Iterative optimization of plasmon resonant nanostructures

Prathamesh Pavaskar[a] and Stephen B. Cronin[b]
Department of Electrical Engineering, University of Southern California, Los Angeles, California 90089, USA

(Received 23 April 2009; accepted 25 May 2009; published online 22 June 2009)

We perform finite difference time domain simulations of two-dimensional clusters of metal nanoparticles with incident planewave irradiation. An iterative optimization algorithm is used to determine the configuration of the nanoparticles that gives the maximum electric field intensity at the center of the cluster. The optimum configurations of these clusters have mirror symmetry about the axis of planewave propagation, but are otherwise nonsymmetric and nonintuitive. The maximum field intensity is found to increase monotonically with the number of nanoparticles in the cluster, producing intensities that are five times larger than linear chains of nanoparticles and 2500 times larger than the incident electromagnetic field. © *2009 American Institute of Physics*.
[DOI: 10.1063/1.3157168]

Plasmon resonant nanostructures have become a topic of growing interest, impacting a wide range of fields, including optics,[1] spectroscopy,[2,3] chemistry[4] and medicine.[5,6] Surface plasmon excitations produce very large enhancements in the electromagnetic fields surrounding these nanostructures. This effect is seen especially for wavelengths near the plasmon resonance energy. Jeanmaire and Van Duyne[7] demonstrated surface enhanced Raman spectroscopy (SERS) using plasmonic nanoparticles as early as 1977. Kneipp *et al.*[2] reported SERS enhancement values of 10^{14} from colloidal silver clusters. A quantitative theoretical understanding of this electric field enhancement came later with Hao and Schatz[8] and Oubre and Nordlander[9] who calculated electric field enhancements for single nanoparticles of different shapes, as well as dimers and linear chains of nanoparticles. Raman intensity enhancement values as high as 10^8 were found in their calculations of dimers. Experimentally, Atay *et al.*[10] found that the plasmon resonant frequency of nanoparticle dimers depends strongly on nanoparticle separation. A similar work was carried out both through simulations and experiments by Su *et al.*[11] confirming these findings.

Adaptive algorithms have been used by Gheorma *et al.*[12] and Seliger *et al.*[13] to optimize nanoscale dielectric structures to achieve preferential angular scattering profiles. The optimum design showed nonsymmetric solutions that could not have been derived by straightforward human logic. An experimental realization of these geometries confirmed the results predicted by these algorithms.[13]

In the work presented here, we simulate the electric field response of metal nanoparticle clusters with incident plane wave irradiation. It should be noted that the two-dimensional (2D) nature of the simulations imply that these nanoparticles are clusters of infinitely long cylinders rather than spheres. We implement optimization of plasmonic materials considering the $2N$-dimensional parameter space (N is the number of nanoparticles), including nonintuitive configurations. We solve Maxwell's equations numerically by discretizing the spatial and temporal dimensions of the electromagnetic fields using the finite difference time domain (FDTD) method.[14] A 2D spatial grid of 300 000 points is used to represent the computational cell. The grid spacing used for our simulations is 1 nm. To justify the grid spacing used for the simulations, the minimum allowed separation between any two nanoparticles is 2 nm. The diameter of the nanoparticles used in simulations is 20 nm. For boundary conditions, we have implemented perfectly matched layers with the number of layers being ten. The dielectric function used is based on a fit of the experimental data obtained by Johnson and Christy[15] to a Lorentz–Drude formula. The temporal grid consists of 10 000 time steps with a spacing of 0.002 fs. We have used a gradient-based algorithm to optimize the electric field at the center of the nanoparticle cluster with respect to all the nanoparticle positions. Downhill movements are allowed in order to avoid local maxima.

Figure 1 shows a flowchart illustrating the algorithm used, which is as follows:

1. Run a FDTD simulation with a broad pulse to determine the resonance frequency of the initial nanoparticle configuration. Initialize all parameters, including number of nanoparticles, nanoparticle positions, frequency and bandwidth of incident radiation, and step size.
2. Calculate electric field intensity gradients with respect to nanoparticle positions in the x and y directions.
3. Move each nanoparticle in the direction of the electric field intensity gradient with respect to its position and with a step size proportional to the distance of the nearest nanoparticle, provided there is no overlap with other nanoparticles.
4. Determine the resonant wavelength of the new nanoparticle configuration and run a full FDTD simulation of the electric fields over the entire simulation grid.
5. Compare the electric field intensity at the center of the nanoparticle cluster with that of the highest previous value (I_{max}).
   a. If this new value exceeds the previous highest value, then the configuration is saved as the new optimum configuration.
   b. If the electric field intensity is found to be lower than the previous highest value, increase the downhill movement counter j by 1 and proceed to the next iteration.

