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Coupled dipole plasmonics of nanoantennas in discontinuous, complex dielectric environments

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ABSTRACT

Two-dimensional metamaterials support both plasmonic and coupled lattice (Fano) resonant modes that together could enhance optoelectronics. Descriptions for plasmon excitation in Fano resonant lattices in non-vacuum environments typically use idealized, homogeneous matrices due to computational expense and limitations of common approaches. This work described both localized and coupled resonance activity of two-dimensional, square lattices of gold (Au) nanospheres (NS) in discontinuous, complex dielectric media using compact synthesis of discrete and coupled dipole approximations. This multi-scale approach supported attribution of experimentally observed spectral resonance energy and bandwidth to interactions between metal and dielectric substrate (s) supporting the lattices. Effective polarizabilities of single AuNS, either *in vacuo* or supported by glass and/or indium tin oxide (ITO) substrates, were obtained with discrete dipole approximation (DDA). This showed plasmon energy transport varied with type of substrate: glass increased scattering, while ITO increased absorption and energy confinement. Far-field lattice interactions between AuNS with/without substrates were computed by coupled dipole approximation (CDA) using effective polarizabilities. This showed glass enhanced diffractive features (e.g., coupled lattice resonance), while ITO supported plasmon modes. This compact, multiscale approach to describe metasurfaces in complex environments could accelerate their development and application.

1. Introduction

Charge polarization of nanoantennas depends on local dielectric environment [1], as described by Clausius–Mossotti [2,3] for electrostatic dipoles embedded in a homogeneous reference. A compact description of localized and coupled resonant modes due to polarization of ordered nanoantennas in complex, discontinuous dielectric environments is needed for energy harvesting [4,5], sensors [6,7], photonic circuits [8,9], and nonlinear optics [10,11]. This calls for a multi-scale, electrodynamic approach beyond dielectric averaging, analytic approximations, or present computational methods. Mass-averaged dielectric values have been shown to oversimplify plasmon and lattice resonant modes [12]. Spectrum-averaged refractive indices insufficiently describe nanoantennas supported by emergent materials like transition metal dichalcogenides [13]. Maxwell-Garnett and effective

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medium [14–17] analytic approaches describe mode energy shifts for random [17–19] and ordered [20–22] nanospheres using Mie theory and the coupled dipole approximation (CDA), respectively, but are limited to real-valued dielectric substrates with near-zero dispersion.

Finite difference time domain (FDTD), boundary/finite element methods (BEM/FEM), and discrete dipole approximation (DDA) are used to describe polarizable electric resonance modes for arbitrarily-shaped nanostructures embedded in a non-dispersive, uniform dielectric environment [23–25] or between dielectric super- and sub-strates [25–31]. Discretization of time and space in FDTD and FEM constrain efficient computation of locally complex dielectrics, particularly for large-area metasurfaces. BEM reduces memory usage, but is limited to describing nanoantennas whose volume may be approximated as a surface [32], e.g., nanodiscs. DDA has been used to compute frequency dependent polarization for single nanoantenna on complex dielectrics at less computational expense than FDTD by discretizing structures into cubic lattices of point dipoles with unique dielectric behavior [33,34]. Schatz et al. used DDA to predict experimental localized surface plasmon resonances (LSPR) from single nanospheres and nanotetrahedrons supported by glass and mica substrates [27,35]. However, coupled plasmon modes between nanoantennas in lattice arrangements described by DDA to date have omitted rigorous analysis of substrate to ease computational expense [36,37]. Comprehensive description of nanoantennas in two-dimensional metamaterials supported by dispersive, complex dielectric substrates requires a more complete approach.

This work inserts effective single-particle polarizabilities computed by DDA in complex (both real and lossy) dielectrics into a rapid, semi-analytical coupled dipole approximation (rsa-CDA) to efficiently describe resonant plasmon, diffractive, and coupled lattice modes for large area, regular lattices of nanoantennas. Predominant features observed in transmission UV–vis spectra from a square lattice of 80 nm radius gold nanospheres (AuNS) supported by indium tin oxide (ITO)-covered glass were reproduced by integrating DDA results at 100 nm scales with rsa-CDA calculations at $>100{,}000$ nm scales. This multi-scale DDA/rsa-CDA approach showed that glass substrates increased resonant scattering which contributed to diffractive features (e.g., coupled lattice resonance) in array spectra; while lossy ITO substrates increased absorption and enhanced energy confinement, contributing to dipole plasmon features in the spectra.

