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

Supporting Information

Simulation Guided Design of Silver Nanostructures for Plasmon-Enhanced Fluorescence, Singlet Oxygen Generation and SERS Applications

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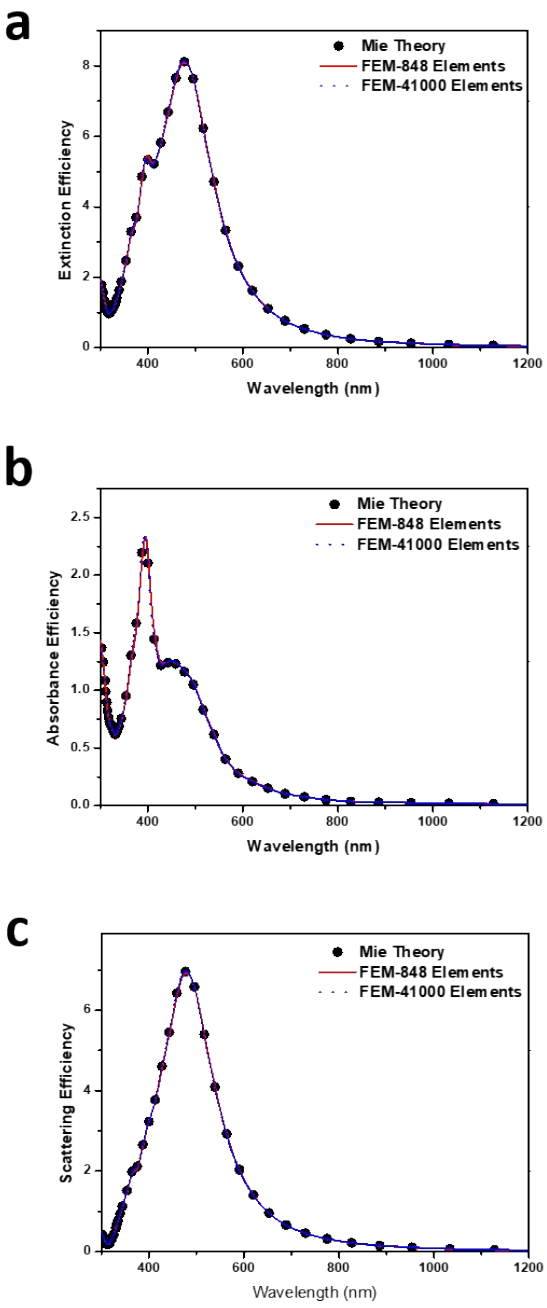


Figure S1. Model Verification: a) extinction efficiency b) absorption efficiency and c) scattering efficiency for analytical Mie theory vs. Finite Element Method for a 90-nm-diameter spherical Ag nanoparticle in water

