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Near-field mapping of three-dimensional surface charge poles for hybridized plasmon modes

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We describe a new computational approach to mapping three-dimensional (3D) surface charge poles and thus to determine complicated and hybridized plasmon modes in metallic nanostructures *via* finite element method (FEM) calculations. 3D surface charge distributions at the near-field resonance energies are calculated directly using Gauss' law. For a nanosphere dimer, we demonstrate that higher-order hybridized plasmon modes can be addressed clearly. As an improvement to conventional mapping approaches, this new approach provides a better understanding of comprehensive physical image of plasmonic systems necessary for fundamental studies and spectroscopy applications. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4934722>]

I. INTRODUCTION

Metallic nanoparticles can undergo light-driven collective oscillations of the conduction electrons known as localized surface plasmon resonances (LSPRs). By virtue of being small, such particles are able to guide and concentrate light at the sub-wavelength scale¹ and provide extremely large, localized enhancements of local electric fields.² These unique properties provide possibilities for applications of plasmonic nanoparticles in a wide variety of fields such as plasmonic waveguiding,³ surface-enhanced spectroscopies,^{4–7} chemical and biological sensing,^{8,9} as well as single molecule detection.^{10,11} Understanding and predicting the fundamental physics governing LSPRs are both necessary to realize and fully optimize potential devices. In particular, mapping the electric fields near plasmonic particles is of primary importance as they determine the enhancement factors and particle-molecule as well as particle-particle coupling. It was only recently fully appreciated that there exists a distinct deviation of spectral positions between the near- and far-field plasmon resonances.^{12–15} In order to achieve the highest local electric field enhancement, this spectral deviation is suggested to be taken into account, while it remains challenging to collect experimentally the entire near-field spectral and spatial characteristics.^{16–18} In addition, experimental mapping of surface plasmons with nanoscale resolution is inherently difficult due to the diffraction limit of light.^{19,20} Various approaches such as cathodoluminescence (CL) spectroscopy,²¹ and near-field optical spectroscopy²² can be employed to overcome this limit and gain information about the local electric fields with few nanometer resolution. Recently, electron energy loss spectroscopy (EELS) performed in the low-loss regime has emerged as a powerful tool for mapping LSPRs.^{23–26} However the interpretation of plasmonic EELS data can be difficult, even more so when trying to correlate

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with near- or far-field light scattering as these techniques do not capture the same information, in particular in the presence of dark modes^{27,28} or hot spots between coupled nanoparticles.²⁹

For better mapping and understanding of plasmon resonances, experimental optical data on plasmonic nanostructures are typically complemented by comparisons obtained from numerical or analytical approaches, including discrete dipole approximation (DDA), finite difference time domain (FDTD), and boundary element method (BEM). For straightforward geometries, simple plasmon modes such as dipoles can readily be recognized by computing the polarization vector directions³⁰ or electric field directions^{31,32} and then deducing surface charge distributions. Alternatively, artificial surface charges and currents can be attached to boundary elements to map out the plasmon modes using BEM.^{23,33} The relative merits and limitations of such methods have been reviewed elsewhere.^{29,34,35}

In this work we describe and discuss a new approach to directly obtain maps of the surface plasmon modes at the near-field resonance energies *via* full electrodynamics calculations. To taken into account spectral deviation between the near- and far-field plasmon resonances, a near-field spectroscopy is proposed to extract the near-field LSPR energies. Firstly conventional plasmon mapping strategy is applied for further comparisons. Then the induced surface charge distributions at the near-field resonance energies are calculated by Gauss' law during FEM calculations. Instead of conventional mapping, the three-dimensional (3D) geometry of surface charge poles is used to determine the symmetry of the plasmon resonance modes. Furthermore, by using a nanosphere dimer we demonstrate that complex structures can also be addressed with this approach. Even higher-order hybridized plasmon modes are presented clearly.

