Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information

Structure-dependent SERS Activity of Plasmonic Nanorattles with Built-in Electromagnetic Hotspots

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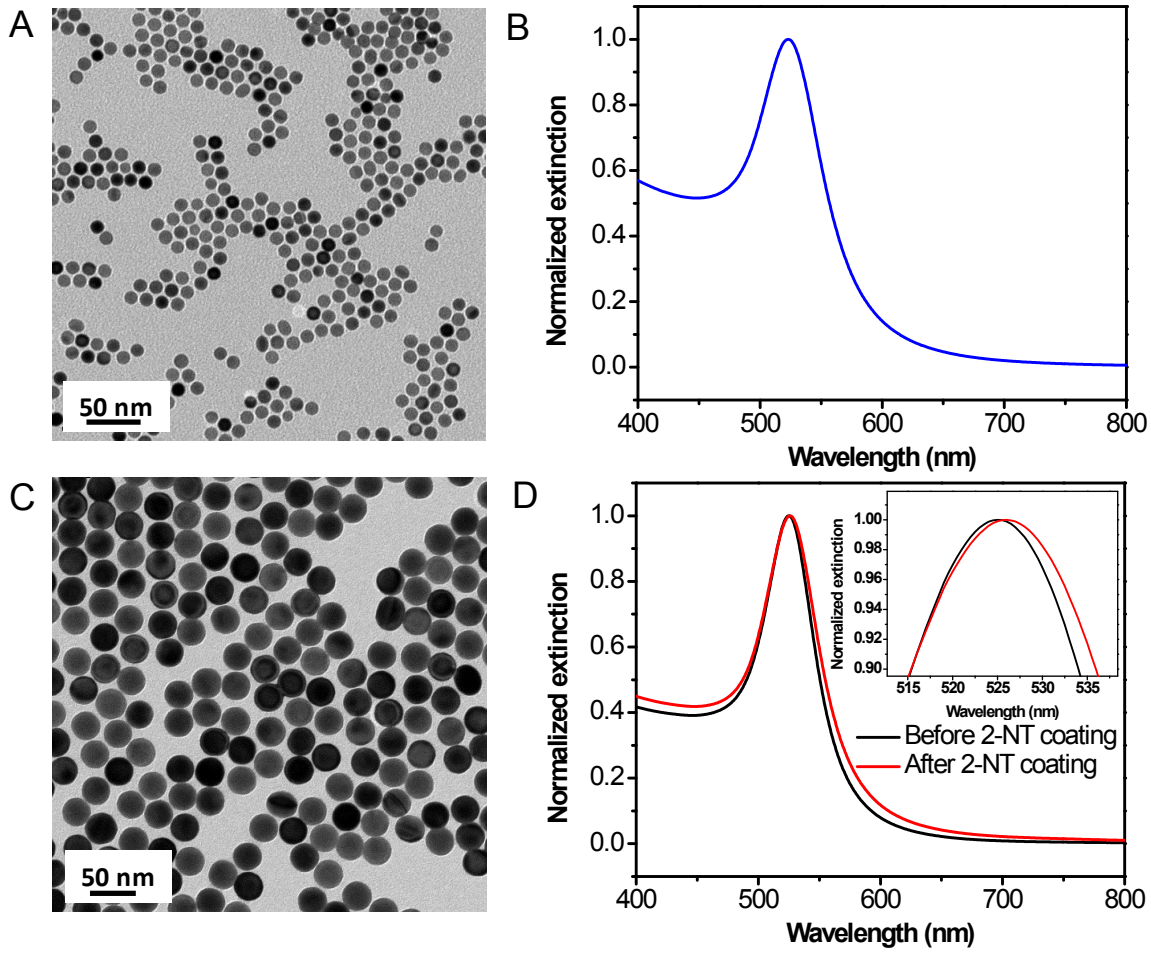

Figure S1. (A) TEM image of 10 nm Au nanospheres. (B) Vis-NIR extinction spectrum of 10 nm Au nanospheres. (C) TEM image of 30 nm Au nanospheres employed as cores for the synthesis of Au@Ag nanocubes. (D) Vis-NIR extinction spectrum of 30 nm Au nanospheres before (black) and after (red) 2-NT coating. Zoom-in spectra in inset reveals a redshift of ~1 nm after 2-NT adsorption.

