

Optical properties of gold nanostructures

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I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

“In particular, she had a wonderful sense of humor, and I learned from her that the highest forms of understanding we can achieve are laughter and human compassion.”

Richard Feynman

to Simina,

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¹<http://cran.r-project.org/>

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¹<http://had.co.nz/ggplot2/>

Abstract

The optical properties of gold in the visible are dominated by the response of the free conduction electrons to light. In gold nanostructures, the surface charge density adopts a configuration that is constrained by the shape of the nanoparticles. As a result, the scattering of light by gold nanoparticles exhibits a resonant response characterised by a strong scattering and absorption in a narrow range of frequencies. The spectral range of this *localised surface plasmon resonance* (LSPR) can be tuned by varying the size and shape of the gold nanoparticle — the nanoparticles act as nanoscale antennas for the visible light. Confirmation of this scaling rule is obtained by conducting experiments with nanoparticles of varying size and aspect ratio. Such particles are fabricated by electron-beam lithography, and characterised by dark-field spectroscopy. Not only does the LSPR shift in frequency with a change of particle size, but its spectral lineshape is also modified. The intensity and width of the LSPR are dictated by a variety of factors that are related to the intrinsic material properties (the complex dielectric function of gold), and to the particle geometry and environment.

The optical response of small gold nanorods is well described by a simple oscillating dipole model — the incident electromagnetic field induces a current in the particle that re-radiates light (scattering). A series of refinements can be made to model more accurately the optical response of realistic particles. If the dipole moment characterising the particle is allowed to vary in phase across the particle, retardation effects provide a correction for the effective dipole moment of the particle. As the particle size approaches the wave length in the surrounding medium, the dipolar approximation breaks down and higher order multipoles need to be considered. The Mie theory provides a very accurate description of the response of spheres of arbitrary size. Further, the T-matrix and other numerical techniques can be employed to accurately reproduce the scattering properties of particles of arbitrary shapes.

When the scattering sample consists of a collection of gold nanoparticles, the collective optical response is affected by two key factors. First, the measured

LSPR is a convolution of the distribution of particle sizes with the individual response of a single particle. This leads to an inhomogeneous broadening of the LSPR lineshape. Second, the light that is scattered by one such particle near resonance can strongly affect its neighbours which scatter light in proportion to the net field they experience, that is the sum of the incident field plus the perturbation arising from the neighbouring particles. The onset of such multiple scattering events is observed even for particle separations that are several times larger than the particle size.

Several regimes of interaction can be distinguished according to the ratio separation / wavelength. First, when the particles are in close proximity (separation \ll wavelength), near-field interactions dominate and result in a spectral shift of the LSPR accompanied with a spectral broadening. Second, when the separation is commensurate with the wavelength, a coherent interaction can develop that couples a large number of particles. In ordered arrays, such coupling gives rise to a geometrical resonance that can strongly affect the LSPR of the particles. In particular a sharp spectral feature is observed that depends on both the single particle response and the geometrical arrangement of the particles in the array.

The coherence of such multiple scattering in diffractive arrays of gold nanoparticles can be broken by introducing disorder in the distribution of particle sizes, or in the particle positions. The optical properties of an irregular array reflect the departure from a periodic system and the spectral lineshape evolves as the level of disorder is increased. In the limit of uncorrelated positions, the diffractive coupling is suppressed and the response of the collection of the particles rejoins the response of isolated particles.

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