

Metal Nanoparticle Ensembles: Collective Optical Properties

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INTRODUCTION

Ensembles of gold and silver nanoparticles in the 10- to 100-nm size range exhibit collective electromagnetic properties, which can be tuned according to particle size and interparticle spacing. Self-assembly is a critical enabling mechanism for organizing nanoparticles into ensembles with well-defined lattice structures or geometries, if particle dispersion forces can be adequately controlled. Presented here are several recent theoretical and experimental studies on metal nanoparticle assemblies with novel and technologically appealing optical properties. For example, gold nanoparticles with intense plasmon resonances can be organized into planar arrays or spherical ensembles around dielectric cores, and serve as substrates for surface-enhanced Raman scattering (SERS). Recent theoretical developments indicate that the electromagnetic field factors responsible for such enhancements can be further tuned by adjusting the diameter-spacing ratio, enabling the optimization of metal nanoparticle ensembles for various applications in sensing and nanophotonics.

SURFACE PLASMONS

Gold and silver nanostructures are well known to exhibit electrodynamic phenomena commonly referred to as surface plasmons (see entry on “Surface Plasmon Spectra of Gold and Silver Nanoparticles”). These are generated by the collective excitation of free electrons in the metal particle, in response to a characteristic electromagnetic frequency. The surface plasmon modes of metal nanostructures have essentially the same function as radio antennas, except that they resonate in the optical and near-infrared (NIR) regions of the electromagnetic spectrum. Surface plasmons can be categorized into two types: localized plasmon resonances, in which incident light is absorbed or scattered by the oscillating electric dipoles within a metal nanoparticle, and surface plasmon polaritons, which propagate along metal surfaces in a waveguide-like fashion until released at some distance from their point of origin (Fig. 1). Localized plasmon resonances generate electromagnetic field factors, which en-

hance linear and nonlinear optical effects near the metal surface. The localized plasmonic responses of individual metal nanoparticles are now quite well understood and have been summarized in several recent works.^[1–3] On the other hand, metal nanoparticle ensembles can support both localized and propagating surface plasmon modes, whose physical relationships are less well defined. Regardless of the complexity of these phenomena, the plasmonic coupling of metal nanostructures with light enhances a broad range of useful optical phenomena, such as resonant light scattering (RLS), surface plasmon resonance (SPR), and SERS, all of which have tremendous potential for ultrasensitive chemical and biomolecular detection and analysis.

The plasmonic responses of coupled metal nanostructures are capable of intensifying local electromagnetic fields by many orders of magnitude. For example, many of the early SERS observations in the late 1970s and early 1980s were performed using kinetically formed aggregates of Ag and Au nanoparticles.^[4] Interest in SERS has been further stoked by reports of single-molecule SERS spectroscopy;^[5–7] however, the reproducibility of such activities has been poor. Despite strong evidence that aggregated nanoparticles can generate “hot spots” that produce enormous enhancements in Raman intensities, these vary widely from sample to sample and often disappear after a few days’ aging. The conditions that enable reproducibly high SERS enhancements have yet to be established, and constitute an important challenge in nanomaterials synthesis.

FABRICATION OF NANOPARTICLE ASSEMBLIES

In the last few years, significant progress has been made in the fabrication and optical characterization of metal nanoparticle assemblies in one, two, and three dimensions. Much of this work has been directed toward the self-assembly and materials properties of nanoparticle assemblies in which the unit particle size is below 10 nm (radius $R < 5$ nm); these have been reviewed elsewhere.^[8–10] More recently, several investigations have focused on



Fig. 1 Incident light on nanostructured metal surfaces can result in localized (standing) plasmon resonances (a), propagation of surface plasmon waves (b), or a combination of the two (c). Excitation of conduction electrons produces local electromagnetic fields (pink) near the metal surfaces. (View this art in color at www.dekker.com.)

metal nanoparticle assemblies with unit structures in the 10- to 100-nm range, the central theme of this entry. Both theoretical considerations and experimental investigations of discrete clusters and extended arrays of these mid-nanometer-sized nanoparticles will be discussed. It will become evident that in addition to particle size, structural parameters such as interparticle distance, lattice geometry, and periodic order also have important roles in the collective optical responses of these ensembles.

