Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information (ESI) for

Nanogap Effects on Near- and Far-Field Plasmonic Behaviors of Metallic Nanoparticle Dimers

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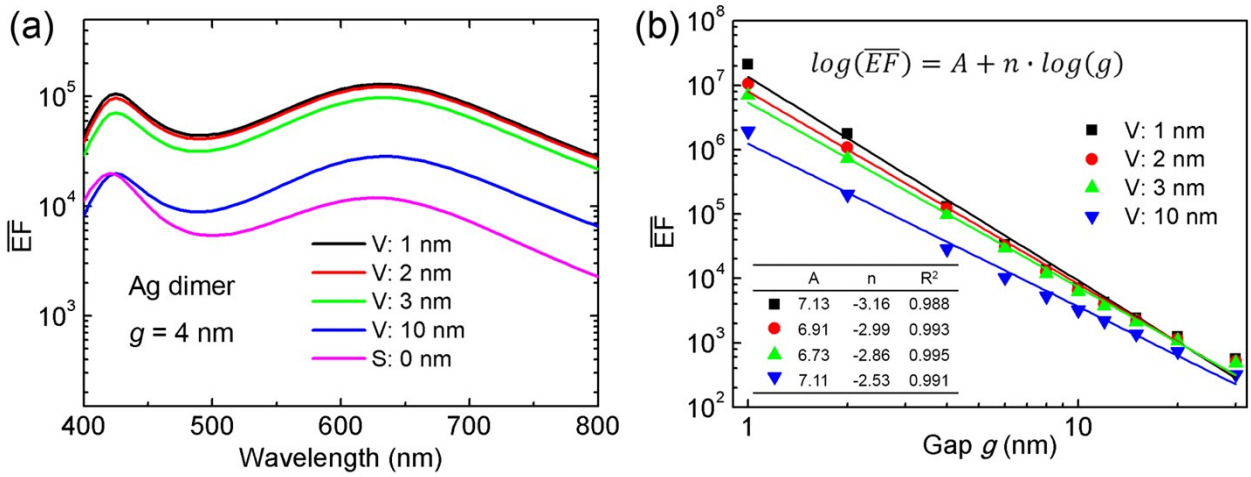

Fig. S1. (a) Calculated $\bar{E}F$ spectra for Ag nanosphere dimer (r = 60 nm, g = 4 nm, as an example) with different expressions of $\bar{E}F$ which are the average of the volume integral of $|E|^4/|E_{inc}|^4$ within 1 nm (black curve), 2 nm (red curve), 3 nm (green curve) and 10 nm (blue curve) above the metal surface, and the surface integral of $|E|^4/|E_{inc}|^4$ at the metal surface (magenta curve). Note that the curve shape and peak positions for different volume integral do not change while both exhibit changes for the surface integral. (b) Log-log plots of $\bar{E}F$ acquired from different volume integral as a function of the gap size g for dimers of Ag nanospheres (r = 60 nm). Fitting parameters A and n for the nearly power-law relationship $\bar{E}F = 10^A \cdot g^n$ are shown in the insert. The value of n increases from -3.16 to -2.53 as the distance above the metal surface for the volume integral increases from 1 to 10 nm.

