Supporting Information for

Crystal Engineering and SERS Properties of Ag-Fe_3O_4 Nanohybrid: from Heterodimer to Core-Shell Nanostructures

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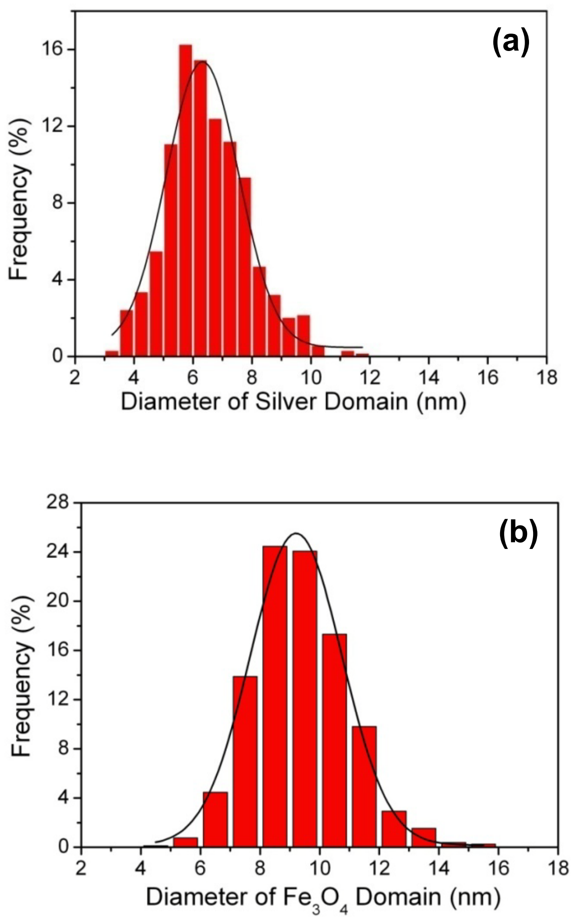

Figure S1. Size distribution of Ag and Fe_3O_4 in the heterodimer nanoparticles.

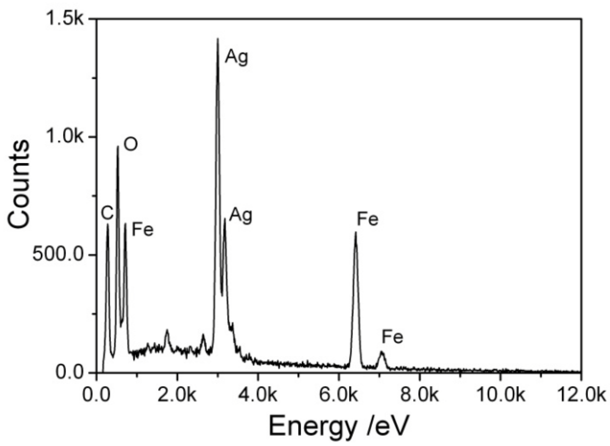

Figure S2. EDS spectra of the Ag-Fe_3O_4 heterodimer nanoparticles.

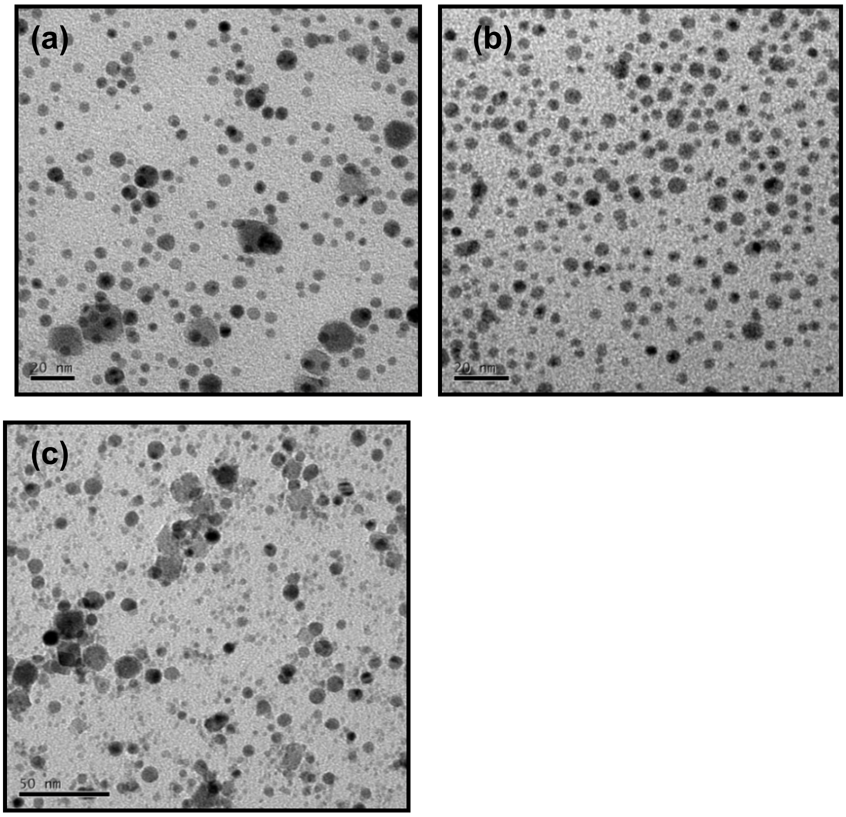

Figure S3. TEM images of the product synthesized without the different surfactants. (a) 1,2-dodecanediol (DDD), (b) oleylamine (OAm); (c) oleic acid (OAc).