Discrete Clusters of Metal Nanoparticles

Plasmon-resonant nanoparticles can experience significant dipolar coupling when their interparticle separation δ is on the order of diameter $2R$ or less where R is nanoparticle radius, giving rise to additional plasmon modes. Effective-medium theories such as the Maxwell-Garnett formula, which can accurately describe the plasmon resonance of isolated metal particles below 30 nm, can provide only a limited approximation of the optical responses by coupled nanoparticles.^[11] These approximations lose their accuracy if δ is much less than one particle diameter ($\delta < 1.5R$), at which point evanescent (near-field) coupling becomes significant.

Simulations of discrete N -particle systems based on generalized Mie theory^[1,12] or numerical approaches such as discrete dipole approximation^[13,14] appear to provide more consistent models of coupled metal nanoparticles. These have been used to predict the extinction and ab-

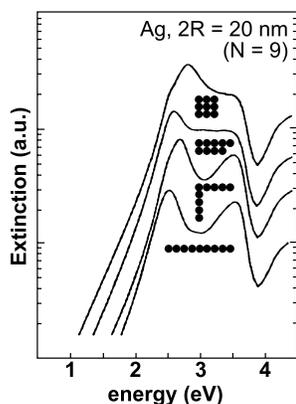


Fig. 2 Extinction spectra of 20-nm Ag particle aggregates in different geometries, as calculated by generalized Mie theory. (Adapted from Ref. [1].)

sorption cross sections of specific aggregate structures, such as chained particles in linear or bent conformations (Fig. 2). Linear chains of Ag nanoparticles produce longitudinal plasmon resonances at strongly redshifted wavelengths, whereas close-packed aggregates exhibit less pronounced shifts in their collective plasmon resonance frequencies. The optical responses of these N -particle clusters in fact correlate closely with anisotropic metal particles of similar overall shape, such as nanorods^[15,16] and nanoprisms.^[13,14,17]

More recent theoretical treatments have given emphasis to the local electromagnetic fields generated near the metal nanoparticle surfaces, with the objective of defining regions with the highest field factors (often quantified as a function of $|E/E_0|$ where E and E_0 are the plasmon-enhanced and incident electric field intensities) for a given frequency ω . This is especially important for surface-enhanced spectroscopies such as SERS, in which signals are amplified as a function of $G_{EM} = |E(\omega)/E_0(\omega)|^2 \cdot |E(\omega')/E_0(\omega')|^2$, where G_{EM} is the local Raman enhancement factor and ω and ω' are the incident and Stokes-shifted frequencies, respectively.^[18] In the simplest case of a two-sphere system, it is widely agreed that local field factors are greatest when the two particles are almost touching. Xu and coworkers have performed electrostatics calculations on pairs of Au and Ag particles (10–90 nm) separated by as little as 1 nm, and suggested G_{EM} values more than 10^{11} for the best cases.^[19] These localized enhancements are exquisitely sensitive to interparticle spacing; changes in δ by just a few nanometers can cause the local enhancements to drop by several orders of magnitude (Fig. 3). These calculations, in conjunction

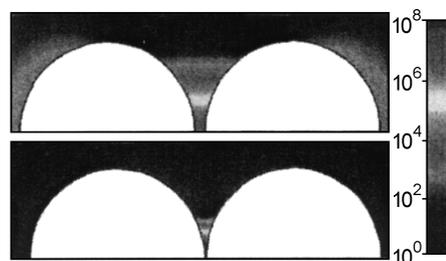


Fig. 3 Electrostatics simulation of local field enhancements (G_{EM}) between two 90-nm Ag particles at interparticle separations of $\delta = 5.5$ and 1.0 nm. (From Ref. [19].)