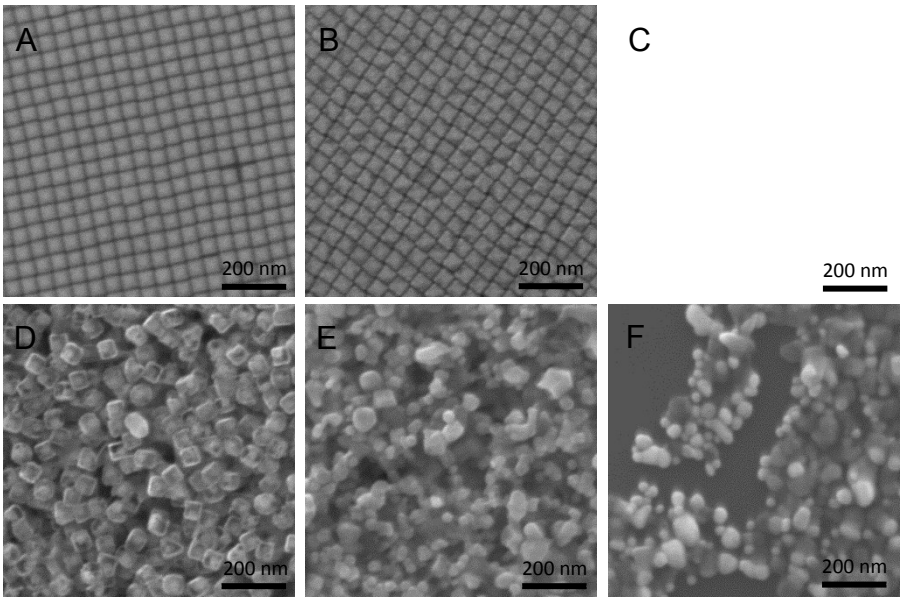

Figure S2. (A)-(F) SEM images of Au@Ag nanocubes and Au nanorattles obtained by adding 0, 20, 40, 60, 80 and 100 μl of 0.5 mM $HAuCl_4$ into 100 μl of NT-Au@Ag nanocubes, respectively.

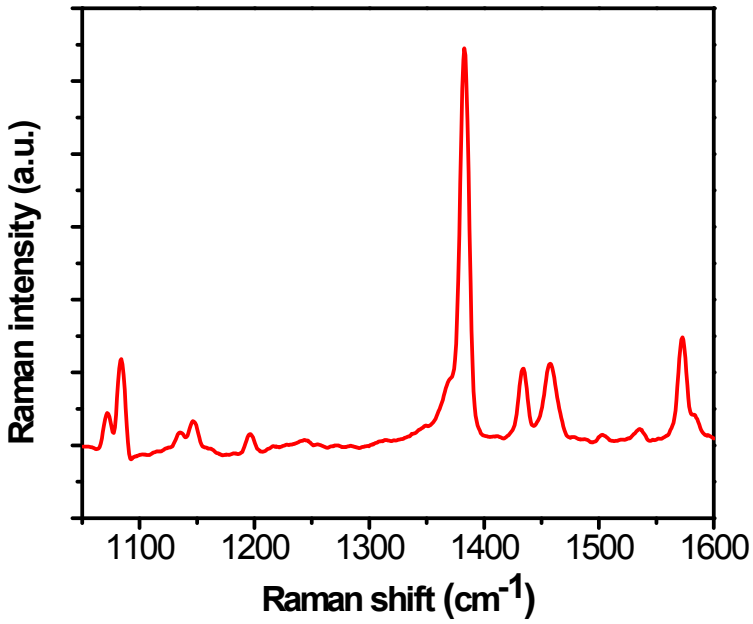

Figure S3. Raman spectrum collected from bulk 2-NT.