II. COMPUTATIONAL METHOD AND THEORY

Finite element method (FEM)^{36,37} calculations were performed in COMSOL Multiphysics (installed on a Quad Intel Xeon CPU, 64 GB RAM workstation).³⁸ Specifically, we solve the vector wave equation for the time-harmonic electric field

$$\nabla \times \left(\frac{1}{\mu_r} \nabla \times \mathbf{E} \right) - k_0^2 \epsilon_r \mathbf{E} = 0 \quad (1)$$

where μ_r and ϵ_r are the relative permeability and permittivity, $\mathbf{E} = (E_x, E_y, E_z)$ is the electric field, and $k_0 = 2\pi/\lambda$ is the incident wave vector with λ the wavelength of the incident plane wave. For far-field scattering properties, extinction spectra are calculated by integrating the time-averaged extinction Poynting vectors $\mathbf{S}_{\text{ext}}$ (i.e. electromagnetic power flow) over an auxiliary surface enclosing the nanoparticle^{39,40}

$$S_{\text{ext}} = \frac{1}{2} \text{Re} \{ \mathbf{E}_{\text{inc}} \times \mathbf{H}_{\text{sca}}^* + \mathbf{E}_{\text{sca}} \times \mathbf{H}_{\text{inc}}^* \} \quad (2)$$

$$C_{\text{ext}} = \frac{-\iint \mathbf{S}_{\text{ext}} dA}{|\mathbf{W}_{\text{inc}}|} \quad (3)$$

where $\mathbf{E}_{\text{inc}}$, $\mathbf{E}_{\text{sca}}$, $\mathbf{H}_{\text{inc}}$ and $\mathbf{H}_{\text{sca}}$ are the incident and scattered electric and magnetic field respectively, C_{ext} is the extinction cross section, $|\mathbf{W}_{\text{inc}}| = 1/2c\epsilon_0 E_0^2$ is the power flow per unit area of the incident plane wave, E_0 (set at 1 V/m here) is the modulus of $\mathbf{E}_{\text{inc}}$, c is the velocity of light and ϵ_0 is the permittivity of vacuum.

Plasmonic nanoparticles are commonly used as enhancing surfaces for spectroscopy, such that computing the near-field enhancement factor for various resonant modes is a valuable tool for spectroscopic applications. The electromagnetic (EM) enhancement factor of SERS is approximately $|\mathbf{E}|^4/|\mathbf{E}_{\text{inc}}|^4$ when the Stokes shift is small.³⁷ Assuming Raman probe molecules are arranged randomly and uniformly on the surface of metallic nanoparticles, the averaged EM enhancement factor can be evaluated by averaging the volume integral of $|\mathbf{E}|^4/|\mathbf{E}_{\text{inc}}|^4$ within a certain distance above the metal surface (here we take 2 nm, see Fig. S1).^{41,42}

$$\overline{EF} = \frac{\iiint (|\mathbf{E}|^4/|\mathbf{E}_{\text{inc}}|^4) dV}{V} \quad (4)$$