[a]Electronic mail: pavaskar@usc.edu.
[b]Electronic mail: scronin@usc.edu.

 © 2009 American Institute of Physics

Downloaded 02 Jul 2009 to 128.125.124.218. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

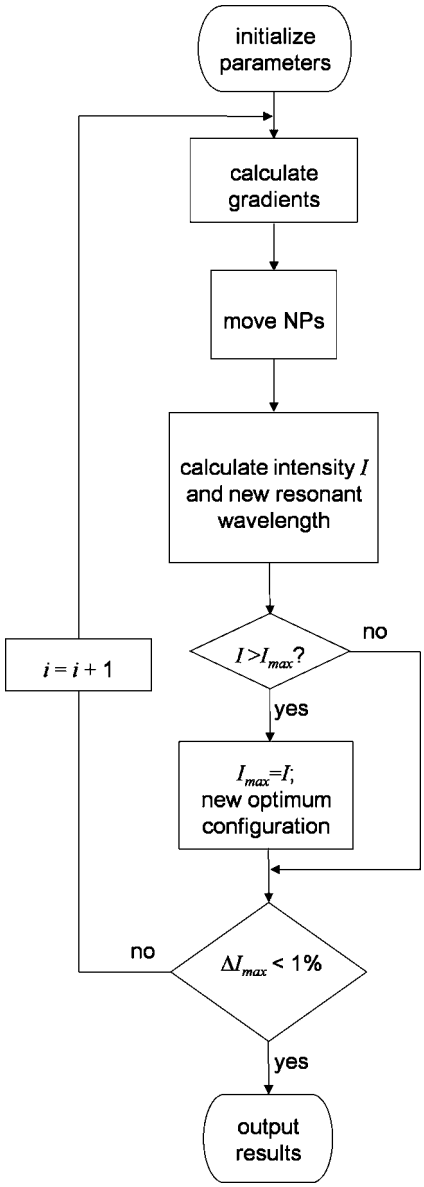

FIG. 1. Flowchart illustrating the algorithm used for optimization.

6. When the maximum field intensity stops changing by more than 1%, the iterative process is stopped, and the highest electric field intensity and corresponding nanoparticle configuration are output.

Figure 2(a) shows an electric field intensity map for the case of three nanoparticles. Here, the two nanoparticles centered about (0,0) are fixed in position, with a separation of 2 nm. The electric field intensity is calculated at the point of interest (shown by "X") as a function of the positions of the third nanoparticle. This figure shows that a maximum intensity can be achieved by placing the third nanoparticle at the top or the bottom of the fixed dimer. Figure 2(b) shows the stepwise results of the optimization algorithm applied to this third nanoparticle. It can be seen from these figures that the algorithm moves the nanoparticle from its initial position (shown in green) to the optimum position (shown in red), as predicted by the intensity map. This optimization was found to reach the convergence criterion after five iterations. Figures 2(c) and 2(d) show the electric field intensity and the resonant wavelengths obtained after each iteration. The electric field intensity is found to increase monotonically with the number of iterations. The resonant wavelength of the cluster also changes slightly during the iterative process but only by 1%–2%. Such a change in the resonant wavelength has been well documented previously in the literature.[10]