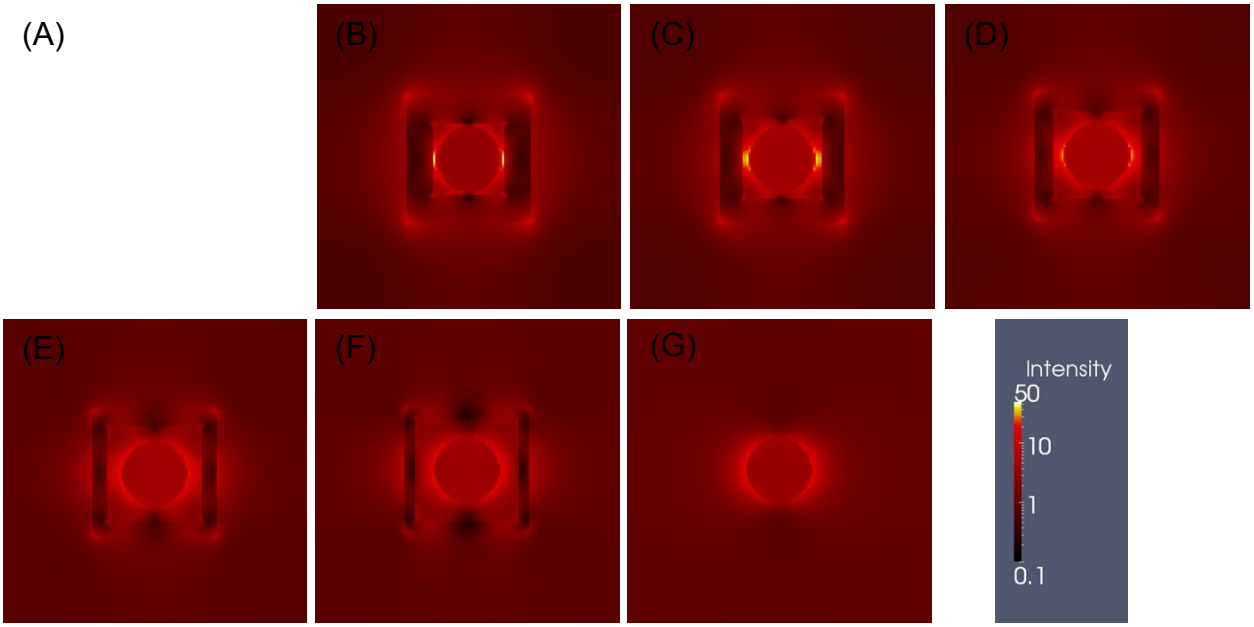

Figure S4. FDTD simulations showing the electric field distribution of Au@Ag nanocube and Au nanorattles of different gaps for electric field polarized along [100] using 514 nm excitation wavelength. (A-G) correspond to electric field distribution of Au@Ag nanocubes and Au nanorattles with a gap of 2, 4, 6, 8, 10 nm and Au core only, respectively.