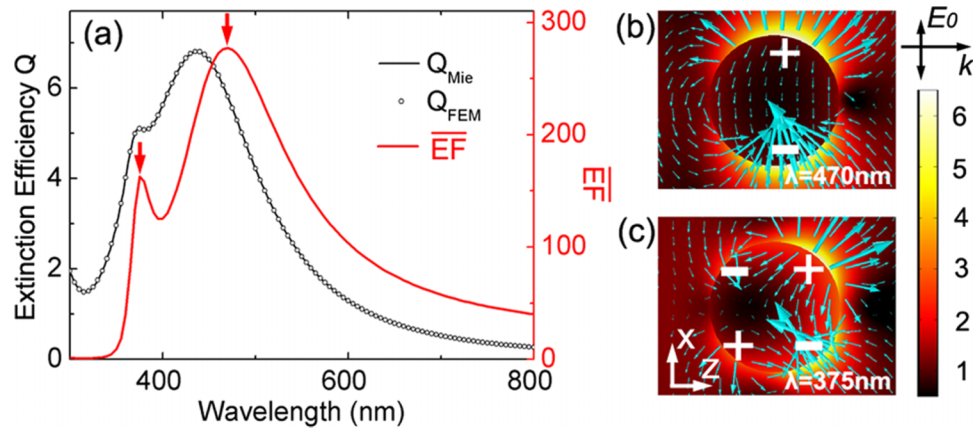


FIG. 1. (a) Extinction efficiency Q of $a = 60$ nm radius Ag nanosphere calculated by Mie theory (black line), finite element method (hollow dots), and near-field $\overline{EF}$ spectrum (red line), calculated with 5 nm steps. The Mie and FEM spectra feature two peaks at $\lambda = 435$ nm and 375 nm, while the near-field displays peaks at $\lambda = 470$ nm and 375 nm. Slice plot of E-field amplitude distribution and transient E-field directions for (b) $\lambda = 470$ nm, $\varphi = 0.34\pi$ (dipole) and (c), $\lambda = 375$ nm, $\varphi = 0.80\pi$ (quadrupole). The incident light propagates along the z -axis with x -axis polarization. The arrow length is proportional to the transient E-field value. The surface charge poles are indicated by “+” and “-” marks.

Plotting the $\overline{EF}$ as a function of energy provides valuable information about the near-field enhancement at various wavelengths that can be used to optimize enhancing substrates for specific resonant molecules. For an entire spectrum (i.e. ~ 100 spectral points) of our model, the computational time is 24–36 h. The excitation energy producing the largest near-field enhancement can be extracted from the $\overline{EF}$ plots (as shown in Fig. 1). Classical Gauss’ law is applied to calculate the surface charge density ρ at these highly enhancing energies, since plasmonic metals such as Ag and Au are good electrical conductors and hence almost all the induced charge distributes on the particle surface. The Gauss’ law in the integral form is: $\Phi_E = \frac{Q}{\epsilon_0} = \oint_S (\mathbf{n} \cdot \mathbf{E}) dS$, where Φ_E is the electric flux through the metal surface S , $Q = \oint_S \rho dS$ is the total charge, thus the surface charge density is:

$$\rho = \epsilon_0 \cdot (\mathbf{n} \cdot \mathbf{E}) = \epsilon_0 \cdot (n_x \cdot E_x + n_y \cdot E_y + n_z \cdot E_z) \quad (5)$$

where $\mathbf{n} = (n_x, n_y, n_z)$ is the outward normal vector of the particle surface.

III. RESULTS AND DISCUSSION

Fig. 1(a) shows the extinction spectrum of a Ag sphere with radius $a = 60$ nm calculated by FEM and Mie theory, respectively.⁴⁰ The extinction efficiency, $Q = \frac{C_{ext}}{\pi a^2}$ was calculated in 5 nm intervals from 300 to 800 nm; silver was modeled by a Lorentz-Drude dispersion function fitting experimental data.^{43,44} Mie theory and FEM results are in excellent agreement, with the maximum relative deviation $\frac{Q_{FEM} - Q_{Mie}}{Q_{Mie}} = 0.4\%$ at $\lambda = 800$ nm (see Fig. S2),⁴¹ where Q_{FEM} and Q_{Mie} are the extinction efficiency calculated by FEM and Mie theory, respectively. Two peaks are present in both the extinction and the $\overline{EF}$ spectrum. They are the result of two kinds of plasmon modes. E-field distributions at near-field LSPR energies ($\lambda = 470$ and 375 nm) indicated by the red arrows in Fig. 1(a) are presented in Fig. 1(b) and 1(c). The incident light is set along the z -axis with x -axis polarization. The sphere center is placed at the origin where the transient incident field is set to be $E_0 \cdot \exp(-i\varphi)$, φ is the phase. The patterns of E-fields and their directions show a pair of surface charge poles at $\lambda = 470$ nm (Fig. 1(b)) and two pairs of surface charge poles at $\lambda = 375$ nm (Fig. 1(c)), revealing a dipole and quadrupole plasmon mode, respectively. As the conventional mapping method, a similar analysis can be used to determine the nature of the plasmon resonances for other highly symmetric structures.

