{-2}\ \mathrm{m})\times\left(4.221\times10^{19}\frac{\mathrm{unit}}{\mathrm{m}^3}\right)\times(6.55\times10^{-23}\ \mathrm{m}^3)]}\Big/{[(5.9\times10^{-4}\ \mathrm{m})^2\times\pi]} = 4.4\times10^{-4}\ \mathrm{m}$$

Here we assumed that all of the Ag-M-dots were aggregated and that the aggregated Ag-M-dots were cylindrical in shape.

(c) Raman laser volume and number density of Ag-M-dots in unaggregated solution are calculated as follows:

V_L (Raman laser volume) = $r^2\times\pi\times L$

$= 3.7534\times10^{-15}$

n_a (number density of Ag-M-dots in unaggregated solution) = N / V

= The amount of Fe in 1 m^3 of Ag-M-dots solution / Fe weight in 1 unit of Ag-M-dot

= 4.221×10^{19} unit/m^3

Where

N is the total number of Ag-M-dots in a volume *V*,

The amount of Fe in 1 m^3 of Ag-M-dots solution = 488.7 g / m^3 (obtained from ICP analysis)

Fe weight in 1 unit of Ag-M-dots = Number of Fe atoms in an Ag-M-dot×Fe Atomic number / Avogadro's number

= 123,900 unit×56.27 g/mol / [(6.022×10^{23}) unit/mol]

= 1.158×10^{-17} g

Where

Number of Fe atoms in an Ag-M-dot = V_p / V_c×(number of Fe atom per V_c) = 123,900

Lattice constant of the Fe_3O_4 unit cell = 0.8395 nm[S3]

V_c (Volume of cubic) = $(0.8395\ nm)^3$= 0.5916 nm^3

Number of Fe atoms per V_c = 24[S4]

V_p (volume of Fe_3O_4 in a Ag-M-dot)

= $4/3\times\pi\times r_{magnetite}^{3}$

= 3,054 nm^3 ($r_{magnetite}$ = 9 nm by TEM analysis)

Here we assumed that all of the Ag-M-dots were aggregated and that the aggregated Ag-M-dot and laser volume were cylindrical in shape.

(d) Probability of overlapping of Ag-M-dots in unaggregated solution is considered as follows.

There were 146 particles in a 450 nm radius cylindrical shaped volume (laser volume). Total observing events were calculated according to the sum of observing particles from 1 to 146 in 324 areas. Here we assumed that the laser penetration depth was ∞. Then, probability of observing particle number (i), Pi, can be calculated as follows.

$$P_i = \frac{{}_{324}C_i}{\sum_{k=1}^{146} {}_{324}C_k}$$

Then, the probability of observing a particle in a range of 135~146 was calculated by the sum of observing probability from 135 to 146.

$$\sum_{i=135}^{146} P_i = 0.97411 \approx 97.4\%$$

Supporting Info II. Calculation of SERS enhancement from Ag-M-dots contact point (hot spot)

If we assume that most enhancement by hot spot comes from a silver NP contact point within 2 nm distance[S5] and that each Ag-M-dot has 12 contact points (FCC), each $HS_{contact}$(Hot spot in contact point) can be calculated as follows:

$HS_{contact}$(Hot spot in contact point)

$$= \frac{A_{Ag-M-Dot}(\text{Area of Ag}-\text{M}-\text{Dot})}{12 \times A_{contact}} \times \text{HS(Calculated Hot spot value; Supporting Info I)}$$

$$= \frac{7854}{12 \times 157.1} \times HS$$

Because $166 \leq HS \leq 518$,

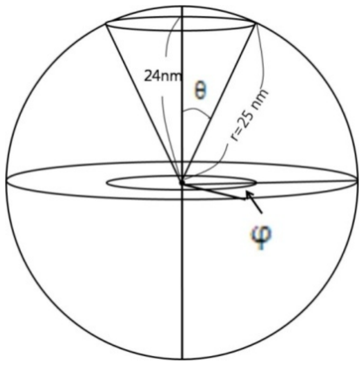
Then $691 \leq HS_{contact} \leq 2{,}158$

Where $A_{contact}$ is the area of contact between two Ag-M-dots

$$= \int_0^{2\pi}\int_0^{\theta} r^2 \sin x \, dx d\varphi$$

$$= r^2 \int_0^{2\pi} [-\cos x]_0^{\theta} \, d\varphi = r^2 \int_0^{2\pi} 1 - \cos\theta \, d\varphi$$

$$= 2\pi r^2 \times 0.04 = 157.0795 \text{ nm}^2$$



Supporting Info III. Calculation of penetration depth

Ag-M-dots were composed of silica NP, magnetite, and silver. Among these materials, silica is the most transparent. We assumed that Raman laser power was decreased 14% per 23 nm penetration in the silica layer.[S2] If we assume that the Ag-M-dots are the same transparent materials, we can prove that a **95%** SERS signal came from a depth of less than **457 nm**, as follows:

$$\pi r^2 \int_0^d e^{-\frac{h}{152.5}} dh = 0.95 \times V_{ra}$$

Then

$$\pi r^2 [-152.5 \times e^{-\frac{h}{152.5}}]_0^d = 0.95 \times (\pi r^2 \times 152.5)$$

Then

$$1 - e^{-\frac{d}{152.5}} = 0.95$$

Where, d = 456.85nm.

Supporting Info References

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