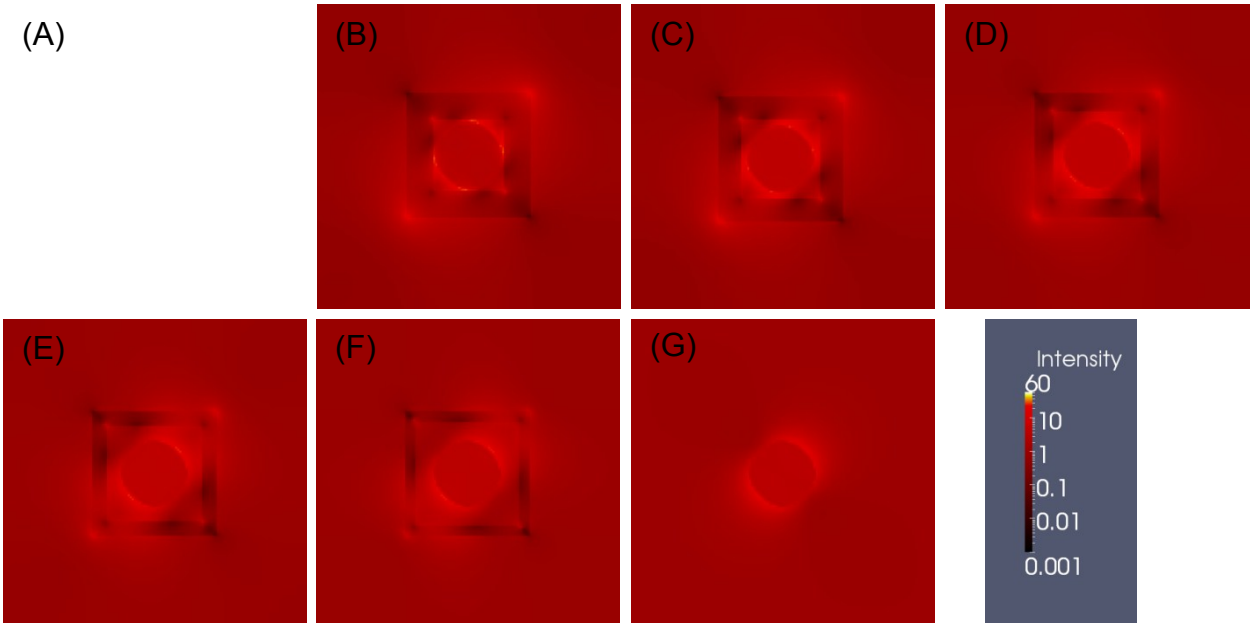

Figure S5. FDTD simulations showing the electric field distribution of Au@Ag nanocube and Au nanorattles of different gaps for electric field polarized along [110] using 514 nm excitation wavelength. (A-G) correspond to electric field distribution of Au@Ag nanocubes and Au nanorattles with a gap of 2, 4, 6, 8, 10 nm and Au core only, respectively.

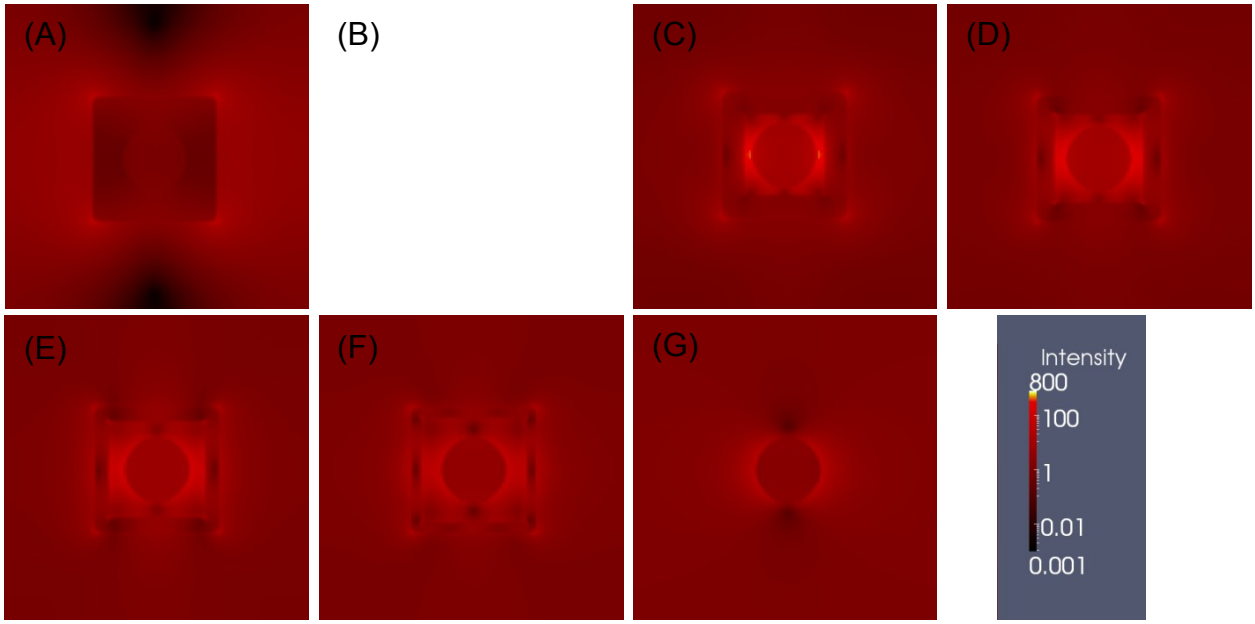

Figure S6. FDTD simulations showing the electric field distribution of Au@Ag nanocube and Au nanorattles of different gaps for electric field polarized along [100] using 553 nm excitation wavelength. (A-G) correspond to electric field distribution of Au@Ag nanocubes and Au nanorattles with a gap of 2, 4, 6, 8, 10 nm and Au core only, respectively.

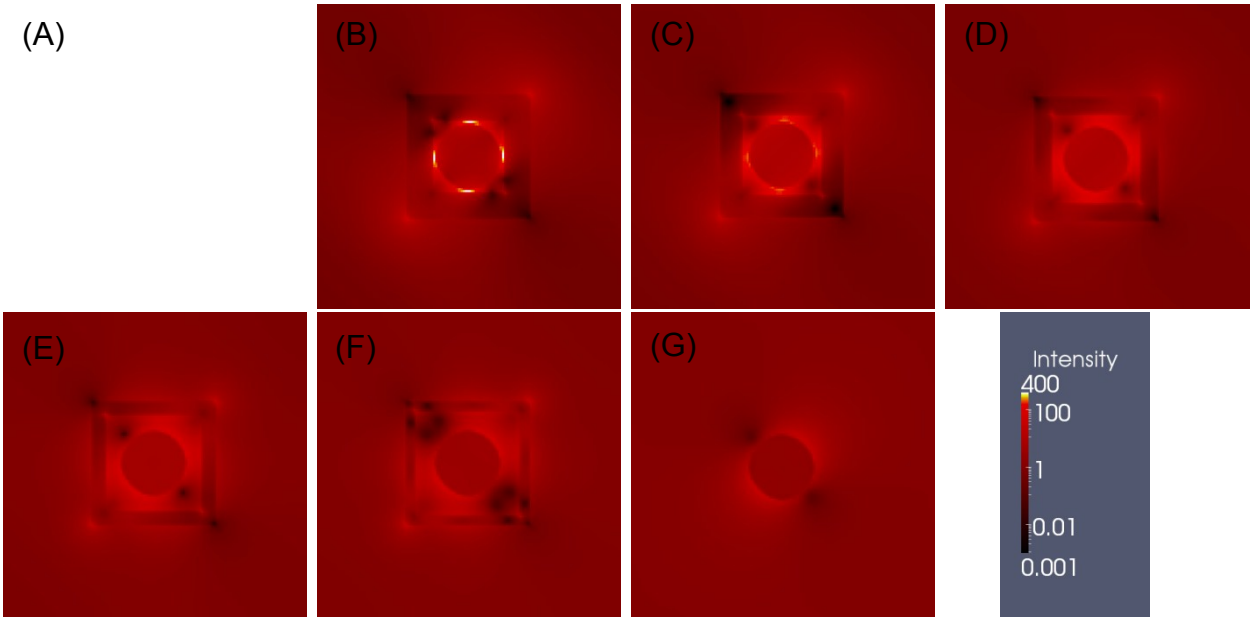

Figure S7. FDTD simulations showing the electric field distribution of Au@Ag nanocube and Au nanorattles of different gaps for electric field polarized along [110] using 553 nm excitation wavelength. (A-G) correspond to electric field distribution of Au@Ag nanocubes and Au nanorattles with a gap of 2, 4, 6, 8, 10 nm and Au core only, respectively.

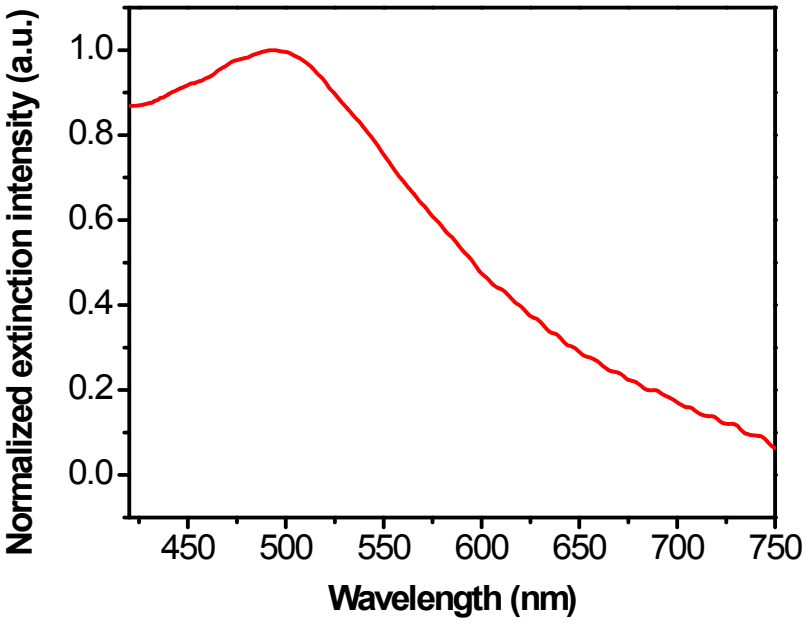

Figure S8. (A) Normalized vis-NIR extinction spectrum obtained from filter paper substrate adsorbed with 20-AuNRT.