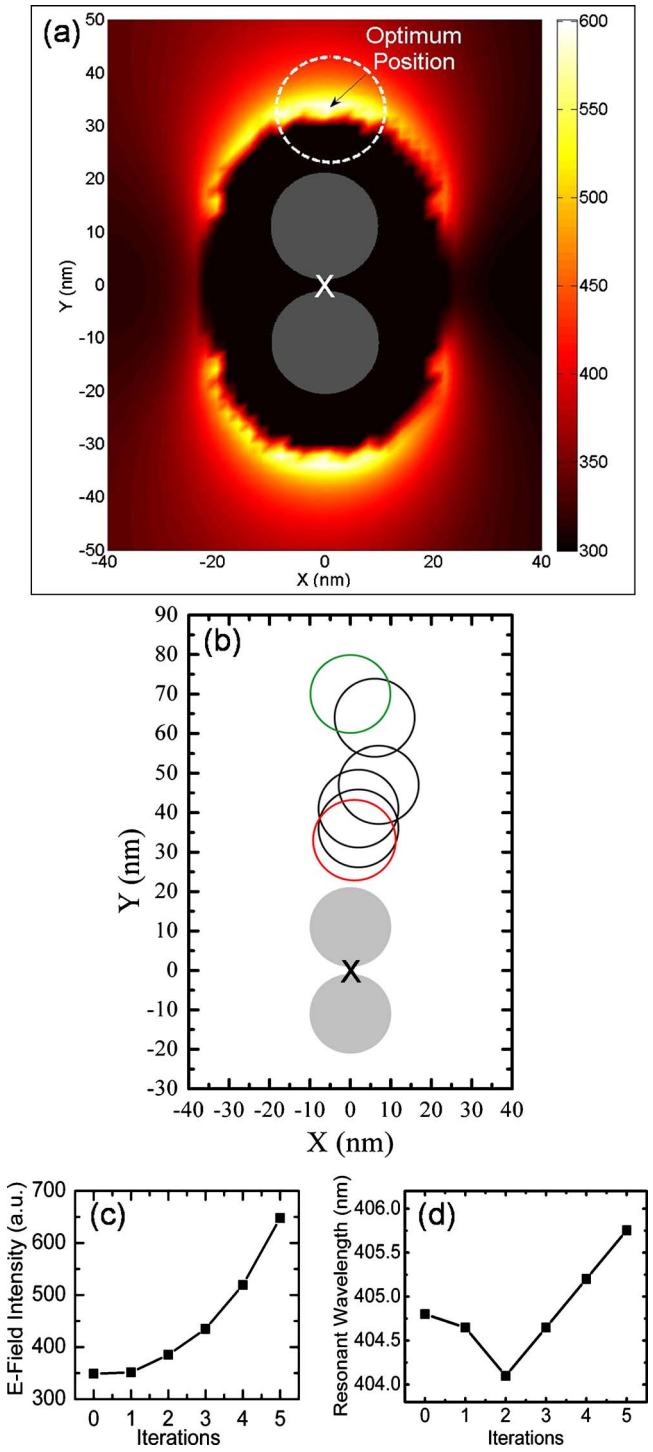

FIG. 2. (Color online) (a) Optimization electric field intensity map with respect to spatial coordinates of the third nanoparticle. (b) Movement of the third nanoparticle with the optimization algorithm. The initial position is shown in green and the final position is shown in red. (c) Change in E-field intensity and (d) resonant wavelength with each iteration.

Using this approach, we add nanoparticles to this cluster, one by one, and optimize the positions of the nanoparticles. The optimized geometric configurations of clusters with 3–20 nanoparticles are shown in the online supporting document.[16] Figure 3 shows the trend in optimum electric

Downloaded 02 Jul 2009 to 128.125.124.218. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

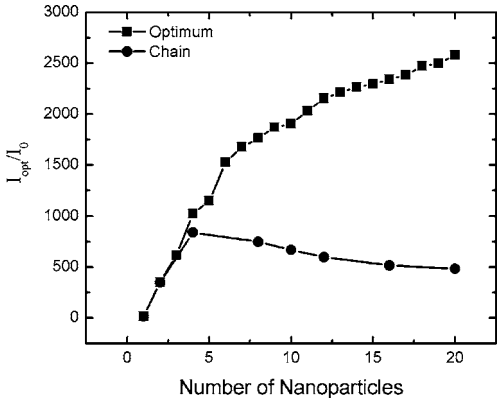

FIG. 3. Optimum electric field intensity enhancement as a function of the number of nanoparticles.

field intensity as a function of the number of nanoparticles together with the electric field intensities of linear chains of nanoparticles with 2 nm separation. A monotonic increase is found in the optimum intensity with increasing number of nanoparticles, whereas the highly symmetric linear chains show a drop in the intensity above four nanoparticles. This is consistent with the previous results in the literature.[17] The electric field intensities of these optimized configurations show a factor of 2000 enhancement over the incident electromagnetic field in the case of ten nanoparticles and a factor of 2500 enhancement in the case of 20 nanoparticles. There are several subtleties that facilitate the practical implementation of this iterative algorithm. The allowance of downhill movements in the optimization routine is necessary to avoid local optima. It is also important to choose the correct step size in the algorithm, in order to achieve convergence. Lastly, we maintain a taboo list of nanoparticle configurations in order to avoid computing the same configuration twice.

The optimum geometric configurations for clusters of 10 and 20 nanoparticles are plotted in Figs. 4(a) and 4(b), together with the resulting electric field intensity. In the figures, the "X" symbol indicates the point of optimum electric field intensity. The direction of planewave propagation in both plots is from left to right. These geometries exhibit mirror symmetry about the *x*-axis. However, their overall

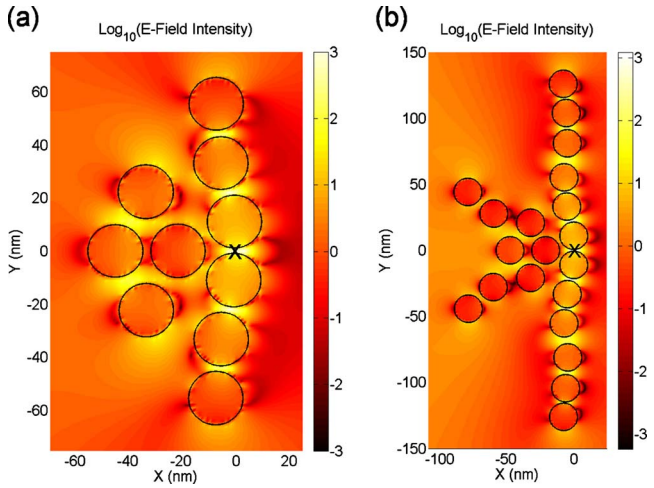

FIG. 4. (Color online) Electric field intensity log plots for (a) 10 and (b) 20 nanoparticle optimum configurations. The "X" symbol indicates the position of optimum electric field intensity.