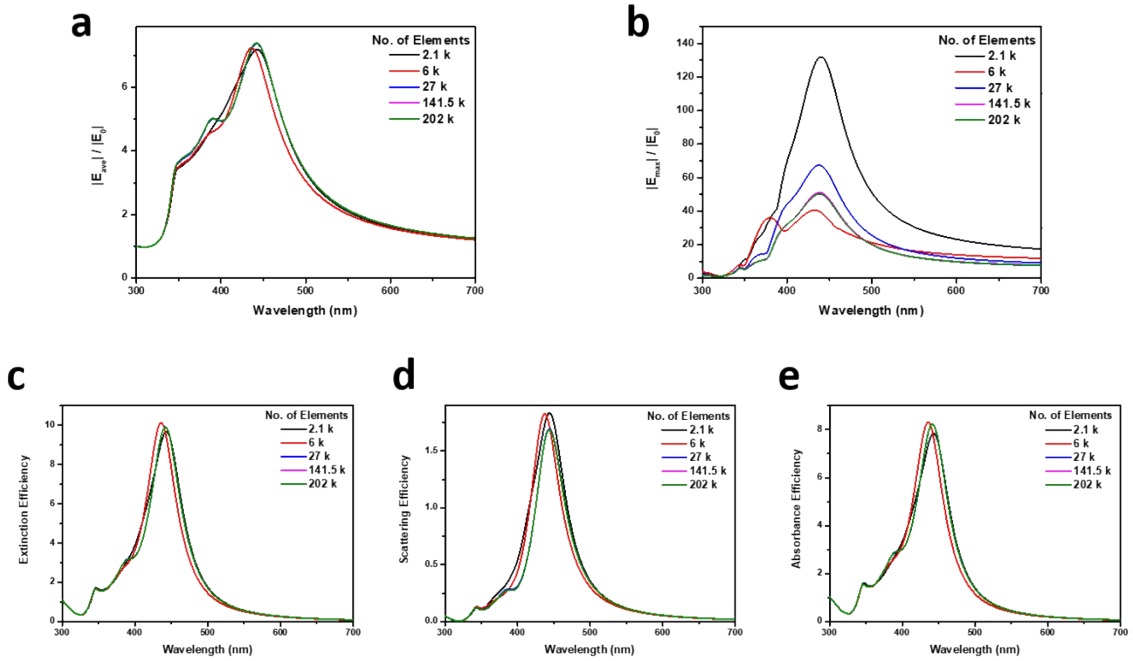


Figure S2. Mesh study for 30 nm Ag nanocube: a) surface average enhanced electric field ($|E_{ave}|/|E_0|$), b) maximum enhanced electric field ($|E_{max}|/|E_0|$) around the Ag nanocube as a function of incident light wavelength. Calculated c) extinction, d) scattering and e) absorbance efficiency spectra for 30 nm Ag nanocube. The *R_c/edge length* was 0.1 in all simulations.

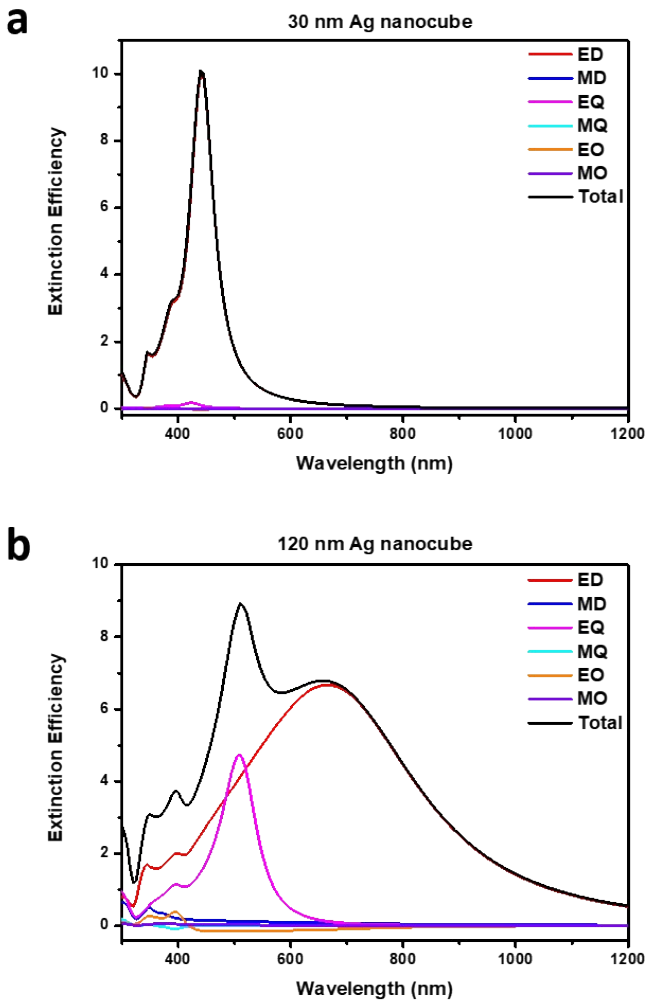


Figure S3. Multipole decomposition of extinction spectra for single (1-Ag) Ag nanocube in water as medium: a) 30 nm edge length, b) 120 nm edge length. R_c to *edge length ratio*=0.1 was used in all simulations.