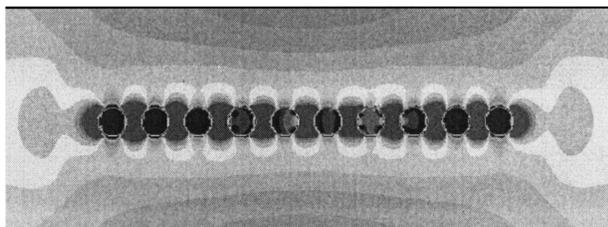


Fig. 4 Finite-difference time-domain simulation of electric fields (red) localized within a linear array of 50-nm Au particles (blue), with interparticle separations of $\delta=75$ nm. (From Ref. [23].)

with experimental studies by the same group,^[7,20] imply that nanoparticle dimers have potential as substrates for routine single-molecule SERS, given a reliable method for localizing analytes in regions of high field.

Linear Arrays of Metal Nanoparticles

Linear (1-D) arrays of metal nanoparticles have attracted much interest for their potential to transport energy in an antenna-like fashion and serve as near-field optical waveguides at subwavelength dimensions, with the possibility of integrating nanophotonics with far-field optical devices.^[21] Theoretical calculations of vectorial energy transport through chains of closely spaced 50-nm Au nanospheres suggest remarkably high levels of transmission at optical resonance, with optimized losses ranging between 10 and 25 dB per micron (Fig. 4).^[22,23] Several methods for producing nanoparticle 1-D arrays have been reported, including self-assembly on prepatterned surfaces^[24] and inside of nanoporous templates^[25,26] as well as by directed assembly using scanning probe microscopy tips.^[21]

Recent experimental studies on plasmonic 1-D nanoarrays have so far been promising. Proof of concept was established by Krenn and coworkers, who used photon scanning tunneling microscopy to image near-field excitations within Au nanoparticle chains.^[27] Near-field optical transport in linear arrays of Au nanoparticles and Ag nanorods was also recently demonstrated by Maier et al.^[23,28] The latter case was shown to support plasmon propagation with losses as low as 6 dB per 200 nm, which suggests their feasible integration into all-photonic device architectures.

Two-Dimensional Arrays of Metal Nanoparticles

Several methods have been employed for arranging metal nanoparticles into periodic and aperiodic two-dimensional (2-D) lattices. Periodically ordered 2-D arrays

with relatively large interparticle spacings ($D/2R=1.5$ to 5, where center-to-center distance $D=2R+\delta$) have been fabricated by electron-beam lithography^[29,30] or by self-assembly on lithographically defined surfaces^[24] (for some recent examples see Refs. [31,32]). Aperiodic 2-D arrays of the same genre have also been produced by self-assembly techniques, mostly by random sequential adsorption onto charged surfaces.^[33–37] For these cases, the collective optical properties of nanoparticles are dominated by dipolar coupling mechanisms; however, their responses are more complex than predicted by classical dipole–dipole interactions, whose strength varies with $1/D^3$. Particles larger than 30 nm can exhibit sizable retardation effects in their dipolar interactions, and this can impact both the wavelength and decay time of their coupled plasmon resonances.^[29,38] For example, Chumanov et al. observed a remarkable blueshifting and narrowing of extinction maxima in submonolayer films of 100-nm Ag particles as a function of packing density.^[33] This was later reproduced in lithographically defined Ag nanoparticle 2-D arrays, and reexamined as a function of particle diameter–spacing ratio.^[37] Recent theoretical analyses by Zhao and coworkers suggest that the blueshifting and narrowing are largely due to radiative dipolar coupling, an electrodynamic term that scales largely with $1/D$.^[39]

Aperiodic 2-D arrays may also provide a practical and straightforward method for preparing SERS substrates.^[34–36] Submonolayer ensembles of colloidal metal particles can be prepared with packing densities of up to 30% (Fig. 5, left), which is well below the close-packing limit ($\sim 90\%$) but sufficient to produce significant electromagnetic coupling and SERS.^[34–36,40] Electrostatic self-assembly of Au nanoparticles on spherical submicron particles has also been reported recently;^[41] in this case, packing densities on the order of 50% can be achieved by increasing the nanoparticles' surface potentials, with a concomitant enhancement in electromagnetic coupling (Fig. 5, right).