Interestingly, for the quadrupole mode, the near-field enhancement peaks at a much lower energy ($\lambda = 470$ nm) than the far-field extinction spectrum ($\lambda = 425$ nm). This red shift in energy of the near-field peak with respect to the far field peak is in agreement what has been reported in

recent works.^{13–17} The deviation is known to depend on the size of the particle, with larger particles displaying more marked shifts, owing to the retardation from the resonance in far-field scattering.^{13,30,45} For large enough particles, this shift has been observed to be comparable to the resonance half-width.⁴⁵ To achieve the highest local electric field enhancement, near-field $\overline{EF}$ spectroscopy (Equation (4)) is thus used.

The surface charge distribution within a full oscillation at a specific resonant frequency is calculated using Gauss' law in the differential form (Equation (5)); results of this novel approach are shown in Fig. 2 for the two modes previously discussed. The 3D surface charge poles can easily be located when the metallic sphere reaches a maximum transient charge polarization. This occurs at $\varphi = 0.34\pi$ and $\varphi = 1.34\pi$ for the dipole mode (Fig. 2(a)) and at $\varphi = 0.80\pi$ and $\varphi = 1.80\pi$ for the quadrupole mode (Fig. 2(b)). These poles alternate between negative and positive as the conduction electrons are driven by the oscillating electric field of light. The response of the electron cloud to the incident electric field is however delayed owing to retardation effects, which can be easily observed as a phase delay between the maximum transient charge polarization and the maximum incident field polarization.

Using Gauss' law to map 3D surface charge poles from numerical results on electric fields is a completely general approach and can readily be applied to complex and arbitrary systems such as coupled nanoparticles, patterned substrates, or rough surfaces. Here, we provide specific examples to demonstrate this broad applicability. Let's take a sphere dimer, an important system in sensing and enhanced spectroscopy owing to the electric hot spot at the nanoparticle junction.^{18,29,46} Results for a dimer composed of two Ag nanospheres (radius $a = 60$ nm) separated by 2 nm are shown in Fig. 3. The gap size is fixed to be 2 nm in order to avoid the invalidation of classic electrodynamics for the reason that below 1 nm the quantum and nonlocal effects need to be considered.⁴⁷ Given the symmetry of the system, three unique polarization/propagation geometries of the incident plane wave exist: (I) propagating along z -axis with x -axis polarization, (II) propagating along x -axis with z -axis polarization, and (III) propagating along z -axis with y -axis polarization. The extinction and $\overline{EF}$ spectra for these three geometries are reported in Fig. 3(b) and 3(c). The far-field extinction peaks are consistent with near-field $\overline{EF}$ peaks in terms of the number of peaks, and a deviation of peak positions between these far- and near-field spectra exists; further investigation would benefit from considering near-field coupling effects. The position of the two lowest order (lowest energy) plasmon resonances in the extinction spectra are $\lambda = 660$ and 430 nm for geometry I, $\lambda = 480$ and 420 nm for II, and $\lambda = 435$ and 375 nm for III, while the peaks in the $\overline{EF}$ enhancement are located at $\lambda = 660$ and 455 nm for I, $\lambda = 480$ and 425 nm for II, and $\lambda = 470$ and 375 nm for III.

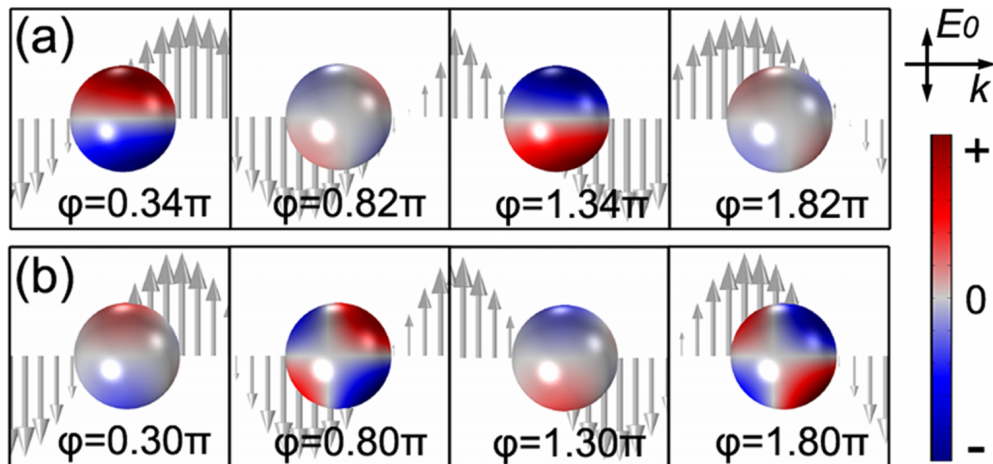


FIG. 2. 3D surface charge distributions for a $a = 60$ nm radius Ag nanosphere within one oscillation. (a) Dipole mode at $\lambda = 470$ nm with $\varphi = 0.34\pi$, 0.82π , 1.34π and 1.82π . (b) Quadrupole mode at $\lambda = 375$ nm, $\varphi = 0.30\pi$, 0.80π , 1.30π and 1.80π . Red and blue color indicate positive and negative charge, respectively. The light is propagating from left to right. The grey arrows represent the transient incident electric field.

