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Nanoshells to nanoeggs to nanocups: optical properties of reduced symmetry core–shell nanoparticles beyond the quasistatic limit

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Abstract. The plasmonic properties of metallodielectric nanoparticles exhibit a highly sensitive dependence on geometry, due to the interaction between primitive plasmon modes associated with the surfaces of the nanoparticle. Changes in nanoparticle geometry that reduce symmetry alter the interactions between plasmon modes and give rise to modified, and altogether new, plasmonic features. Here, we have examined the near- and far-field optical properties of three variants of a core–shell nanoparticle: nanoshells, nanoeggs and nanocups. Nanoshells, consisting of a spherical silica core coated with a thin gold shell, convert to ‘nanoeggs’ by offsetting the core within the shell. Offsets of the core greater than the thickness of the shell layer, where the core pierces the shell, result in ‘nanocups’. The absorption and scattering spectra of a nanoegg reveal the emergence of multipolar peaks strongly redshifted relative to those of nanoshells and larger near-field enhancements. The wavelength of maximum field enhancement increases with increasing core offset, distinct from the dipole resonance of the nanoparticle. For larger nanoeggs beyond the quasistatic regime, variations in the relative contribution of scattering and absorption to the nanoparticle extinction depend upon both the core–shell offset and on overall particle size. These observations may lead to new opportunities to tailor near- and
far-field properties of plasmonic nanoparticles for specific applications, such as high performance surface-enhanced spectroscopy, bioimaging and nanoparticle-based therapeutics.

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1. Introduction

A rapidly expanding army of metallodielectric nanoparticles has taken the world of nanophotonics by storm, offering solutions to decades-old problems and opening up new avenues of exploration. Cancer research has been expanded from a focus in pharmaceuticals and radiotherapy to include engineered nanoparticle therapies [1, 2]. Spectroscopic measurements have been revolutionized by field enhancements previously unavailable outside of specialized laser facilities [3]–[5]. Eventually, such nanoparticles may even form the basis of inexpensive optical metamaterials [6]. Many of these developments have relied on variations of the core–shell geometry, including nanoshells, nanoeggs and nanocups.

The near- and far-field optical properties of all three core–shell geometries have been well studied [7]–[13]. Here, we will focus on the transitional behaviour between these three classes of nanoparticles. Moving a spherical core away from the centre of a spherical gold shell, and then allowing the core to emerge from the outer shell, effectively converts a nanoshell to a nanoegg, and then a nanocup, solely as a function of core offset. Examining the physical basis for the calculated shifts in the plasmonic response may allow for the design of optimized, application-specific nanoparticles. Reliably creating such particles to meet future industry demands may inspire the development of improved synthesis techniques.

The optical response of nanoshells can be calculated using the Mie theory [14]; nanoeggs and nanocups require alternate methods of solution. In the quasistatic limit, where the size of the nanoparticle is substantially smaller than the vacuum wavelength of light, nanoeggs have been solved analytically using the plasmon hybridization theory [15, 16]. Larger particles with a significant degree of asymmetry, such as nanoeggs and nanocups, require numerical methods of solution to include the effects of phase retardation.

In this study, we have used the finite element method (FEM) to examine the transition from gold–silica nanoshells to nanoeggs and nanocups. Both the near- and far-field effects of core offset and total particle size are considered, with an emphasis on spectral evolution and focused field enhancements. We conclude that, for a given pair of inner and outer shell radii, phase retardation and core offsets can be used together to design nanoparticles with a desired scattering and absorption ratio at the dipolar resonance.

2. Calculating nanoparticle spectra

The near- and far-field optical properties of nanoshells, nanoeggs and nanocups were solved numerically in the frequency domain using the scattered field formulation. Problem definition, solution and analysis were all conducted using Matlab (R2007a) in conjunction with the scripting functions of a commercially available FEM package (COMSOL Multiphysics 3.4 with the RF module).

The 3D simulation space was composed of four spherical volumes: a core, a shell, an embedding medium and a perfectly matched layer (PML). The nanoparticle core was silica ($\varepsilon_1 = 2.04$), embedded in a gold shell modelled using the empirically determined bulk dielectric constants by Johnson and Christy with linear interpolation [17]. The embedding medium was air. A plane wave, used for excitation, was inserted on the inside of PMLs surrounding the embedding medium [18].

The dimensions of the embedding volume and the PML were chosen such that increasing the size of the nanoparticle further would not affect the simulation results. For symmetric nanoshells, the absorption and extinction spectra calculated using COMSOL matched Mie theory in both extinction amplitude and peak wavelength (figure 1(a)).