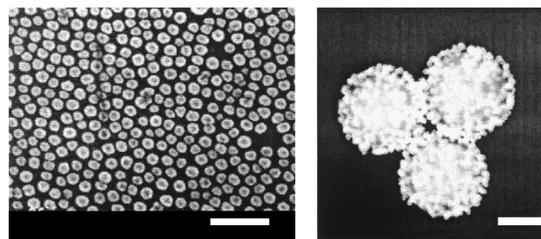


Fig. 5 Left: planar ensemble of 40-nm Au particles adsorbed onto thiol-functionalized SiO_2 . (From Ref. [40]. Copyright 1995, American Chemical Society.) Right: spherical core-shell ensembles of 30-nm particles adsorbed onto amine-functionalized 390-nm SiO_2 particles. (From Ref. [41].) Scale bar=200 nm in both images.



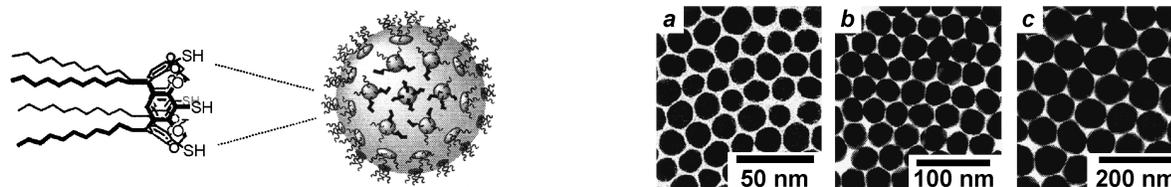


Fig. 6 Self-organized 2-D arrays of resorcinarene-encapsulated Au nanoparticles. Unit particle sizes: (a) 16 nm; (b) 34 nm; (c) 87 nm. (From Ref. [45]. Copyright 2001, American Chemical Society.)

2-D nanoparticle arrays with much smaller interparticle spacings ($D/2R < 1.1$) are likely to support strong near-field coupling as well as dipolar coupling, and should be excellent substrates for generating SERS and other surface-enhanced spectroscopies. In principle, such nanoparticle ensembles should also be accessible by thermodynamic self-assembly; however, metal particles in the midnanometer size range experience strong interaction potentials that can promote kinetic aggregation, resulting in poorly defined structures. This can be viewed as a problem in dispersion control: If repulsive interactions can offset particle self-attraction at close range, conditions for thermodynamically controlled self-organization can be achieved. Earlier demonstrations by Schmid et al.^[42] and by Giersig and Mulvaney^[43,44] have indicated that colloidal Au particles can be organized into close-packed domains with local 2-D order.

A general method for organizing metal nanoparticles into hexagonal close-packed 2-D arrays has recently been developed by Wei and coworkers, using multivalent macrocyclic surfactants known as resorcinarenes.^[45,46] These compounds are capable of extracting colloidal Au particles from aqueous suspensions and dispersing them in-

to organic solvents or at air–water interfaces.^[47] In the latter case, resorcinarene-stabilized nanoparticles as large as 170 nm have been organized into 2-D arrays with excellent local order (Fig. 6). Here the $D/2R$ ratios are well below 1.1; careful inspection of the TEM images reveals an inverse correlation between array periodicity and interparticle spacing δ , most likely due to greater van der Waals attraction with unit particle size.