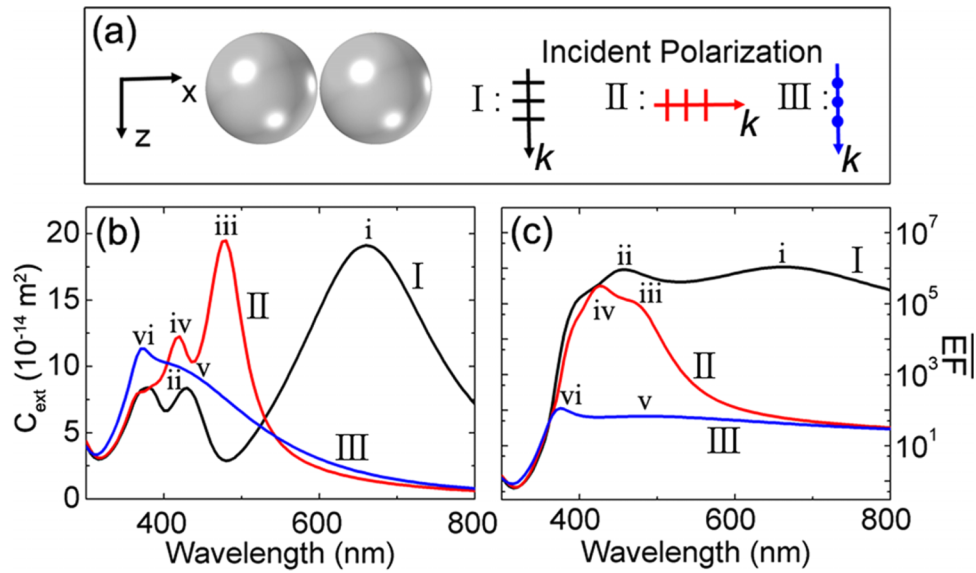


FIG. 3. (a) Dimer structure composed of two Ag nanospheres with 60 nm radius and 2 nm inter-particle separation. The three unique excitation geometries are indicated by I, II, and III. (b) Extinction cross section C_{ext} for the three geometries. The positions of extinction peaks due to low-order plasmon resonances are $\lambda = 660$ (i) and 430 nm (ii) for geometry I, $\lambda = 480$ (iii) and 420 nm (iv) for geometry II, and $\lambda = 430$ (v) and 375 nm (vi) for geometry III. (c) Near-field $\overline{EF}$ spectra of the three geometries. Low-order plasmon resonance energies are $\lambda = 660$ (i) and 455 nm (ii) for geometry I, $\lambda = 470$ (iii) and 425 nm (iv) for geometry II, and $\lambda = 470$ (v) and 375 nm (vi) for geometry III.

Electric field distributions and 3D surface charge pole maps at the $\overline{EF}$ peak energies mentioned above, are plotted together in Fig. 4, highlighting the strong correlation between resonant mode geometry and local field enhancement. The resonant modes are labeled (i) to (vi) as identified in Fig. 3(c). Depending on the nature of the coupling between the particles, modes can be bonding, non-bonding, or antibonding following the plasmon hybridization model.⁴⁸ Fig. 4 shows these types of hybridization: (i) bonding dipole mode, (ii) bonding second-order standing-wave mode, (iii) asymmetric bonding dipole mode, (iv) asymmetric bonding quadrupole mode, (v) antibonding dipole mode, (vi) antibonding quadrupole mode. The four bonding modes sustain “hot spots”, highly enhancing regions at the interparticle junction, desirable for spectroscopy applications,^{2,4} while the two antibonding modes show poor near-field enhancement. The maximum local EF for the bonding modes is as high as 10^9 while it is lower than 10^4 for the antibonding modes.

In particular, the bonding second-order standing-wave mode (ii) is easily confused with the bonding quadrupole mode (iv). If Fig. 4(ii) were simply a two-dimensional plot similar to Fig. 1(b) and 1(c), it would be recognized as four charge poles for each sphere judging from the boundary charge distributions. Actually seen from the 3D surface charge plot, the two poles in the middle part of the sphere merge into a big pole, thus only three poles charge are present for each sphere. This mode is the second-order standing-wave plasmon mode commonly observed in plasmonic nanorods^{20,49} at an energy just above that of the dipole. The plasmon hybridization theory predicts a red shift in wavelength (i.e., decreased resonance energy) for the bonding mode and a small blue shift (i.e., increased resonance energy) for the antibonding mode with respect to the isolated, single particle resonance energy. The red shift is obvious in all of our results, but our 5 nm calculation spacing makes it difficult to assess the presence of a slight blue shift. We thus performed more finely spaced (1 nm) calculations in the energy region of interest (370–380 nm) for the antibonding dipole mode (vi). The single particle quadrupole $\overline{EF}$ and extinction spectrum maximum was found to be 375 nm and 372 nm, respectively; these values were 376 and 375 nm for mode (vi). A slight blue shift was thus indeed observed: 1 nm in the $\overline{EF}$ spectrum (376 – 375 nm) and 3 nm in the extinction spectrum (375 – 372 nm) (see Fig. S4).⁴¹

Beyond assessing mode geometry and observing near-field and far-field differences, this FEM-based approach is also useful because of its applicability to arbitrary experimental geometries. In