Discretization of the simulation space was conducted using the built-in free meshing algorithm in COMSOL, which partitioned the simulation space into a collection of tetrahedral finite elements. Large field enhancements, resulting from plasmon resonances, required the application of mesh constraints to ensure convergence of the simulation in the visible and near-infrared (NIR) ($\lambda = 400–1500$ nm). The nanoshell and nanoegg surfaces were restricted to a maximum triangle mesh side length of 10 nm with an element growth rate of 1.40, specifying that elements adjoining the nanoparticle surface could be no more than 1.4 times the size of surface elements. Nanocups, where the abrupt core–shell intersection results in high field gradients, required a maximum edge mesh length of 1 nm and an element growth rate of 1.3 for convergence. Typical nanoparticle meshes using the constraints listed here resulted in $1 \times 10^5–5 \times 10^5$ degrees of freedom (the number of parameters required for describing the scattered electric field in a simulation space).

The core offset parameter $D$ is defined as the dimensionless quantity $D = \text{offset}/(r_2 - r_1)$, where $r_1$ and $r_2$ are the radii of the nanoparticle core and shell, respectively. The $D$ parameter defines particles in this paper as nanoshells when $D = 0$, nanoeggs ($0 < D < 1$), and nanocups ($D > 1$). Due to unphysical field enhancements, and the associated difficulty in reaching convergence, results have been omitted for nanocups with core offsets of $D = 1–1.4$

Far-field extinction spectra were obtained by summing the far-field absorption ($Q_{\text{abs}}$) and scattering ($Q_{\text{scat}}$) efficiencies. Scattering spectra were calculated on a spherical boundary using

$$Q_{\text{scat}} = \frac{1}{\pi r_2^2 E_{\text{inc}}^2} \int |E_{\text{far}}|^2 R_t^2 \cdot d\Omega,$$

where $R_t$ is the radius of the boundary used for calculating the far-field transform, $E_{\text{far}}$ is the vectorial far-field component of the scattered field calculated with the COMSOL implementation of the Stratton–Chu formula [19] and $E_{\text{inc}}$ is the incident electric field amplitude. The factor of $R_t^2$ inside the integral is introduced automatically by COMSOL as a normalization factor during the boundary integration, and must be removed during post-processing to obtain the correct magnitude of $Q_{\text{scat}}$. Absorption efficiencies were determined
similarly by integrating the time-averaged resistive heating ($U_{av}$):

$$Q_{abs} = \frac{1}{\pi r_2^2} \frac{2}{\sqrt{\varepsilon_0/\mu_0}} \int (U_{av}) \, dV.$$  \hspace{1cm} (2)

Near-field enhancements at a point $p$ are defined as the total electric-field amplitude ($E_{tot}$) at the nanoparticle surface normalized to the incident field magnitude ($\eta_p = E_{tot}/E_{inc}$) where, on resonance, the total electric field near the particle surface is dominated by scattering ($E_{tot} \approx E_{scat}$). In the context of this study, the enhancement is determined by taking the average of the ten largest scattered field elements above the nanoparticle surface. Spectral peak wavelengths and amplitudes were determined using a custom analysis code in conjunction with a cubic spline interpolating function to reduce granularity in the calculated spectra.

The computational cost of calculating scattering and absorption spectra for a given geometry was significant, with a single particle geometry requiring 5–10 h using the PARDISO direct solver with shared memory parallelism enabled. Simulations for multiple geometries were performed in parallel on multiple 64-bit compute nodes, each with 16 GB of RAM and eight 2.83 GHz Intel® Xeon® cores. Desktop workstations performing these same calculations, using 64-bit single- or dual-core processors and 8 GB of RAM, required 4–8 times longer.

3. Simulation results

3.1. Far-field spectra of nanoparticles

The far-field spectra of $[r_1, \ r_2] = [30, \ 35]$ nm nanoshells, nanoeggs and nanocups as a function of core offset parameter $D$, along with their associated multipolar resonances, are shown in figure 1. For nanoshells ($D = 0$), the FEM and Mie calculations agree with each other (figure 1(a)). For core offsets ranging from $0 < D < 0.32$, the spectra continue to closely resemble that of a nanoshell. As $D$ is increased beyond that range, several multipolar peaks begin to appear, subsequently redshifting with increasing core offset. Once the core pierces the shell, forming a nanocup, we observe a very similar multipeaked, redshifted spectrum. Additional increases in $D$, as the core moves further outside the shell, cause the peaks to blueshift until they are resonant with the interband transitions of Au and are damped. Qualitatively similar spectral properties were obtained for $[45, \ 52.5]$ nm and $[60, \ 70]$ nm particles, indicating that the trends observed here are quite general for particles beyond the quasistatic regime.

The formation of multipolar spectra when $D \approx 1$ for both nanoeggs and nanocups can be understood simply as the mixing, or hybridization, of primitive sphere and core plasmons. For nanoeggs, plasmon hybridization has produced an analytical solution [20]; however, no such solution yet exists for nanocups. The plasmon hybridization picture, however, allows us to develop a physical understanding of the calculated resonances without the need for an explicit solution [21]–[23].

In the spherically symmetric case, multipoles of the primitive plasmon modes can interact only with modes of the same angular momentum index: dipolar sphere modes hybridize only with dipolar cavity modes, for example. With the reduced symmetry of nanoeggs, this selection rule is relaxed and the multipolar primitive sphere plasmon modes, for example, can hybridize with all multipolar cavity plasmon modes. The resulting hybridized energy levels can then contain elements of the many multipolar modes. As $D \rightarrow 1$, an increasing number of optically active modes appear, and the modes redshift, even in the quasistatic limit, due to the increased...
Figure 1. Far-field extinction properties of \([r_1, r_2] = [30, 35]\) nm nanoeggs and nanocups composed of a gold shell surrounding a silica core with displacement \(D = \text{offset}/(r_2 - r_1)\). (a) Extinction spectra for a plane wave polarized as indicated in diagram (spectra offset for clarity). Black lines were calculated using FEM; red dots overlaid on the \(D = 0\) spectra are the corresponding Mie theory result. (b) Peak wavelengths of multipolar extinction spectra shown in (a). Coloured lines indicate peak wavelengths (red squares, \(l = 1\); green circles, \(l = 2\); purple triangles, \(l = 3\); light blue inverted triangles, \(l = 4\); dark blue diamonds, \(l = 5\)). Grey circles denote wavelength of maximum \(E\)-field enhancement.

interaction between primitive plasmon modes. Following previous notation, we refer to these mixed mode resonances using the multipolar index \(l\) corresponding to the orthogonal modes of a symmetric nanoshell \([12]\).

For nanocups \((D > 1)\), the pure cavity and sphere hybridization model no longer applies. However, due to geometry and different dielectric embedding media, there are distinct plasmons associated with the cavity inside the cup, which is in contact with silica, and the outer surface of the shell, which is in contact with air. As with nanoeggs, these two primitive plasmons hybridize and form mixed mode resonances which may also be referred to using the multipolar index \(l\). As \(D\) increases, and the core moves further outside of the shell, the primitive plasmon modes hybridize more weakly, resulting in a subsequent blueshift of the multipolar modes. Nanocup modes without strong inherent dipolar components, such as the \(l = 4\) and
3 peaks, weaken and vanish as $D \to \infty$, since they can only be excited in the case of strong hybridization.

These results show strong similarity to previous work by Cortie and Ford [6], which included the calculated extinction spectra of a [35, 50] nm nanocup with flat edges. A quantitative comparison between their semi-shell nanocup geometry and the offset-core geometry reported here is not possible due to differing sizes, core–shell aspect ratios and embedding media. However, they do observe a strong resonance (which they denote as $\alpha$) at 610 nm for light polarized parallel to the cup’s axis of symmetry which corresponds to the dipole-active $l = 3$ multipolar resonance of the offset-core nanocups. As Cortie and Ford decrease the cut-off height of the semi-shell, which is analogous to increasing $D$, they observe a blueshifting and weakening of this resonance, in agreement with figure 1.

The two weakest, and most redshifted, plasmon resonances for nanocups (figure 1(b)) have not been observed in previous experiments [10, 13]. The absence of these peaks could be partially due to modification of the bulk dielectric function by size-dependent electron scattering [24] for large core–shell offsets, as the electron mean free path may be significantly reduced due to shell thinning which would weaken and broaden plasmon peaks, while leaving the peak wavelengths essentially unchanged [6, 25, 26]. However, whether or not the bulk dielectric function needs to be modified is controversial. Single-particle spectroscopic measurements of nanoshells correlated with the Mie theory suggest that inhomogenous broadening may be the dominant factor in plasmon linewidth broadening, not deviations from the bulk dielectric function [27].

3.2. Nanoegg near-field properties

Changing of the core offset $D$ causes significant changes in both the spatial volume and intensity of the enhanced near-fields of the nanoegg structure. The near-field focusing of a nanoegg can be increased in two ways: offsetting the core and, for a given core offset, exciting the nanoegg at a higher-energy multipolar resonance.

Increasing core offsets always causes more intense focusing of the $l = 1$ peak. Higher energy hybridized modes will also increase the field enhancement, as shown in the near-field plots in figures 2(a)–(d), calculated at the four extinction peaks. For all plasmon resonances, enhancement occurs on the outer shell surface and is strongest on the thinnest part of the nanoegg.

Field enhancements at the $l = 1$ peak, along with the maximum field enhancement attainable for a given nanooegg core offset, are shown in figure 2(f) for three sizes of nanooegg with identical core/shell ratios. Most experimentally accessible geometries will have $D = 0–0.8$, where the maximum enhancement occurs at the $l = 1$ peak.

The field enhancements shown in figure 2(f) were independent of meshing, as the continuous layer of gold around the nanoegg core lacks sharp edges or discontinuities in the simulation space. Enhancements for nanocups are not reported, however, since the sharp tips that result from a simple core-offset model produce unphysical field enhancements (up to 700) with a strong dependence on meshing parameters. Spectra for the cups reported here do show good qualitative agreement with previously reported cup structures without sharp tips [6, 13], suggesting that their far-field properties are not completely dominated by tip effects. For both structures, the field enhancements reported here could be significantly affected by the surface roughness and shell defects inherent to chemically synthesized particles [6, 16].
Figure 2. Local field enhancement properties of nanoeggs as a function of core offset. (a)–(d) Field enhancements ($G$) of a [30, 35] nanoegg with a 4.6 nm core offset ($D = 0.92$) at the four scattering peaks. Scale bars are 2 nm. (e) Far-field extinction spectra corresponding to field enhancement plots. (f) Comparison between the maximum $E$-field enhancement at the dipole scattering peak ($G_{\text{ext}}^{l=1}$, solid lines) and the maximum enhancement calculated within the entire spectrum for each offset ($G_{\text{max}}$, dashed lines). Red [30, 35] nm, green [45, 52.5] nm and blue [60, 70] nm. (g) Blueshifting of $E$-field enhancement peak compared to the extinction peak for the $l = 1$ mixed mode.

The difference between the wavelength of maximum field enhancement and the extinction wavelength for the mixed $l = 1$ mode ($\Delta \lambda = \lambda_{\text{max}}^{l=1} - \lambda_{\text{ext}}^{l=1}$) is shown in figure 2(g). For nanoshells, it is well known that the maximum field enhancement is always redshifted relative to the extinction peak [28]. For nanocups, we find that the enhancement peak blueshifts relative
to the extinction peak for increasing $D$. This offset is more significant for larger nanoeggs, and could prove critical when designing nanoeggs with a desired field enhancement maximum.

3.3. Tuning relative absorption and scattering efficiencies

In the quasistatic regime, the extinction spectrum of nanoparticles is dominated by absorption; larger particles tend to be dominated by scattering [29]. Controlling the relative magnitudes of scattering and absorption will facilitate further optimization of nanoparticles for use in the NIR.

Scattering and absorption efficiencies for three core-offset nanoparticles calculated at their $l = 1$ extinction peak are shown in figure 3. In panel (a) the absorption and scattering efficiencies of a quasistatic [30, 35] nm nanoegg decrease as the core is offset, and then increase slowly after the core pierces the shell to form a nanocup. Panel (b) shows a larger, [45, 52.5] nm particle. While absorption still slightly dominates when $D = 0$, increasing offsets increase the absorption efficiency slightly until $D > 0.5$. Panel (c) shows that an even larger [60, 70] nm nanoegg, solidly beyond the quasistatic limit and dominated by scattering when $D = 0$, can have a dipole extinction peak dominated by absorption for sufficiently large offsets.

4. Concluding remarks

Much as lenses can be used for focusing light onto an object of interest, nanoeggs may be viewed as tuneable nanoscale optical lenses that can be used for illuminating a molecule or molecules of interest for surface-enhanced spectroscopies. Just as one must select a lens with the correct properties, a nanoparticle lens must be designed to focus light into a hotspot matched to the size of the molecule of interest. The varying degrees of hotspot confinement corresponding to both offset and multipolar order show that a nanoegg functions as a highly chromatic nanolens,
with the volume of the enhanced field associated with each multipolar resonance optimized for different sizes of analyte.

We have shown that controlling this type of tuning is possible by varying the core offset parameter $D$, and by choosing which multipolar resonances should be excited. Taking into account the relative blueshift between the $l = 1$ enhancement and extinction peaks could prove important for further optimizing nanoeggs as active SERS substrates.

For applications where absorption is a desirable property, small nanoshells with their tunable plasmon frequency and strong absorption characteristics are ideal. If a larger particle is required, or dictated by the available chemical synthesis methods, we have shown that the relative contribution of absorption to the extinction spectrum can be increased by offsetting the particle core. Such offsets could be achieved experimentally by electroless plating [12] or evaporation onto spherical templates [7].

For medical imaging applications, where scattering is desirable, large symmetric nanoshells give significantly larger signals than either gold nanoparticles, or asymmetric structures such as nanoeggs, cups, or rods [30]. These results suggest that an admixture of large nanoshells, for imaging and tuneable absorbers, such as nanorods or nanoeggs, for photothermal therapy, may improve the efficacy of hybrid biomedical imaging and treatment applications, including cancer treatment [2].

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