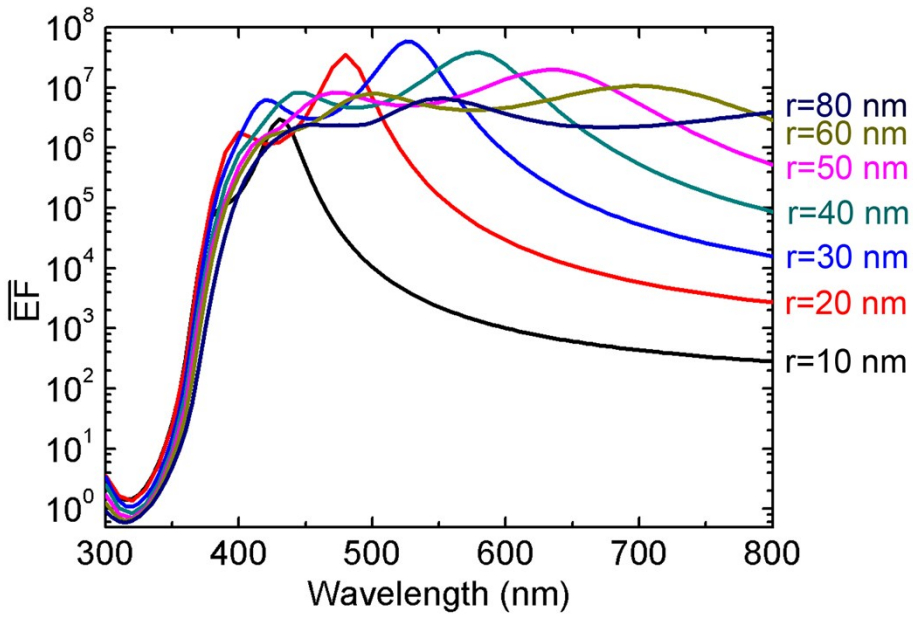

Fig. S2. Calculated near field $\bar{E}F$ spectra by fixing the gap size g = 1 nm and varying Ag nanosphere radius *r* from 10 to 80 nm. The near field enhancement becomes almost 'flat' in the visible range when *r* > 50 nm. As is known, for large individual plasmonic nanospheres (e.g. *r* > 50 nm), multipole resonances can be excited besides the fundamental dipole resonance. For the dimer structure, the continuous arising of bonding dipole resonances in longer wavelength regions and bonding multipole resonances in shorter wavelength regions can lead to the flat near field enhancement.