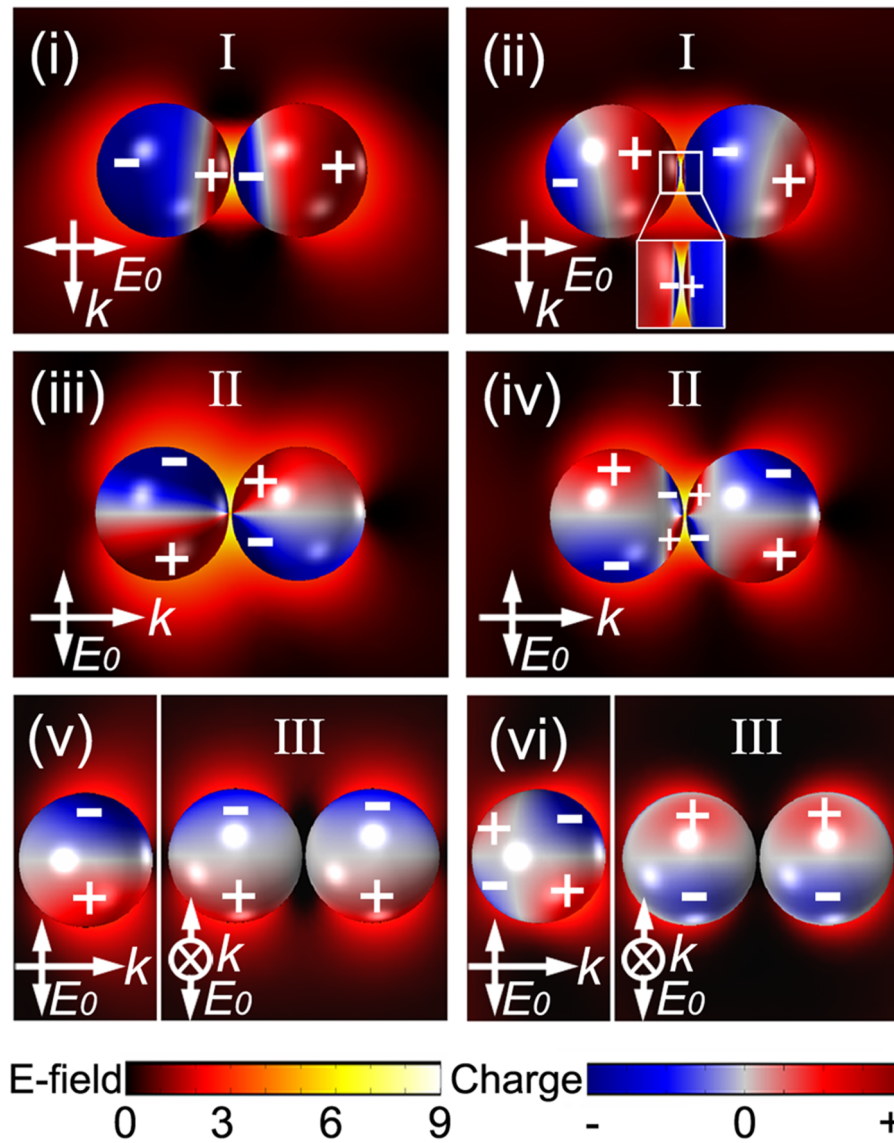


FIG. 4. Mapping of the plasmon modes corresponding to the peaks identified in Figure 3(c). Slice logarithmic $|E|^4$ distributions and 3D surface charge distributions with the maximum transient charge polarization are plotted together. (i) Geometry I, $\lambda = 660$ nm, $\varphi = 0.48\pi$, bonding dipole mode. (ii) Geometry I, $\lambda = 455$ nm, $\varphi = 0.20\pi$, bonding second-order standing-wave mode. (iii) Geometry II, $\lambda = 470$ nm, $\varphi = 0.18\pi$, asymmetric bonding dipole mode. (iv) Geometry II, $\lambda = 425$ nm, $\varphi = 0.82\pi$, asymmetric bonding quadrupole mode. (v) Geometry III, $\lambda = 470$ nm, $\varphi = 0.68\pi$, antibonding dipole mode. (vi) Geometry III, $\lambda = 375$ nm, $\varphi = 0.30\pi$, antibonding quadrupole mode. The inset in (ii) shows the two small but strong poles located in the junction area. Higher order modes for I and II are reported in the Supplemental Material.⁴¹