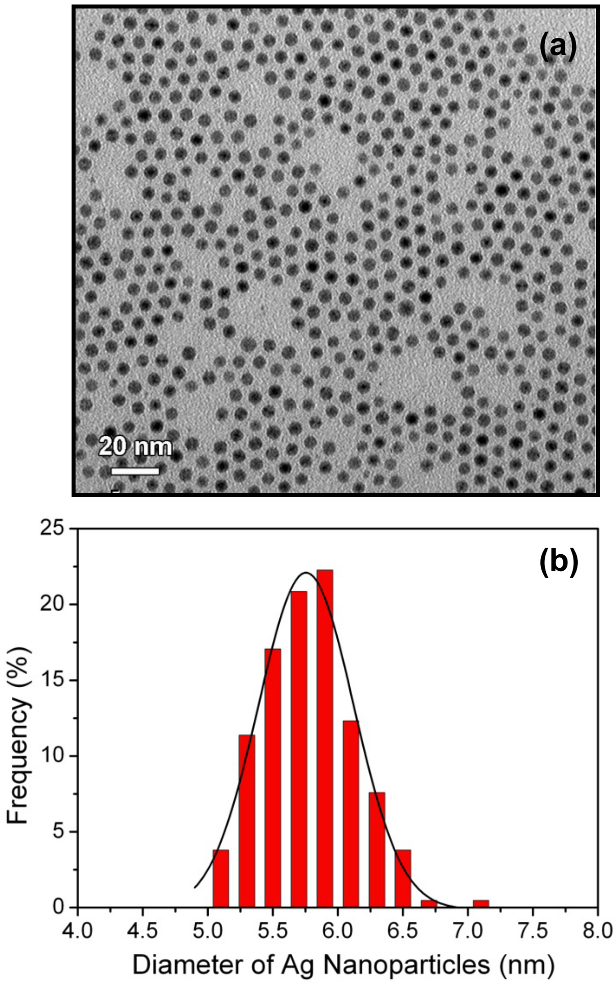

Figure S4. (a) TEM image and (b) size distribution of Ag nanoparticles.

***Calculation of Enhancement Factor*:**

1) Enhancement Factor of Ag Nanoparticles
The amount of Ag derived from ICP AAS techqniue: 0.09064 mg
The weight of each Ag nanoparticle based on the average diameter (6.6 nm):

$$W = \rho_{Ag} * V_{Ag} = 10.53\ g/cm^3 * \frac{4}{3}\pi * (3.3\ nm)^3 = 1.584*10^{-15}\ mg$$

Then, the number of Ag nanoparticles:

$$N = 0.09064\ mg / 1.584*10^{-15}\ mg = 5.72*10^{13}$$

The molar number of Ag nanoparticles:

$$n = 5.72*10^{13} / 6.02*10^{23} = 9.50*10^{-11}\ mol$$

So, the concentration of Ag nanoparticles:

$$C_{Ag\ NPs} = 9.50*10^{-11}\ mol / 1\ mL = 9.50*10^{-8}\ mol/L$$

On the other hand, the surface area of each Ag nanoparticle:

$$4\pi(d/2)^2 = 4*3.14*(3.3\ nm)^2 = 136.78\ nm^2$$

The surface area of a 2D unit cell with 8 Ag binding sites: 1.724 nm^2 (Ref 1,2)
Then, the number of binding sites on each Ag NP:

$$(136.78\ nm^2 / 1.724\ nm^2) \times 8 = 634.7$$

So, the concentration of binding sites:

$$9.50*10^{-8} mol/L \times 634.7 = 6.03*10^{-5}\ mol/L$$

If each binding site is occupied by a probe molecule, the concentration of probe molecules for SERS measurement is $6.03*10^{-5}$ mol/L.
The Raman intensity (I_{Raman}) of 0.1 M 2-NT (C_{Raman}) is 368.73.

$$\text{Thus, } EF = \frac{I_{SERS}}{I_{Raman}} * \frac{C_{Raman}}{C_{SERS}} = \frac{68.72}{368.73} * \frac{0.1}{6.03 * 10^{-5}} = 310$$

2) Enhancement Factor of Ag-Fe_3O_4 heterodimer nanoparticles

Because the Ag nanoparticle in the heterodimer nanohybrid is closely contacted with Fe_3O_4, the exposed surface for the binding of the probe molecules is significant reduced. Here, it is assumed that 75% of the surface area of the Ag nanoparticle is still available for the binding of the probe molecules. Then, the effective surface area of each Ag nanoparticle for the probe molecules is

$$\frac{3}{4} * 4\pi(d/2)^2 = \frac{3}{4} *4*3.14*(3.3\ nm)^2 = 102.58\ nm^2$$

Then, the number of the binding sites on each Ag NP:

$$(102.58\ nm^2 / 1.724\ nm^2) \times 8 = 476$$

So, the concentration of binding sites:

$$9.50*10^{-8} mol/L \times 476 = 4.52*10^{-5}\ mol/L$$

The concentration of probe molecules for SERS measurement: $4.52*10^{-5}$ mol/L

$$\text{Thus, } EF = \frac{I_{SERS}}{I_{Raman}} * \frac{C_{Raman}}{C_{SERS}} = \frac{189.66}{368.73} * \frac{0.1}{4.52 * 10^{-5}} = 1.14*10^3$$

(1) Y. Feng, S. Xing, J. Xu, H. Wang, J. W. Lim and H. Chen, *Dalton Trans.* **2010**, *39*, 349.
(2) J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, **2005**, *105*, 1103.