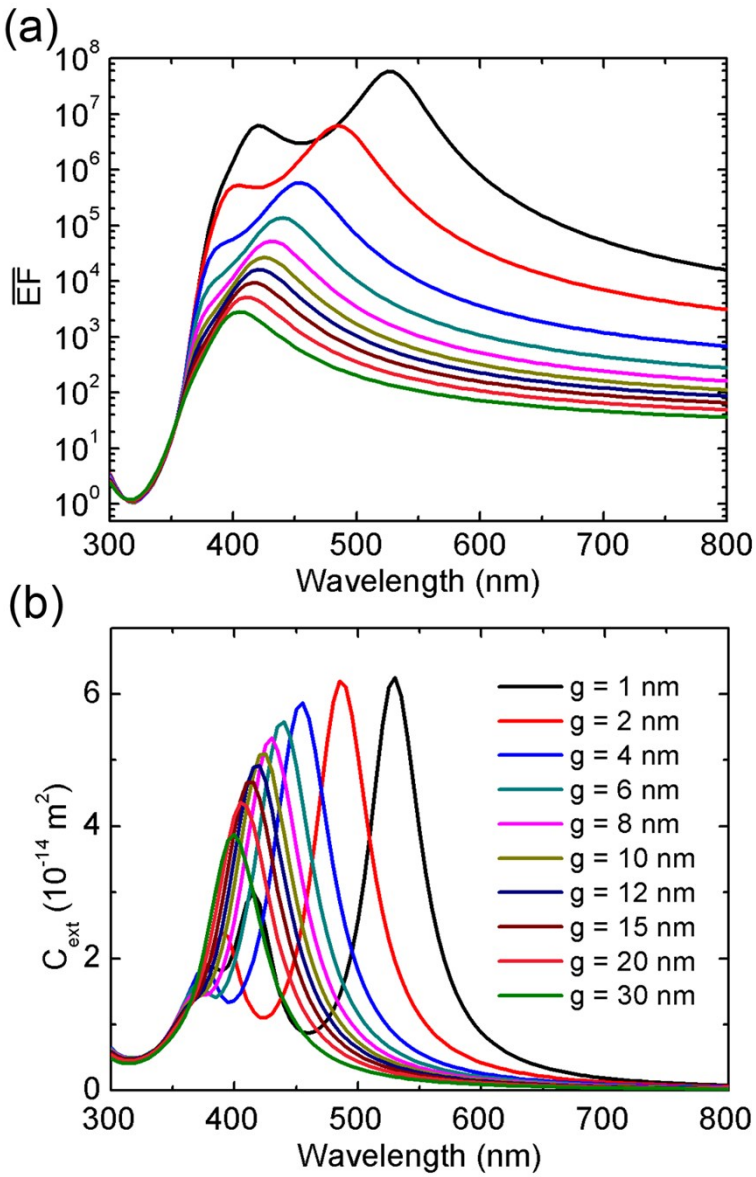

Fig. S3. FEM calculated near-field $\bar{EF}$ (a) and corresponding far-field extinction cross section C_{ext} (b) spectra with 5 nm wavelength spacing for Ag nanosphere (r = 30 nm) dimers. The gap size g varies from 1 to 30 nm.

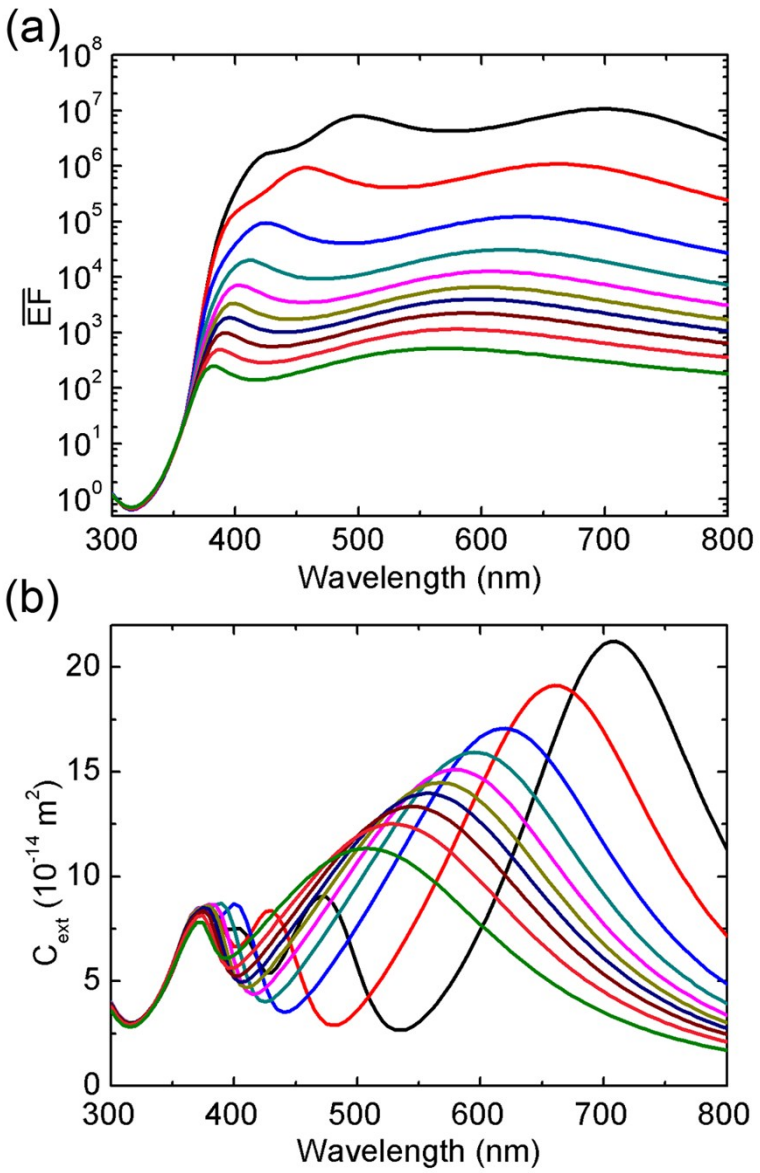

Fig. S4. $\overline{EF}$ and corresponding C_{ext} spectra with 5 nm wavelength spacing for Ag nanosphere (r = 60 nm) using the same legend as in Fig. S2.

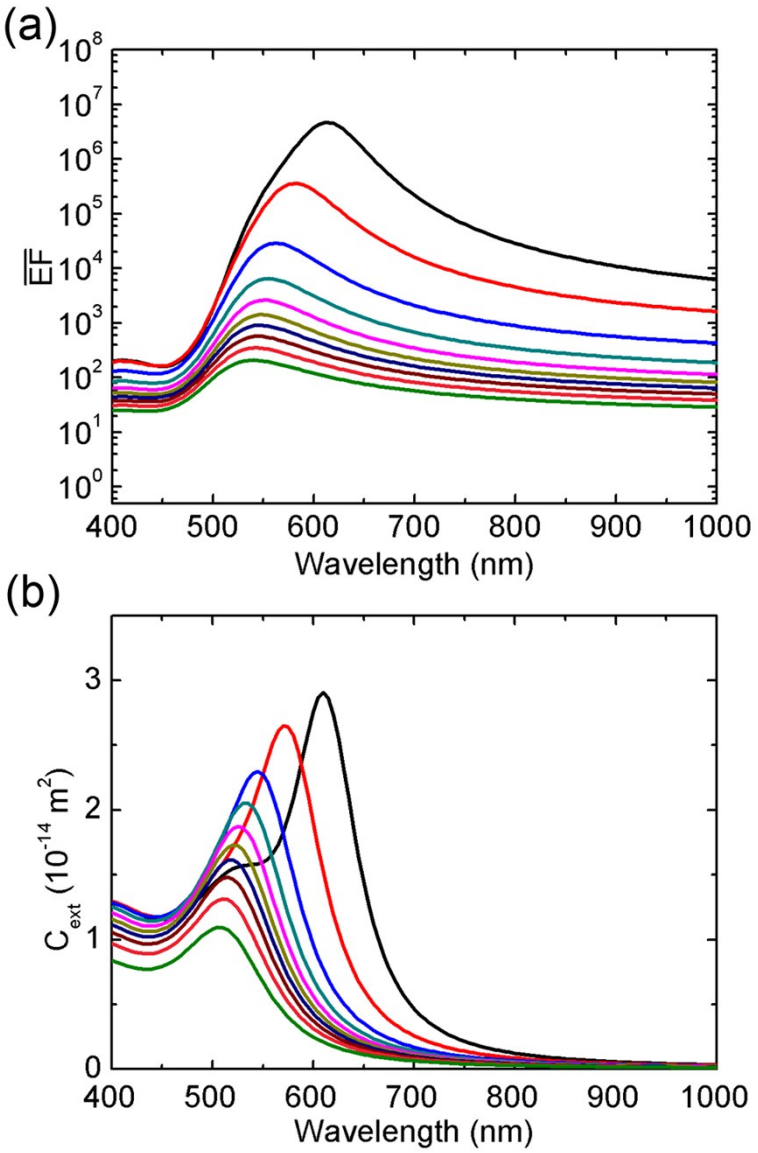

Fig. S5. $\bar{EF}$ and corresponding C_{ext} spectra with 5 nm wavelength spacing for Au nanosphere (r = 30 nm) using the same legend as in Fig. S2.

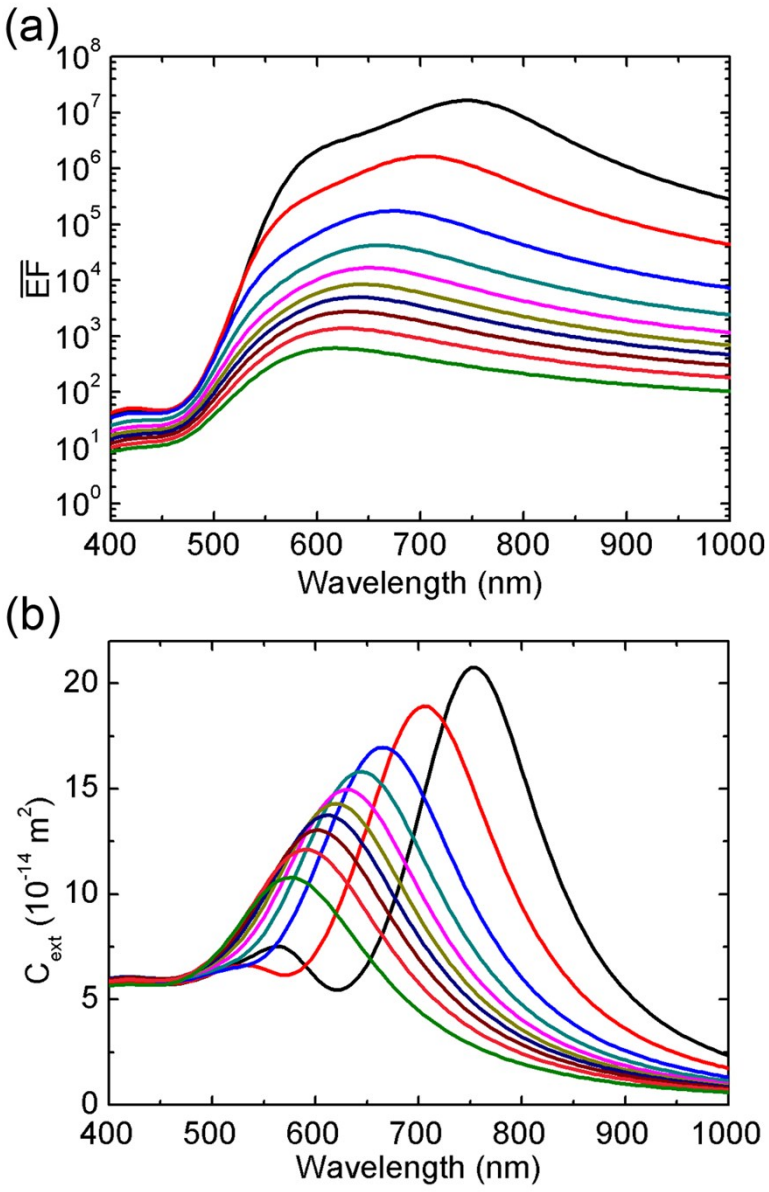

Fig. S6. $\bar{EF}$ and corresponding C_{ext} spectra with 5 nm wavelength spacing for Au nanosphere (r = 60 nm) using the same legend as in Fig. S2.

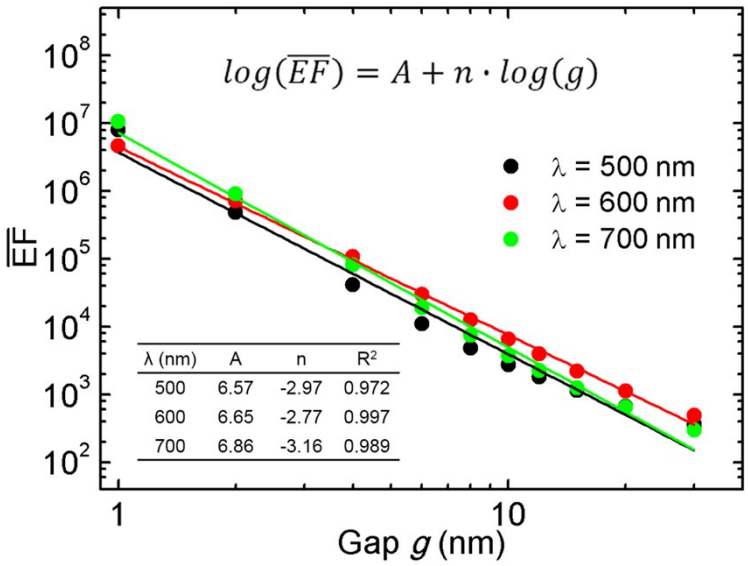

Fig. S7. Log-log plots of $\bar{EF}$ values at λ = 500, 600 and 700 nm as a function of the gap size *g* for *r* = 60 nm Ag nanosphere dimer. The slopes *n* are -2.97, -2.77 and -3.16 respectively.

Movie S1: Three dimensional surface charge distributions within one full oscillation for Fig. 2(e).