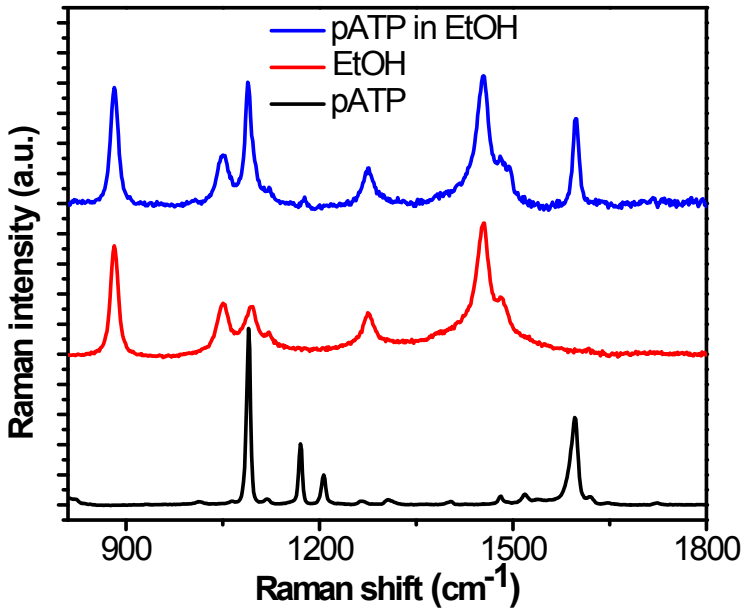

Figure S9. Raman spectra collected from bulk-pATP, ethanol and pATP in ethanol.

SERS Enhancement factor (EF):

The SERS enhancement factor (EF) of each Au nanorattle was calculated by using the following equation[1,2,3]:

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{bulk}/N_{bulk}}$$

Where I_{SERS} and I_{bulk} are intensities of the same band for the SERS and bulk spectra, N_{SERS} is the number of the 2-napthalnethiol (2-NT) bound to the surface of Au nanorattles and N_{bulk} is the number of the 2-NT in the excitation volume.

For 20-AuNRT, I_{SERS} =~29000 counts and I_{bulk}=~125 counts. Raman spectrum of 2-NT in bulk was collected using 20x microscopy objective (with a numerical aperture (NA) =0.4). The approximate laser spot size of 20X objective can be obtained using the following expression:

$$\omega_0 = 4\lambda/\pi NA$$

Where ω_0 is the minimum waist diameter for a laser beam of a wavelength λ focused by an objective with a numerical aperture NA. So for 20x objective,

$$\omega_0 = \frac{(4)(0.514)}{\pi(0.4)} = 1.64\ \mu m \quad z_0 = \frac{2\pi{\omega_0}^2}{\lambda} = \frac{2\pi(1.64)^2}{0.514} = 32.9\ \mu m$$

So, the focal volume $(\tau) = (\frac{\pi}{2})^{1.5}{\omega_0}^2 z_0 = (\frac{\pi}{2})^{1.5} \times 1.64^2 \times 32.9 = 174.2\ \mu m^3$

Density of the 2-NT is $1.55\ g/cm^3$, molecular mass of 2-NT is 160.24 (g/mol)

$$N_{bulk} = \frac{(1.55 g/cm^3)(174.2 \mu m^3)}{160.24} = 1.69 \times 10^{-12}\ mol$$

The volume of individual 20-AuNRT with edge length of 59 nm is estimated to be $(59-24)^3\ nm^3$

$$N_{SERS} = \frac{(1.55 g/cm^3)(59-24)^3 nm^3}{160.24} = 4.15 \times 10^{-19}\ mol$$

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{bulk}/N_{bulk}} = \frac{29000/4.15 \times 10^{-19}}{125/1.69 \times 10^{-12}} = 9.45 \times 10^8$$

So the EF for 40-AuNRT, 60-AuNRT, 80-AuNRT, and 100-AuNRT is

2.83×10^8, 5.27×10^7, 4.04×10^6, 6.32×10^5.

1. P. L. Stiles, J. A. Dieringer, N. C. Shah and R. P. Van Duyne, *Annual Review of Analytical Chemistry*, 2008, **1**, 601-626.
2. T. Itoh, M. Iga, H. Tamaru, K.-i. Yoshida, V. Biju and M. Ishikawa, *J. Chem. Phys.*, 2012, **136**, 024703.
3. L. Tian, N. Gandra and S. Singamaneni, *ACS Nano*, 2013, **7**, 4252-4260.