Supporting Information: Plasmon-Coupled Resonance Energy Transfer II: Exploring the Peaks and Dips in the Electromagnetic Coupling Factor

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Derivation of quasi-static expression of the total electric field experienced by the acceptor

To calculate the coupling factor between the donor and the acceptor, we need the total electric field due to the donor at the position of the acceptor. When a nanoparticle is present, the donor will induce a dipole at the nanoparticle center that in turn generates a response dipole field.[1] Therefore, the total electric field experienced by the acceptor is the superposition of the donor electric field in vacuum and the induced dipole field in vacuum. We thus need to obtain several quantities, namely the vacuum solution of electric field due to the donor at the position of the acceptor, the vacuum field due to the donor at the position of the nanoparticle (treating it as a point), and the vacuum field due to the induced nanoparticle dipole at the position of the acceptor. We will start from the general expression of electric field due to an oscillating dipole, then use appropriate assumptions and approximations, such as the quasi-static approximation.

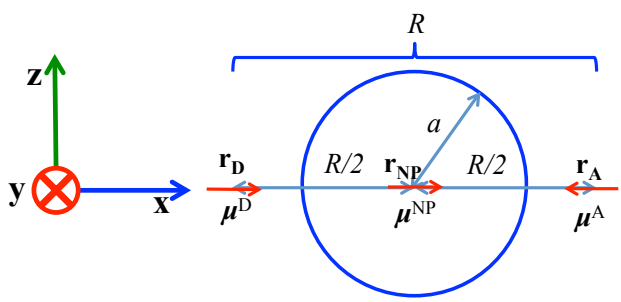

Figure S1: Scheme showing the variables in the derivation for the quasi-static expression.

Fig. S1 shows the related variables for configurations of the donor, the acceptor, and the nanoparticle. In vacuum, a donor dipole moment ($\boldsymbol{\mu}^{\mathrm{D}} = \mu^{\mathrm{D}}\hat{\mathbf{x}}$) is located at position $\mathbf{r_D}$, while the acceptor ($\boldsymbol{\mu}^{\mathrm{A}} = -\mu^{\mathrm{A}}\hat{\mathbf{x}}$) is separated from the donor by the distance $R_{DA} = |\mathbf{r_A} - \mathbf{r_D}|$. A nanoparticle at position $\mathbf{r_{NP}}$ with radius a is centered at the midpoint of the donor and the acceptor, i.e. $|\mathbf{r_{NP}} - \mathbf{r_D}| = |\mathbf{r_{NP}} - \mathbf{r_A}| = R_{DA}/2$. The exact solution of the electric field at a point $\mathbf{r}'$ in vacuum (without the nanoparticle) due to an oscillating point dipole $\mathbf{p}$ from a

distance of $R'(\mathbf{r}', \mathbf{r_p}) = |\mathbf{R}'(\mathbf{r}', \mathbf{r_p})| = |\mathbf{r}' - \mathbf{r_p}|$ is:[2]

$$\mathbf{E}^{\mathbf{p}}_{exact}(\mathbf{r}') = k^3 e^{ikR'} \left\{ (\mathbf{n} \times \mathbf{p}) \times \mathbf{n} \frac{1}{kR'} + [3\mathbf{n}(\mathbf{n} \cdot \mathbf{p}) - \mathbf{p}] \left[\frac{1}{(kR')^3} - \frac{i}{(kR')^2} \right] \right\} \tag{S1}$$

where $k = 2\pi/\lambda$ is the wave number (λ being the wavelength), and $\mathbf{n}$ is the directional unit vector of $\mathbf{R}'$, i.e. $\mathbf{n}(\mathbf{r}', \mathbf{r_p}) = \mathbf{R}'(\mathbf{r}', \mathbf{r_p})/R'(\mathbf{r}', \mathbf{r_p})$. For the configuration in Fig. S1, both $\mathbf{n}(\mathbf{r_{NP}}, \mathbf{r_D})$ and $\mathbf{n}(\mathbf{r_A}, \mathbf{r_D})$ are the vector (1, 0, 0), i.e. $\mathbf{n}(\mathbf{r_{NP}}, \mathbf{r_D}) = \mathbf{n}(\mathbf{r_A}, \mathbf{r_D}) = \hat{\mathbf{x}}$. Hence, the cross term in Eq. S1 is zero for both $\mathbf{E}^{\mathrm{D}}(\mathbf{r_{NP}})$ and $\mathbf{E}^{\mathrm{D}}(\mathbf{r_A})$. We then adopt the quasi-static approximation ($kR' << 1$), which leads to the two expressions: $e^{ikR'} \approx 1$ and $1/(kR')^3 >> 1/(kR')^2$. Therefore, the quasi-static electric field at the center of the nanoparticle ($\mathbf{r_{NP}}$) due to the donor dipole is

$$\mathbf{E}^{\mathrm{D}}_{quasi}(\mathbf{r_{NP}}) = \frac{2\mu^{\mathrm{D}}}{(R_{DA}/2)^3} \hat{\mathbf{x}} \tag{S2}$$

which can induce a dipole moment at this position[3]

$$\boldsymbol{\mu}^{\mathrm{NP}} = \alpha \mathbf{E}^{\mathrm{D}}_{quasi}(\mathbf{r_{NP}}) = \frac{16\alpha\mu^{\mathrm{D}}}{R^3_{DA}} \hat{\mathbf{x}} \tag{S3a}$$

$$\alpha = g_d a^3 = \frac{\epsilon_{Ag} - 1}{\epsilon_{Ag} + 2} a^3 \tag{S3b}$$

with the nanoparticle radius (a) and the size-dependent spherical dipole polarizability (α). The variable ϵ_{Ag} is the complex, wavelength-dependent dielectric function of the nanoparticle, i.e. $\epsilon_{Ag}(\lambda) = \epsilon'_{Ag}(\lambda) + i\epsilon''_{Ag}(\lambda)$. At the position of the acceptor, the total electric field is the sum of the field from the donor dipole and the field from the induced dipole of the

nanoparticle:

$$\mathbf{E}_{quasi}^{total}(\mathbf{r_A}) = \mathbf{E}_{quasi}^{\mathrm{D,vac}}(\mathbf{r_A}) + \mathbf{E}_{quasi}^{\mathrm{NP,vac}}(\mathbf{r_A}) \tag{S4a}$$

$$\mathbf{E}_{quasi}^{\mathrm{D,vac}}(\mathbf{r_A}) = \frac{2\mu^{\mathrm{D}}}{R_{DA}^3}\hat{\mathbf{x}} \tag{S4b}$$

$$\mathbf{E}_{quasi}^{\mathrm{NP,vac}}(\mathbf{r_A}) = \frac{2\mu^{\mathrm{NP}}}{(R_{DA}/2)^3}\hat{\mathbf{x}} = \frac{256 g_d a^3 \mu^{\mathrm{D}}}{R_{DA}^6}\hat{\mathbf{x}}. \tag{S4c}$$

Rearranging the terms arrives at the dipole-resonance quasi-static expression in the main text:

$$\mathbf{E}_{quasi}^{total}(\mathbf{r_A}) = \mathbf{E}_{quasi}^{\mathrm{D,vac}}(\mathbf{r_A}) \times \Gamma \tag{S5a}$$

$$= \frac{2\mu^{\mathrm{D}}}{R_{DA}^3}\left(1 + \frac{128 g_d a^3}{R_{DA}^3}\right)\hat{\mathbf{x}}. \tag{S5b}$$

Additional figures

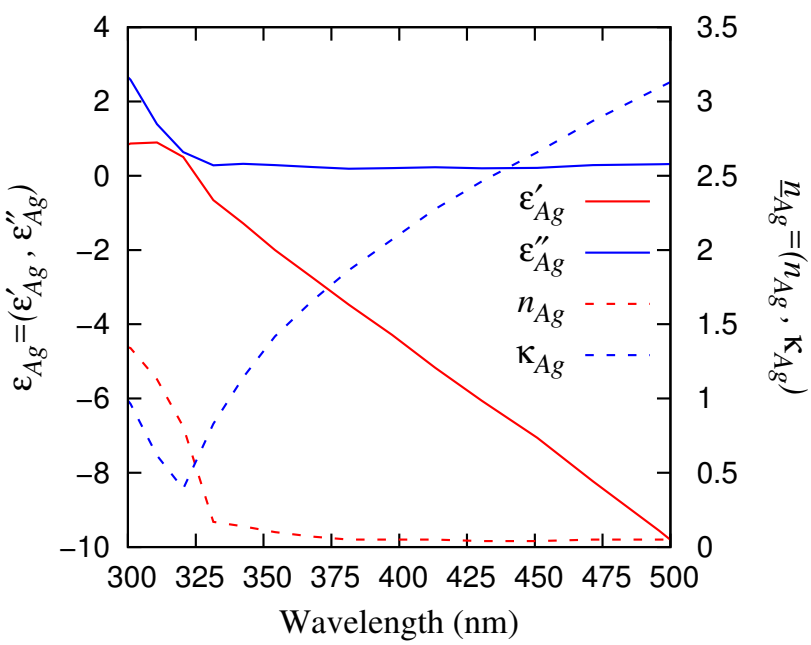

Figure S2: Experimental dielectric function (solid lines) and refractive index function (dashed lines) for silver as provided by Johnson and Christy.[4]

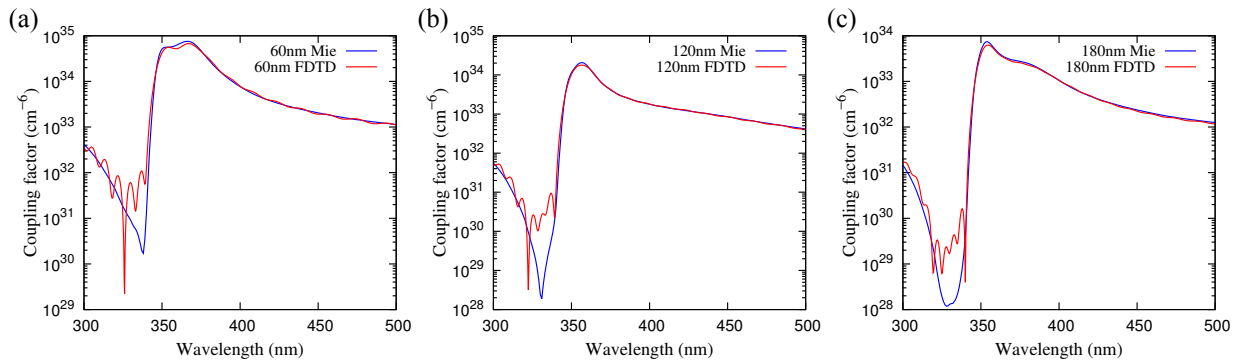

Figure S3: Comparison between coupling factors calculated using electric fields from Mie theory and from FDTD method. The results mostly agree with each other, with variations in small values of CF using FDTD due to numerical noise.

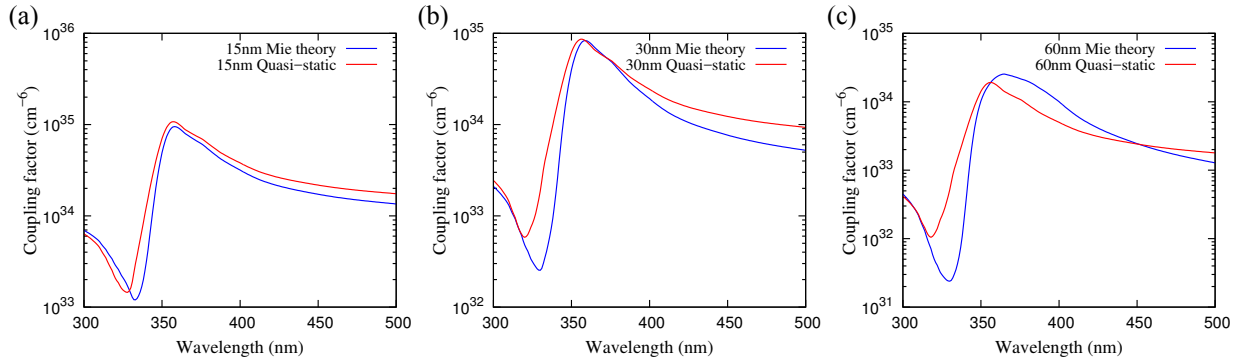

Figure S4: Comparison between coupling factors calculated using electric fields from Mie theory and from quasi-static expression, both using dielectric function provided by Palik.[5]

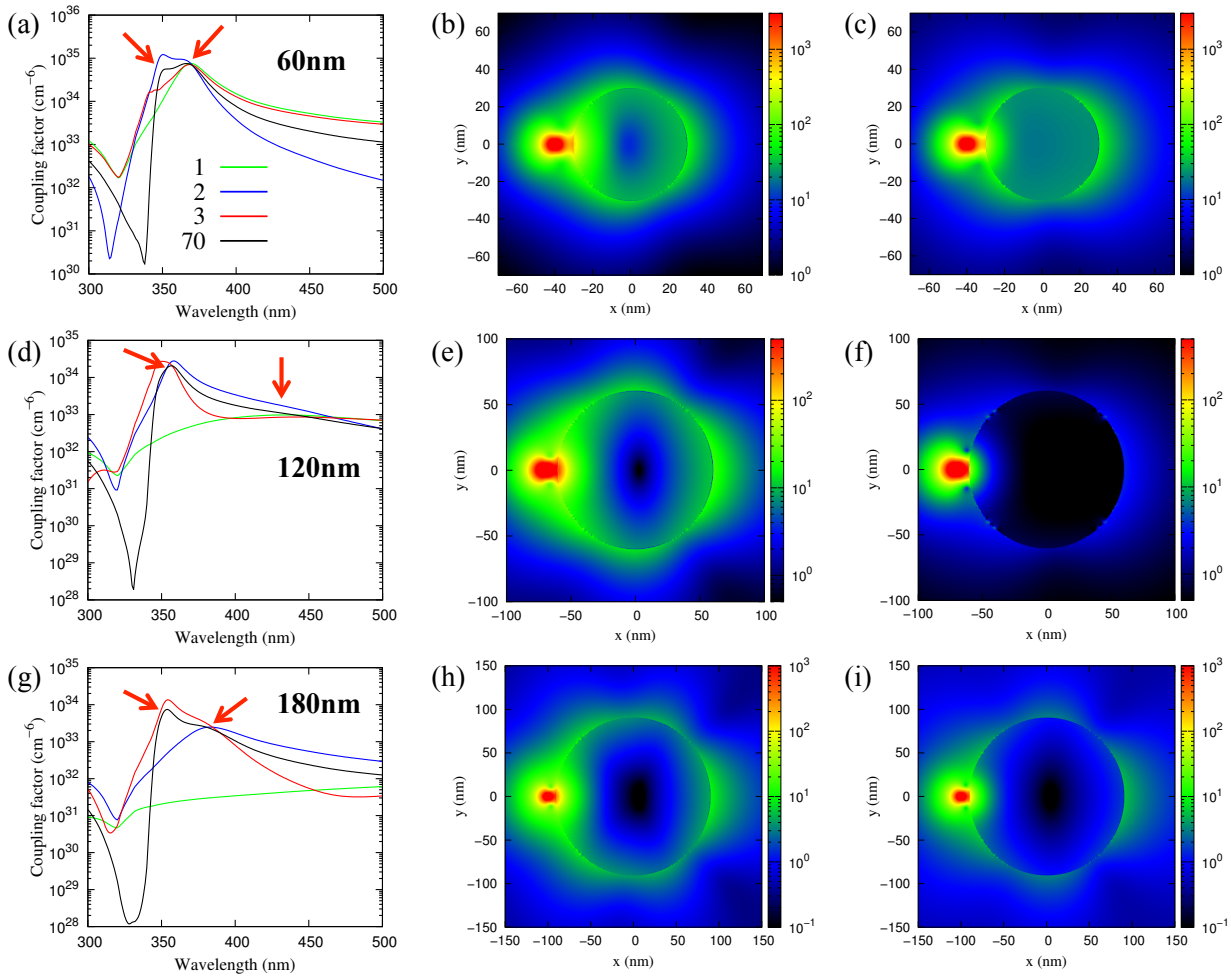

Figure S5: Coupling factor spectra (left column) and electric field magnitude maps (center and right columns) for nanoparticles with sizes of 60nm (a-c), 120nm (d-f), and 180nm (g-i) in diameter. The center column plots correspond to the higher energy peaks in their respective CF spectra (b and e for quadrupole, h for octupole), while the right column plots correspond to the lower energy peaks (c and f for dipole, i for quadrupole). The CF spectra are from Mie theory, while the field magnitude maps are from FDTD calculations.

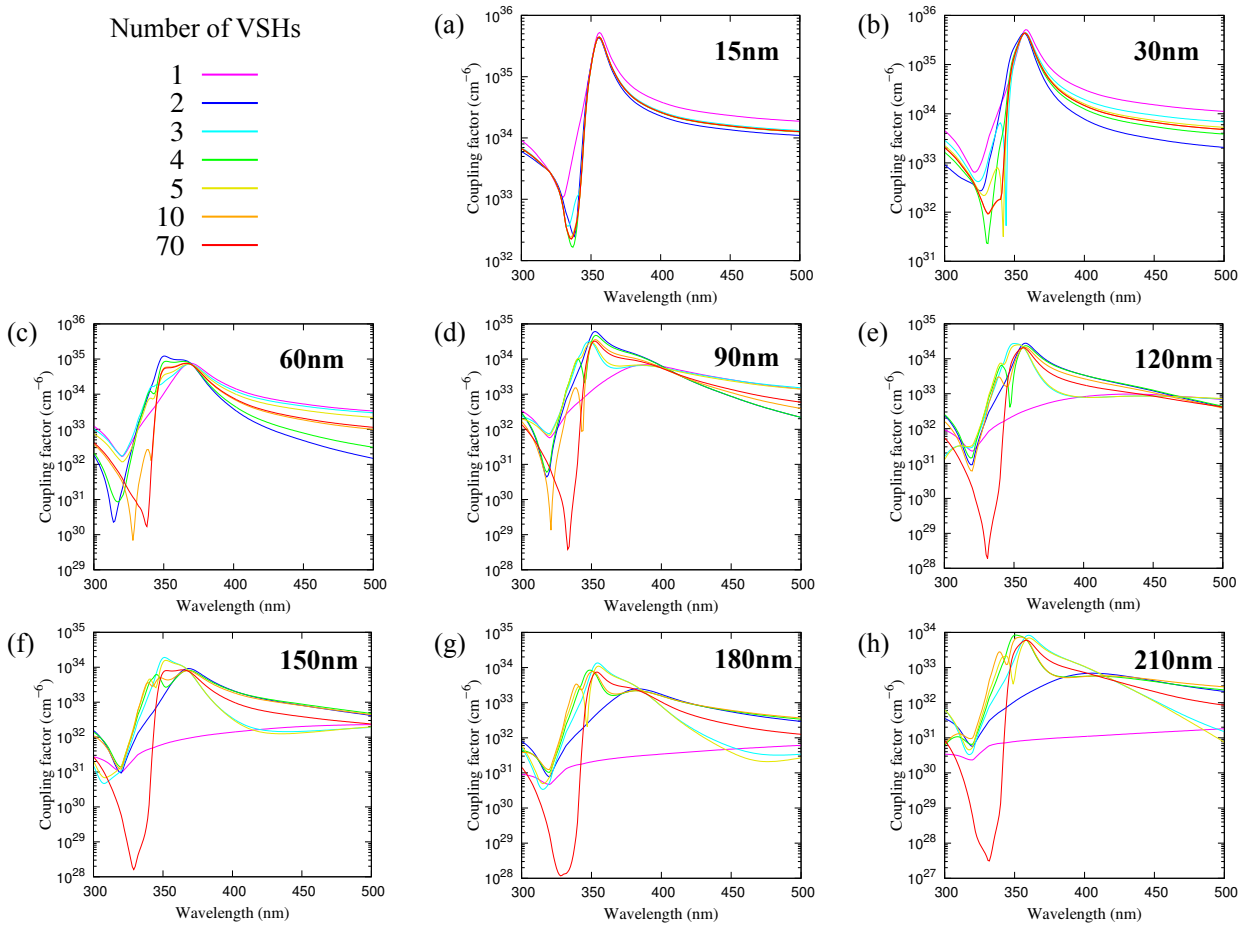

Figure S6: VSH decomposition of coupling factor spectra for nanoparticles with different sizes.

References

(1) Kerker, M.; Wang, D.-S.; Chew, H. Surface Enhanced Raman Scattering (SERS) by Molecules Adsorbed at Spherical Particles: Errata. *Appl. Opt.* **1980**, *19*, 4159–4174.

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(3) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *J. Phys. Chem. B* **2003**, *107*, 668–677.

(4) Johnson, P. B.; Christy, R. W. Optical Constants of the Noble Metals. *Phys. Rev. B* **1972**, *6*, 4370–4379.

(5) Palik, E. D.; Ghosh, G. *Handbook of Optical Constants of Solids*; San Diego: Academic Press., 1998.