configuration is still largely nonsymmetric and nonintuitive. We would like to emphasize that these complex geometries are obtained independent of the initial positions of the nanoparticles, before optimization.

The FDTD calculations performed in this work are 2D. As such, they represent infinitely long cylindrical rods rather than spherical nanoparticles. In order to treat spherical nanoparticles, three-dimensional (3D) simulations must be carried out, which requires significantly more computational resources. In 2D, moving each nanoparticle requires roughly 5 min of computation time. However, in 3D, parallel processors are required, and computation times are on the order of hours rather than minutes for each computational iteration. The biggest problem of implementing these simulations, in 3D, is this additional computational cost.

In conclusion, we have implemented an iterative optimization algorithm to determine the geometric configurations of metal nanoparticle clusters that produce the strongest electric field intensity from an incident electromagnetic plane wave. The optimum configurations of these clusters are found to have mirror symmetry about the axis of planewave propagation, but are otherwise nonsymmetric and nonintuitive. The optimized electric field intensity increases monotonically with the number nanoparticles in the cluster. The electric field intensity enhancement for 20 nanoparticles is 2500 times larger than the incident electromagnetic field. This enhancement is significantly higher than a linear chain of nanoparticles or the centermost dimer alone. If these optimized nanoparticle configurations can be achieved experimentally, this method could enable new devices based on near-field and nonlinear effects.

This research was supported in part by ONR Award No. N00014-08-1-0132 and AFOSR Award No. FA9550-08-1-0019.

[1]S. A. Maier, M. L. Brongersma, P. G. Kik, S. Meltzer, A. A. G. Requicha, B. E. Koel, and H. A. Atwater, Adv. Mater. (Weinheim, Ger.) **15**, 562 (2003).
[2]K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari, and M. S. Feld, Phys. Rev. Lett. **78**, 1667 (1997).
[3]R. Kumar, H. Zhou, and S. B. Cronin, Appl. Phys. Lett. **91**, 223105 (2007).
[4]W. H. Hung, I. K. Hsu, A. Bushmaker, R. Kumar, J. Theiss, and S. B. Cronin, Nano Lett. **8**, 3278 (2008).
[5]T. Endo, K. Kerman, N. Nagatani, H. M. Hiepa, D. K. Kim, Y. Yonezawa, K. Nakano, and E. Tamiya, Anal. Chem. **78**, 6465 (2006).
[6]M. Y. Sha, H. Xu, S. G. Penn, and R. Cromer, Nanomedicine **2**, 725 (2007).
[7]D. L. Jeanmaire and R. P. Van Duyne, J. Electroanal. Chem. Interfacial Electrochem. **84**, 1 (1977).
[8]E. Hao and G. C. Schatz, J. Chem. Phys. **120**, 357 (2004).
[9]C. Oubre and P. Nordlander, J. Phys. Chem. B **109**, 10042 (2005).
[10]T. Atay, J. H. Song, and A. V. Nurmikko, Nano Lett. **4**, 1627 (2004).
[11]K. H. Su, Q. H. Wei, X. Zhang, J. J. Mock, D. R. Smith, and S. Schultz, Nano Lett. **3**, 1087 (2003).
[12]I. L. Gheorma, S. Haas, and A. F. J. Levi, J. Appl. Phys. **95**, 1420 (2004).
[13]P. Seliger, M. Mahvash, C. Wang, and A. F. J. Levi, J. Appl. Phys. **100**, 034310 (2006).
[14]A. Taflove and S. C. Hagness, *Computational Electrodynamics: The Finite-Difference Time-Domain Method*, 3rd ed. (Artech House, Boston, 2005), p. xxii.
[15]P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).
[16]See EPAPS supplementary material at http://dx.doi.org/10.1063/1.3157168 for optimized geometric configurations of clusters with 3 to 20 nanoparticles.
[17]Z. B. Wang, B. S. Luk'yanchuk, W. Guo, S. P. Edwardson, D. J. Whitehead, L. Li, Z. Liu, and K. G. Watkins, J. Chem. Phys. **128**, 094705 (2008).

Downloaded 02 Jul 2009 to 128.125.124.218. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp