Supporting Information

Two–step Decomposition of Plasmon Coupling in Plasmonic Oligomers

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1. Derivation of the total dipole moments of detuned plasmonic heterodimers

For a plasmonic heterodimer, the polarizability of each sphere at frequency $\omega = \omega_0 + \delta$ can be written as

$$\begin{aligned}\alpha_1 &= \frac{A(\omega_0+\Delta)^2}{(\omega_0+\Delta)^2 - (\omega_0+\delta)^2 - i\gamma_n(\omega_0+\delta)} \\ \alpha_2 &= \frac{B(\omega_0-\Delta)^2}{(\omega_0-\Delta)^2 - (\omega_0+\delta)^2 - i\gamma_n(\omega_0+\delta)}\end{aligned} \tag{S1}$$

where $A = a_1^3$, $B = a_2^3$. From Eq. 6 we have the total dipole moment

$$\mathbf{p}^{\text{Tot}} = \mathbf{p}_1 + \mathbf{p}_2 = \frac{\alpha_1 + \alpha_2 + 2\alpha_1\alpha_2 G}{1 - \alpha_1\alpha_2 G^2} \tag{S2}$$

By substituting Eq. S1 into Eq. S2, and neglecting second and higher order terms of Δ/ω_0, γ/ω_0 and δ/ω_0 , we can get with the first-order approximation of $\mathbf{p}^{\text{Tot}}$

$$\mathbf{p}^{\text{Tot}} = \frac{\omega_0\left[(A+B)(i\gamma+2\delta)+2(A-B)\Delta-2ABG\omega_0\right]}{(\gamma-2i\delta)^2+4\Delta^2+ABG^2\omega_0^2} \tag{S3}$$

Therefore, the the imaginary part of $\mathbf{p}^{\text{Tot}}$ is

$$\text{Im}[\mathbf{p}^{\text{Tot}}] = \frac{\gamma\omega_0\left[4A(\delta+\Delta)^2+4B(\delta-\Delta)^2-8ABG\omega_0\delta+(A+B)\left(\gamma^2+ABG^2\omega_0^2\right)\right]}{16\left(\delta^2-\Delta^2\right)^2+8\gamma^2\left(\delta^2+\Delta^2\right)+ABG^2\omega_0^2\left(2\gamma^2-8\delta^2+8\Delta^2+ABG^2\omega_0^2\right)+\gamma^4} \tag{S4}$$

2. The effective radius for the plasmonic trimer

The coupled dipole equations for a plasmonic trimer can be written as

$$\begin{aligned}\mathbf{p}_1 = &\quad \alpha_1 + \alpha_1 \left[G_{21}\mathbf{p}_2 + G_{31}\mathbf{p}_3\right] \\ \mathbf{p}_2 = &\quad \alpha_2 + \alpha_2 \left[G_{12}\mathbf{p}_1 + G_{32}\mathbf{p}_3\right] \\ \mathbf{p}_3 = &\quad \alpha_3 + \alpha_3 \left[G_{13}\mathbf{p}_1 + G_{23}\mathbf{p}_2\right]\end{aligned} \tag{S5}$$

For the detuned plasmonic trimer as illustrated in Fig. 1b, if we ignore the coupling between the side particles, we have the following relations: $\alpha_1 = \alpha_3$, $G_{21} = G_{12} = G$, and $G_{31} = G_{13} = 0$. The solution for each dipole moment is consequently

$$\begin{aligned}\mathbf{p}_1 = \mathbf{p}_3 &= \frac{\alpha_1 + \alpha_1\alpha_2 G}{1 - 2\alpha_1\alpha_2 G^2} \\ \mathbf{p}_2 &= \frac{\alpha_2 + 2\alpha_1\alpha_2 G}{1 - 2\alpha_1\alpha_2 G^2}\end{aligned} \tag{S6}$$

and the total dipole moment is

$$\mathbf{p}^{\mathrm{Tot}}_{\mathrm{trimer}} = \frac{2\alpha_1 + \alpha_2 + 4\alpha_1\alpha_2 G}{1 - 2\alpha_1\alpha_2 G^2} \tag{S7}$$

If we substitute $\alpha'_1 = 2\alpha_1$ into Eq. S7, we can get

$$\mathbf{p}^{\mathrm{Tot}}_{\mathrm{trimer}} = \frac{\alpha'_1 + \alpha_2 + 2\alpha'_1\alpha_2 G}{1 - \alpha'_1\alpha_2 G^2} \tag{S8}$$