addition to the particle geometry and structure, the incident light direction (α) can be manipulated. An example is shown in Fig. 5, where $\alpha = 45^\circ$. In this case, the calculated extinction spectrum reveals three peaks, at $\lambda = 660$, 475, and 415 nm, coinciding with the peak of modes (i), (iii) and (iv) in Fig. 3(b) (See Fig. S5).⁴¹ The $\overline{EF}$ spectrum displays two peaks: the peak at $\lambda = 660$ nm corresponds to the bonding dipole mode (i), while the broad peak around $\lambda = 460$ nm is a superposition of other bonding modes including (ii), (iii), and (iv) (see Fig. S6).⁴¹ This correspondence confirms that the results of $\alpha = 45^\circ$ excitation is a combination of the two unique excitation geometries I and II discussed previously. This mode combination can easily be discerned graphically, as shown in Fi. 5(b) and 5(c), where the modes at $\lambda = 660$ and 460 nm are plotted. Thus the pole patterns and the spectra appear as a combination of modes from geometry I and II. Despite this

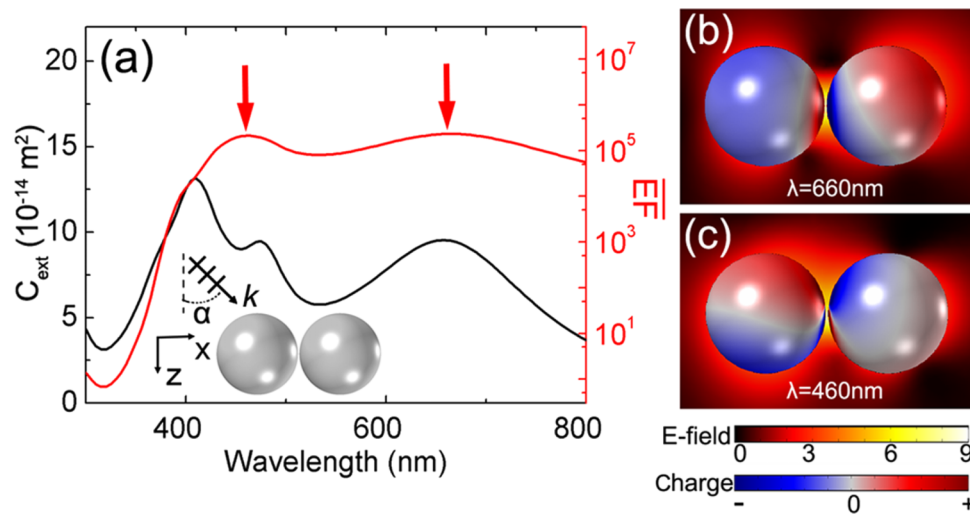


FIG. 5. Oblique incident excitation for the Ag nanoparticle dimer, with $\alpha = 45^\circ$. (a) Extinction cross-section C_{ext} (black) and $E\vec{F}$ spectrum (red). Plasmon mapping at (b) $\lambda = 660$ nm, $\varphi = 0.46\pi$ and (c) $\lambda = 460$ nm, $\varphi = 0.14\pi$ using the same strategy as in Fig. 4.

excellent correspondence, it is worth mentioning that the explanation surrounding mode mixing is an approximation and is not quantitative at this point.

IV. CONCLUSION

In conclusion, we have introduced and applied a FEM-based tool to calculate and map 3D surface charge poles directly and thus to determine complicated or hybridized plasmon resonance geometries in arbitrary shapes. For a nanosphere dimer, a map of the electric field enhancement alone could not discern between a second order standing wave bonding mode and a quadrupole bonding mode; the model presented here clearly shows the difference. This approach is based on Gauss' law and allows the investigation of near-field enhancement while providing a better understanding of plasmon resonance symmetry and surface charge distribution. This new tool is expected to be of wide appeal given that it can provide the comprehensive physical image of a plasmonic system necessary for fundamental studies and spectroscopy applications.

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