Supporting Information for
Crystal Engineering and SERS Properties of Ag-Fe₃O₄ Nanohybrid: from Heterodimer to Core-Shell Nanostructures
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Figure S1. Size distribution of Ag and Fe₃O₄ in the heterodimer nanoparticles.
Figure S2. EDS spectra of the Ag-Fe$_3$O$_4$ 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 technique: 0.09064 mg

The weight of each Ag nanoparticle based on the average diameter (6.6 nm):

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

Then, the number of Ag nanoparticles:

\[ N = \frac{0.09064 \text{ mg}}{1.584 \times 10^{-15} \text{ mg}} = 5.72 \times 10^{13} \]

The molar number of Ag nanoparticles:

\[ n = \frac{5.72 \times 10^{13}}{6.02 \times 10^{23}} = 9.50 \times 10^{-11} \text{ mol} \]

So, the concentration of Ag nanoparticles:

\[ C_{Ag\text{NPs}} = \frac{9.50 \times 10^{-11} \text{ mol}}{1 \text{ mL}} = 9.50 \times 10^{-8} \text{ mol/L} \]

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

\[ 4\pi(d/2)^2 = 4 \times 3.14 \times (3.3 \text{ nm})^2 = 136.78 \text{ nm}^2 \]
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:

\[
(136.78 \text{ nm}^2 / 1.724 \text{ nm}^2) \times 8 = 634.7
\]

So, the concentration of binding sites:

\[
9.50 \times 10^{-8} \text{ mol/L} \times 634.7 = 6.03 \times 10^{-5} \text{ mol/L}
\]

If each binding site is occupied by a probe molecule, the concentration of probe molecules for SERS measurement is $6.03 \times 10^{-5}$ mol/L.

The Raman intensity ($I_{\text{Raman}}$) of 0.1 M 2-NT ($C_{\text{Raman}}$) is 368.73.

\[
\frac{I_{\text{SERS}}}{I_{\text{Raman}}} \cdot \frac{C_{\text{Raman}}}{C_{\text{SERS}}} = \frac{68.72}{0.1} \cdot \frac{368.73}{6.03 \times 10^{-5}} = 310
\]

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

2) Enhancement Factor of Ag-Fe$_3$O$_4$ heterodimer nanoparticles

Because the Ag nanoparticle in the heterodimer nanohybrid is closely contacted with Fe$_3$O$_4$, the exposed surface for the binding of the probe molecules is significantly 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

\[
\frac{3}{4} \times 4\pi (d/2)^2 = \frac{3}{4} \times 4 \times 3.14 \times (3.3 \text{ nm})^2 = 102.58 \text{ nm}^2
\]

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

\[
(102.58 \text{ nm}^2 / 1.724 \text{ nm}^2) \times 8 = 476
\]

So, the concentration of binding sites:

\[
9.50 \times 10^{-8} \text{ mol/L} \times 476 = 4.52 \times 10^{-5} \text{ mol/L}
\]

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

\[
EF = \frac{I_{\text{SERS}}}{I_{\text{Raman}}} \cdot \frac{C_{\text{Raman}}}{C_{\text{SERS}}} = \frac{189.66}{4.52 \times 10^{-5}} = 1.14 \times 10^3
\]