This is similar to the the total dipole moment of a plasmonic dimer (Eq. S2), since the polarizability α is proportional to the cube of radius, the effective radius of the two side particles is consequently

$$a'_1 = \sqrt[3]{2}a_1 \tag{S9}$$

3. Comparison of the optical cross sections calculated by CDA and GMM for silver pentamer

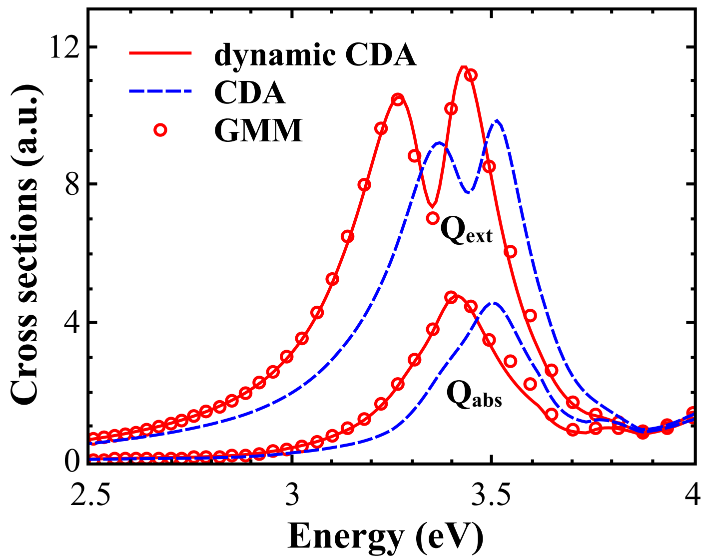

Figure S1: Optical cross sections for the silver pentamer as illustrated in Fig. 2 calculated by CDA and GMM method.

4. Dipolar fit for the silver pentamer

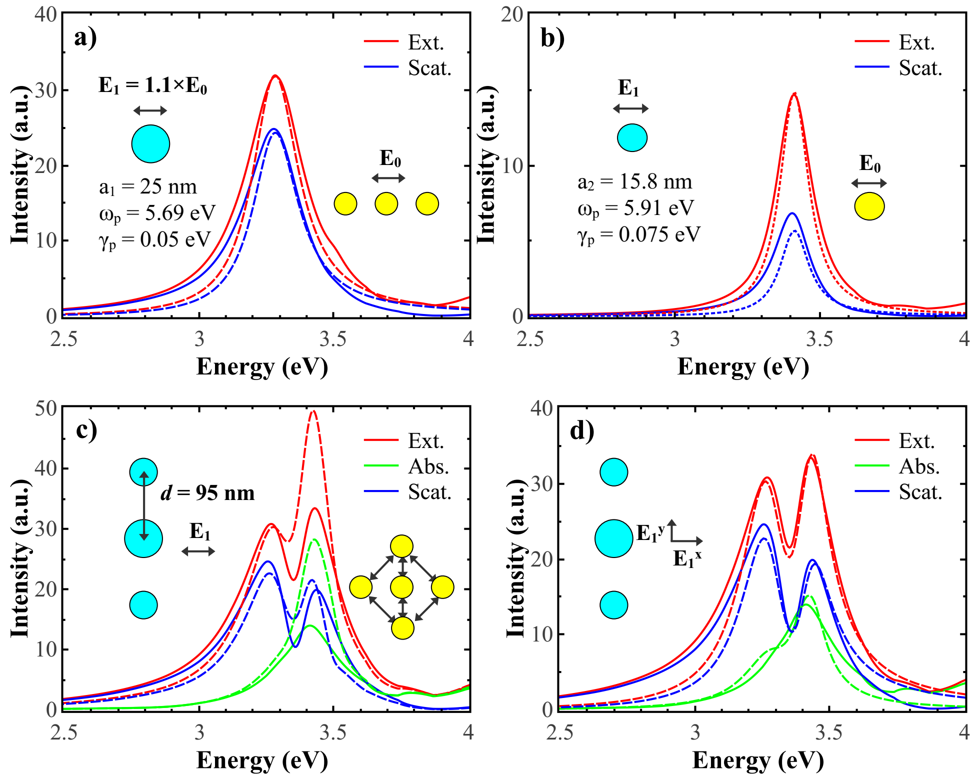

Figure S2: Dipolar fitting for the silver trimer (a) and individual particle (b), and calculated cross sections for the coupling dipolar scatters under transverse (c) and slant (d) excitations. The cross sections are normalized by πa_0^2 (a_0 = 25 nm), and the dashed lines are the fitted spectra.

We use the Drude model to fit the dielectric functions for the dipolar scatters, the parameters (plasma frequency ω_p, damping frequency γ_p, and radius a) are determined from the spectral feature (Fig. S2a,b). To satisfy the optical theorem, the polarizability α of the scatter is modified with the formalism[1] of

$$\alpha = \frac{1}{1 - i2k^3\alpha_{\text{static}}/3} \tag{S10}$$

Since cross sections of the trimer are relatively high compared with a single scatter, we increase the incident electric field ($E_1 = 1.1E_0$) in the fitting calculations. The individual silver particles also need to be fitted, because the cross sections in Fig. 2a are calculated by the dynamic CDA method.

The cross sections of the coupling dipolar scatters are calculated by the CDA method (not dynamic CDA), and the interparticle distance d = 95 nm is determined from the resonance frequencies of the pentamer (Fig. S2c). However, the absorption spectrum doesn't fit very well, most likely because the coupling between the vertical outer particles and the middle trimer is under a mixture of transverse and longitudinal excitations. Thus, we change the electric polarization angle to simulate the slant excitation, and get an excellent fit when $E_1^y : E_1^x = 0.66$ (Fig. S2d).

References

(1) Draine, B. T. The Discrete–dipole Approximation and its Application to Interstellar Graphite Grains. *Astrophys. J.* **1988**, *333*, 848–872.