2. Materials and methods

2.1. Numerical modeling

The CDA describes electrodynamics of a nanoantenna lattice comprising a metasurface by treating each constituent antenna as a point dipole with scalar polarizability [20,38,39]. Charge density polarization of each antenna, $\boldsymbol{P}$, is calculated according to antenna polarizability (α) and cumulative contributions from the incident field, $\boldsymbol{E}_o$, and adjacent dipoles comprising the lattice, $\boldsymbol{E}_{lat}$, *viz.*,

$$\boldsymbol{P} = \alpha(\boldsymbol{E}_o + \boldsymbol{E}_{lat}) \tag{1}$$

The retarded dipole sum calculates $\boldsymbol{E}_{lat}$ by summing interactions of all nanoantennas in the lattice on each individual antenna. An analytical α is available for symmetric shapes such as spheres, spheroids, and toroids [35,40,41] in homogenous media, but external numerical calculation (e.g., DDA) is required for complex shapes [42] or most cases of non-uniform media. Polarizability corrections exist for spherical nanoantenna within non-lossy, multi-layered media [43], however they are not extendable to arbitrary antenna shapes or lossy substrates.

This work used DDA package DDSCAT 7.3 to compute effective polarizabilities of 80 nm radius AuNS in a vacuum and mounted on ITO or soda lime glass substrates [44–46]. DDSCAT solves Maxwell's equations by discretizing arbitrary geometries into a cubic lattice of point dipoles. Targets were discretized according to their Cartesian description using a MATLAB (v8.3, MathWorks, Natick, MA, USA) tool available on nanoHUB [47]. Each point dipole within a target was assigned a polarizability, α_{di}, according to the "lattice dispersion relation" described by Gutkowicz-Krusin [48] to permit calculation of its polarization $\boldsymbol{P}_{di}$ in response to $\boldsymbol{E}_o$. DDSCAT was modified to output complex effective polarizability, α_{eff}, for each AuNS–substrate pair by summing the polarizability of each dipole within the target [7,42], calculated as a function of the inter-dipole spacing (d_{di}), $\boldsymbol{P}_{di}$ for the i^{th} dipole per unit volume, and $\boldsymbol{E}_o$ at the i^{th} dipole:

$$\alpha_{eff} = \sum_{i=1}^{n} \frac{{d_{di}}^3 (\boldsymbol{P}_{di})_i}{(\boldsymbol{E}_o)_i} \tag{2}$$

DDA simulations were performed with $d_{di}=5$ nm for incident vacuum wavelengths between 400 nm and 800 nm at 1 nm resolution on a 16-core supercomputer node with 32 GB of memory. Near-field enhancement plots were generated using $d_{di}=2$ nm for convergence. Wave vector (k) was incident orthogonal to the substrate (along x-axis) and polarized along the z-axis. Substrates were modeled as a cylinder in the y–z plane with radius and height equal to $2x$ the particle radius [27,35] i.e., 160 nm. Interaction between AuNS and substrate was considered at 0%, 15%, and 30% particle surface area for two scenarios: (1) AuNS embedded into the substrate and (2) AuNS "cut-off" at the substrate surface. Percentage interaction values were based on analytic weighting factors characteristic of $1/e$ plasmon interaction distance from the nanoantenna surface [17]. Dielectric data for soda lime glass and ITO reported by Rubin and König et al., respectively, were used [49,50].

Computed polarizabilities were then used to calculate far-field lattice spectra from square 301×301 arrays of AuNS using rsa-CDA [7,42]. The rsa-CDA [20,38,40] reduced computational time by taking advantage of $\pi/2$ rotational symmetry in square lattices [40]. Dielectric data for Au reported by Johnson and Christy was used in all simulations [51]. This multi-scale DDA/rsa-CDA technique has been shown to reduce computation time more than 40,000-fold for nanoring lattices *in vacuo* relative to full volume DDA models [42].