SI-4-The effect of edge length on absorbance and scattering cross-sections

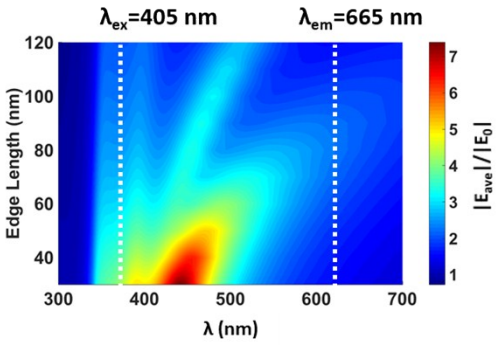
Similar to spheroidal particles, this phenomenon is due to the fact that the absorption is proportional to the third power of the edge length, whereas the scattering is proportional to the sixth power as expressed in *eq.1* and *eq.2*. Thus, as the diameter increases, absorption becomes less efficient, and scattering starts to dominate. For the quasistatic limit where $\lambda <$ (scatterer dimensions), the absorption and scattering cross-sections of a spheroid are given as[1]:

$$\sigma_{abs} = \frac{2\pi n_{water}}{\lambda} Im[\alpha] \qquad \textbf{eq. S1}$$

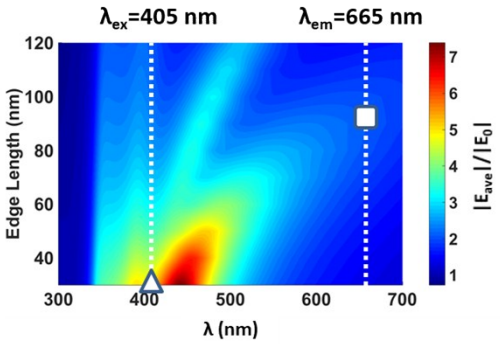
$$\sigma_{scat} = \frac{8\pi^3 n_{water}^{\ 4}}{3\lambda^4} |\alpha|^2 \qquad \textbf{eq. S2}$$

where n_{water} is refractive index of water and α is the dipolar polarizability of the spheroid that is proportional to particle volume, rendering the absorption and scattering cross-sections proportional to the third and sixth power of the edge length for a cube.[1, 2]

1)Draw a line at excitation and emission wavelengths of the fluorophore



2)Find the points with the highest enhanced electric field at each line



3)Find the corresponding sizes for each of the above points

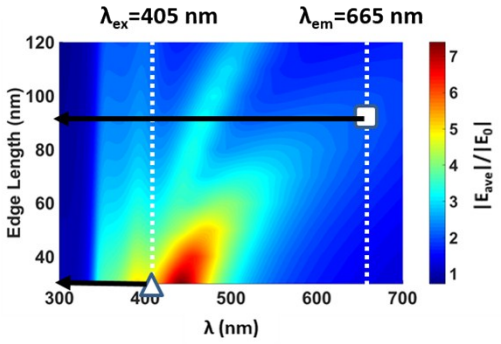


Figure S4. Schematic illustration on the procedure to find the best sizes of Ag nanocubes for MEF studies of a fluorophore with large stocks shift. The above excitation/emission wavelengths are corresponding to an red-emissive aggregation-induced emission dye as reported in the literature (Hu et al, *Chemical Science*, 2018, 9, 2756-2761)

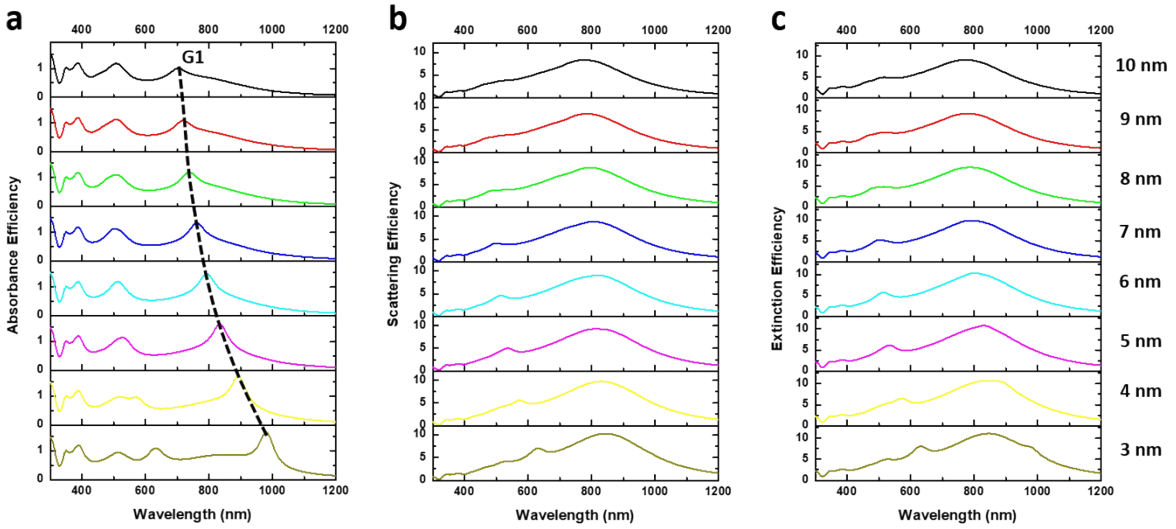


Figure S5. Effect of separation distance on a) absorbance spectra, b) scattering spectra, and c) extinction spectra of 90 nm Ag nanocube dimers in water. Curvature radius (R_c) to *edge length ratio*=0.1. The black-colored dashed line in the absorbance efficiency figure indicates the blue shift of gap surface plasmon resonance (G1, black dashed line) with an increase in the gap between the nanocubes as indicated next to each row.

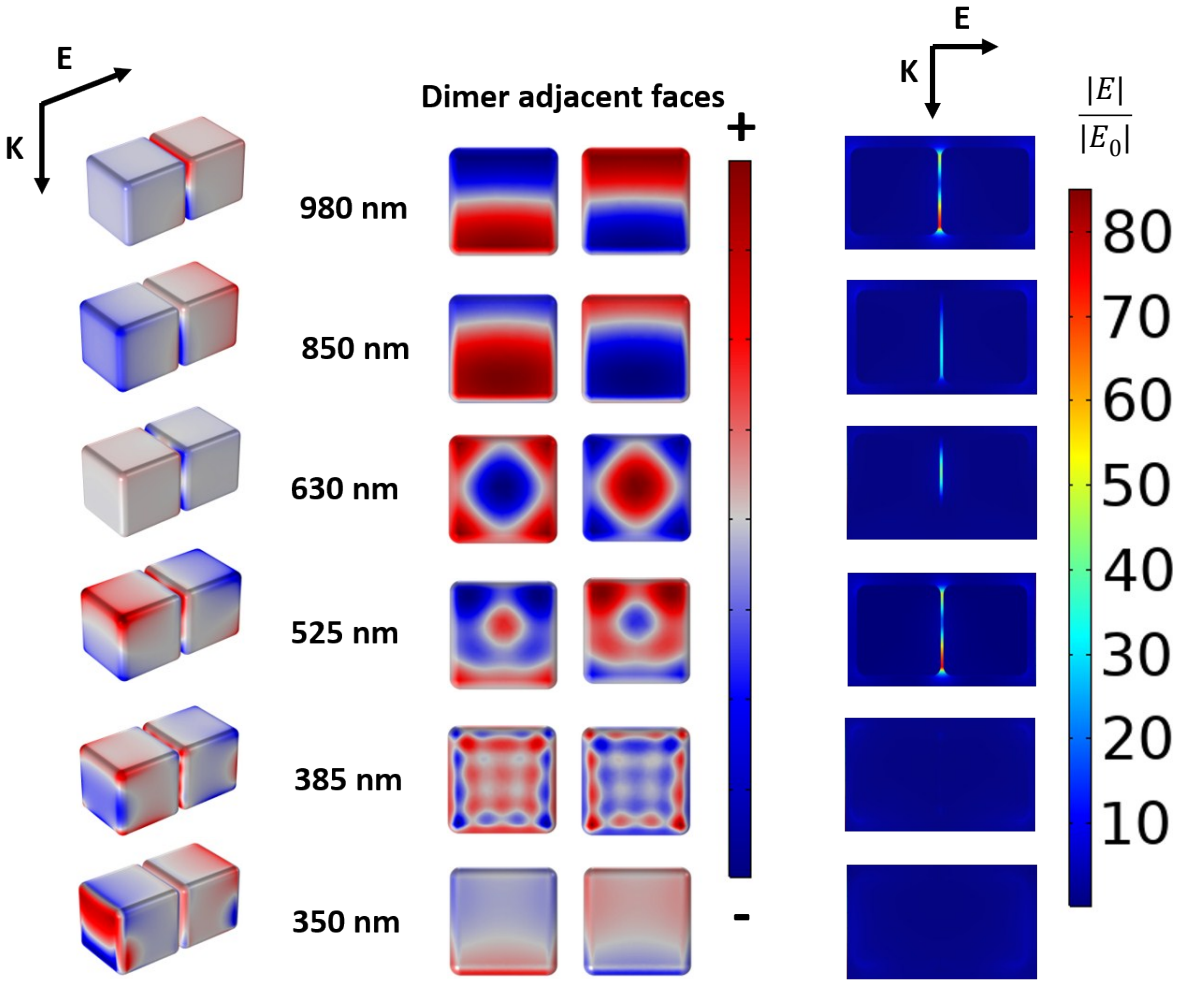


Figure S6. Surface charge distribution (left and middle columns) and enhanced electric field ($|\vec{E}|/|E_0|$) distribution for dimer (2-Ag) of 90 nm Ag nanocubes with gap of 3 nm under different excitation wavelength. Curvature radius (R_c) to *edge length ratio* is 0.1. The medium is water. The arrows for E and K indicate the direction of electric field polarization and incident light propagation, respectively

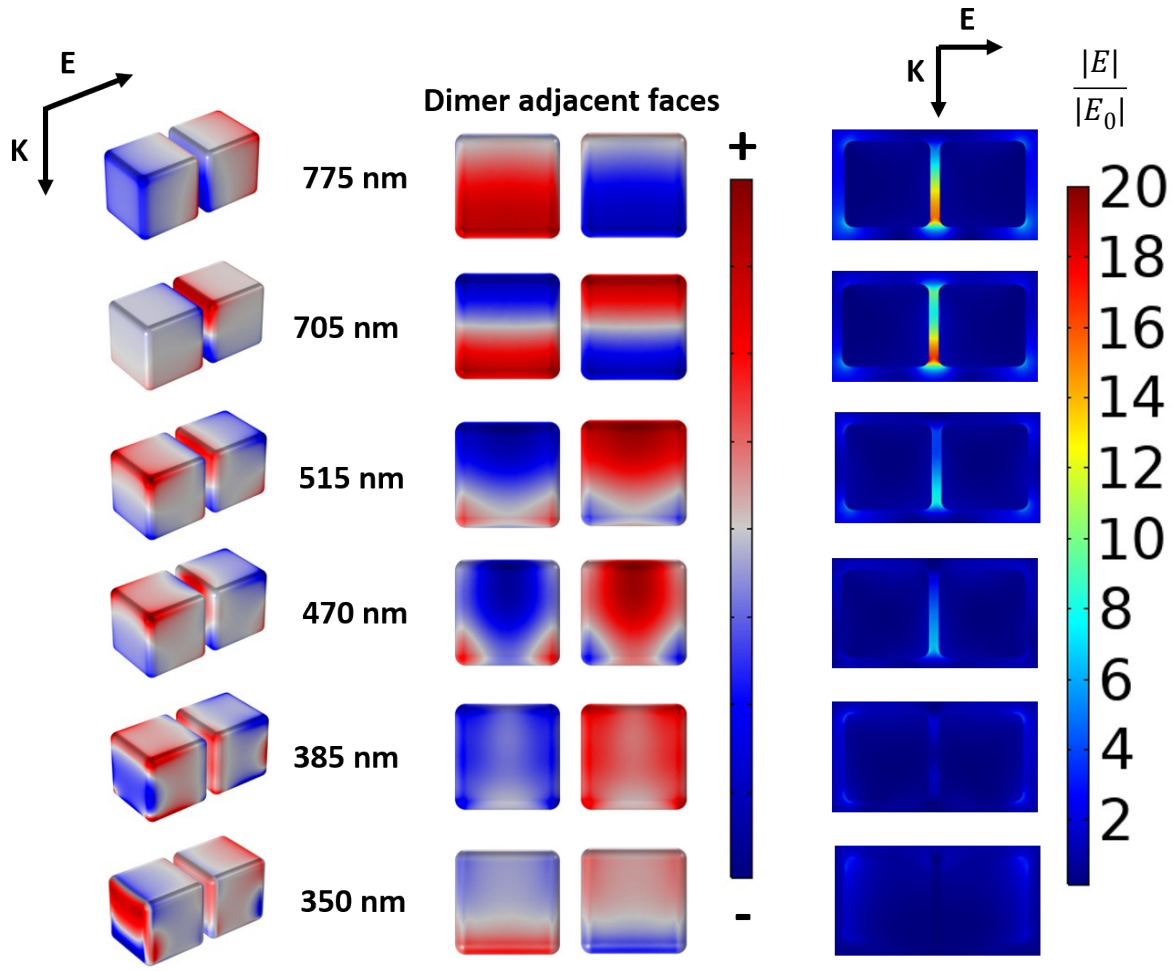


Figure S7. Surface charge distribution (left and middle columns) and enhanced electric field ($|\vec{E}|/|E_0|$) distribution for dimer (2-Ag) of 90 nm Ag nanocubes with a gap of 10 nm under different excitation wavelength. Curvature radius (R_c) to edge length *ratio* is 0.1. The medium is water.

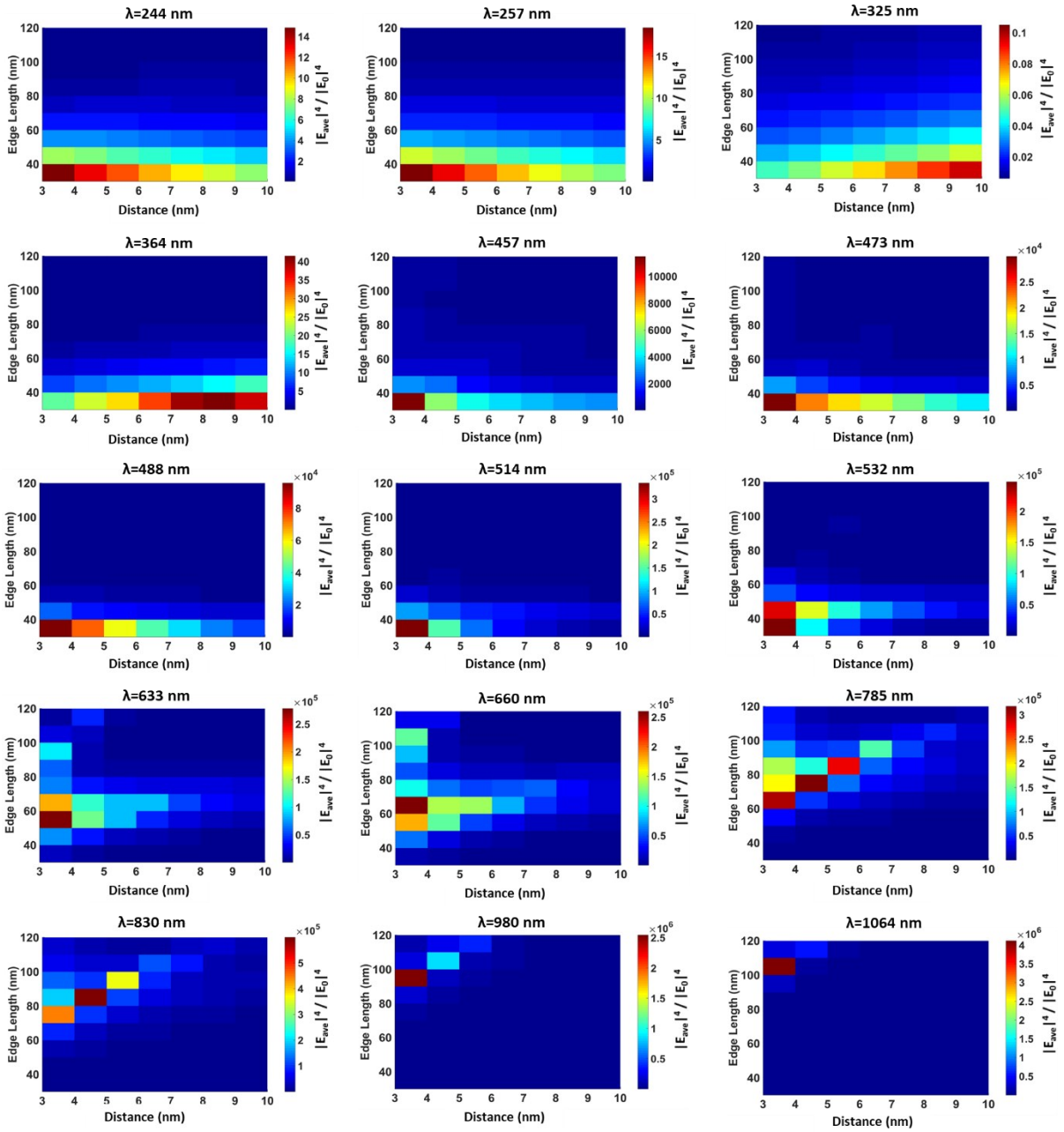


Figure S8. The fourth power of volumetric average enhanced electric field in the gap area between the face-to-face Ag nanocube dimers (2-Ag) with different edge lengths and gaps under different common Raman spectroscopy laser wavelengths (as indicated on the top of each figure)

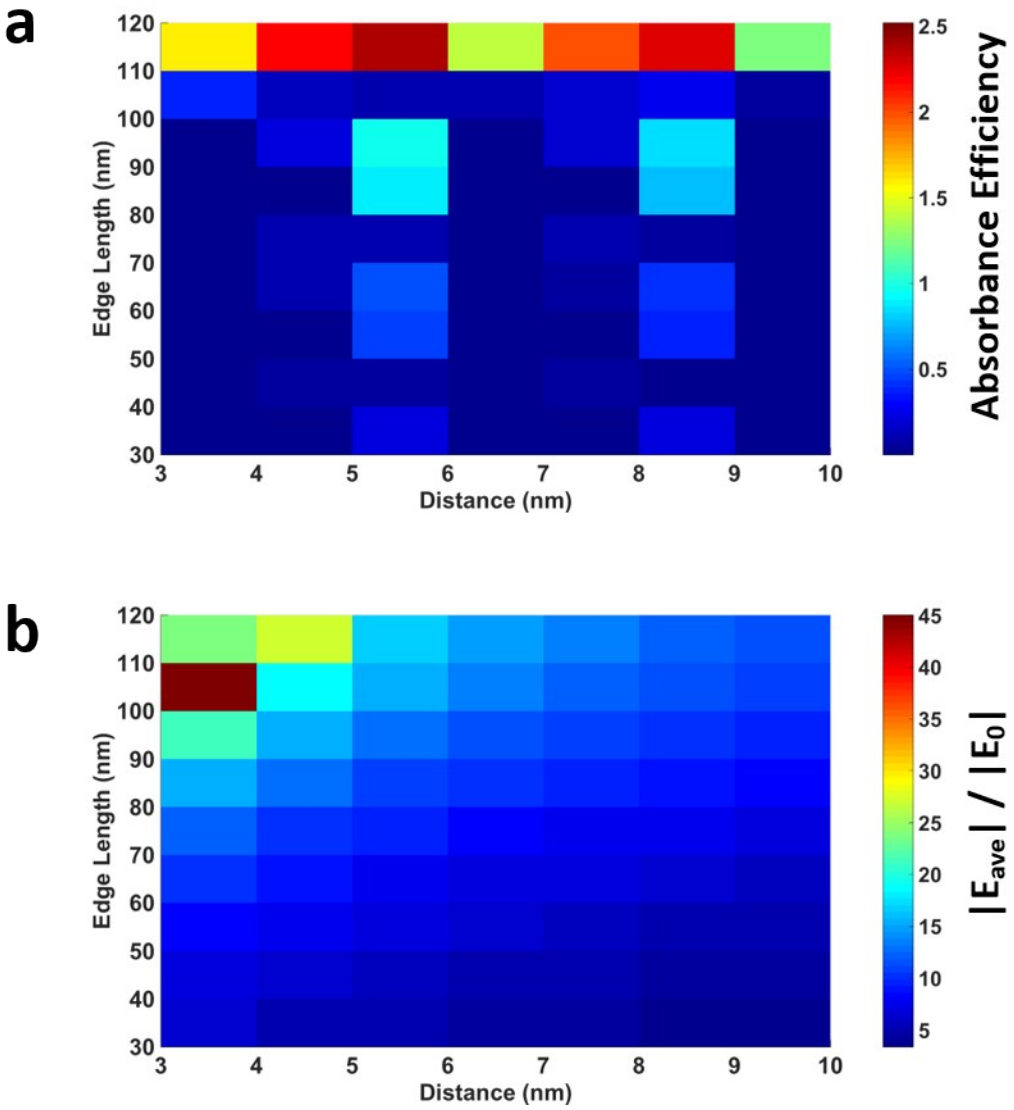


Figure S9. a) The absorbance efficiency and b) volumetric average enhanced electric field in the gap area of Ag nanocube dimers with different edge length and gap under 1064 nm incident light.

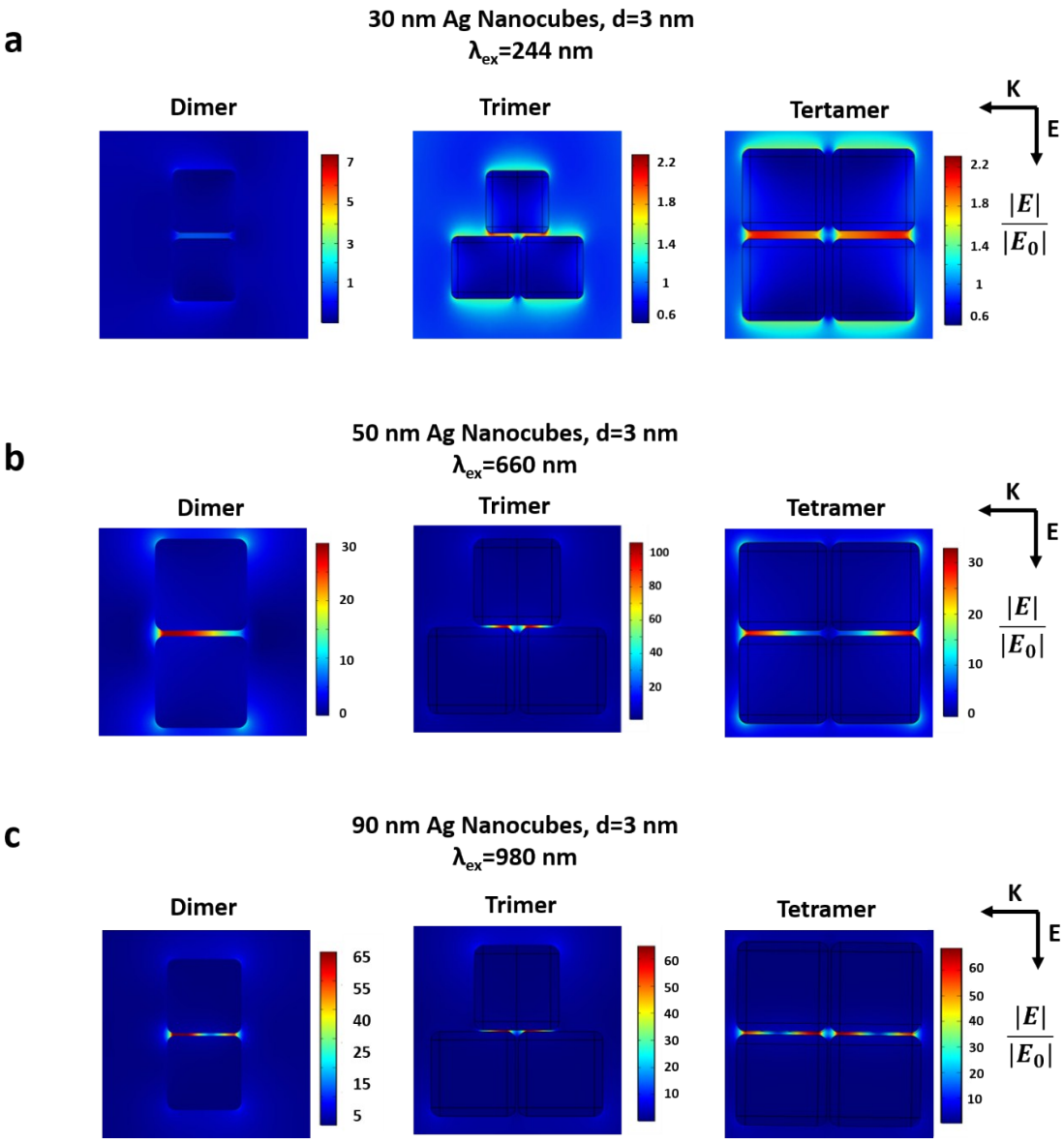


Figure S10. The enhanced electric field ($|E|/|E_0|$) in dimer, trimer, and tetramer Ag nanocubes with similar gap (*d*=3 nm) under different Raman spectroscopy wavelengths: a) 30 nm Ag nanocubes under 244 nm Raman laser wavelength, b) 50 nm Ag nanocubes under 660 nm Raman laser wavelength and, c) 90 nm Ag nanocubes under 980 nm Raman laser wavelength.