The periodic 2-D nanoparticle arrays exhibit size-dependent optical properties at visible and NIR wavelengths. The gold nanoparticle films vary in hue from blue ($2R = 16$ nm) to a faint gray ($2R > 70$ nm), the latter being strongly absorptive in the NIR region (Fig. 7). The specular reflectance is also dependent on periodic structure, with maximum reflectance of white light observed for $2R$ between 40 and 70 nm.^[48] These variable reflectivities can be attributed to several effects: 1) an angular dependency in attenuated reflection as a function of surface roughness, a well-studied phenomenon in metallic thin films;^[49] 2) size-dependent optical absorption, with significant absorptivities in the visible region for nanoparticle arrays with periodicities below 40 nm; and 3) size-dependent increases in Mie scattering, a phenomenon that has been

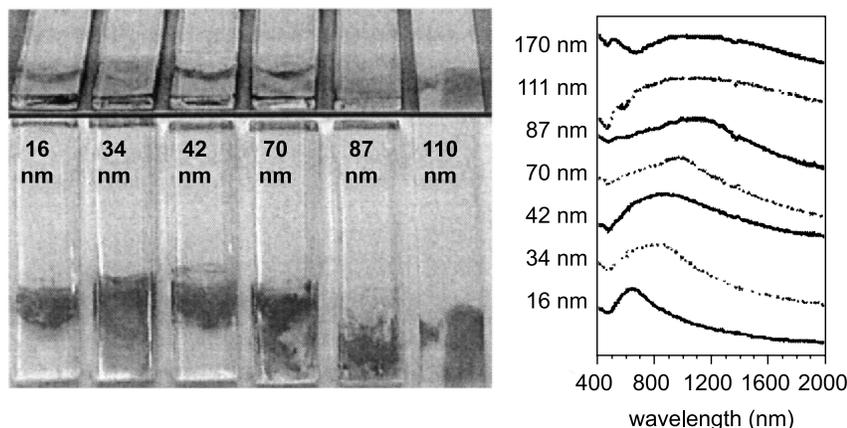


Fig. 7 Size-dependent optical properties of Au nanoparticle arrays. (From Refs. [45,48].) Left: 2-D nanoparticle arrays transferred onto annealed quartz substrates, as viewed directly (bottom) and with specular reflectance (top, $\theta_i = 60^\circ$). Substrates are approximately 1 cm wide. (Reproduced by permission of the Materials Research Society.) Right: extinction spectra of 2-D nanoparticle arrays. (Copyright 2001, American Chemical Society.)



characterized for nanoparticles and nanostructured metal surfaces with roughnesses on the order of 40 nm or more.^[1,2,49]

The 2-D nanoparticle arrays also exhibit size-dependent SERS activities, with excellent levels of signal enhancement in many cases.^[50] Surface-averaged Raman signals generated from the adsorbed resorcinarenes could be optimized as a function of periodicity and excitation wavelength, with enhancements as high as 10^7 . The observed trends are in accord with previous theoretical calculations describing electromagnetic SERS,^[51–54] and also with SERS studies on disordered metal colloid aggregates.^[55–57] However, the resorcinarene-stabilized nanoparticle arrays have considerable advantages in reproducibility and stability, and retain essentially all SERS activity more than a year after self-assembly. Additional signal enhancement could be obtained by increasing the solid angle of incidence and collection; the angle-dependent Raman intensities suggest that propagating surface plasmons in the Au nanoparticle films contribute significantly to the SERS effect.

The colloidal Au nanoparticle arrays are capable of detecting exogenous analytes by SERS and thus have potential as spectroscopic chemical sensors.^[50] Volatile organic compounds adsorbed onto the array surface produce a detectable signal within seconds; removal of the surfactant layer by plasma treatment further increases the arrays' sensitivities and enables the reproducible detection of analytes in aqueous solutions at micromolar concentrations.^[58] However, recent theoretical calculations indicate that detection limits can be further lowered by adjusting the interparticle spacing. An incremental change in δ delocalizes field intensities but at the same time increases the available sampling space for analyte detection. Recent calculations by Genov et al. indicate that the surface-averaged enhancement factor G_R (as opposed to the local factor G_{EM}) from periodic nanoparticle arrays can be maximized as a function of excitation wavelength

at a given value of $2R/\delta$, and can surpass that produced by disordered metal–dielectric films by several orders of magnitude (Fig. 8).^[59]

3-D Superlattices of Metal and Metallodielectric Nanoparticles

In addition to enhancing spontaneous emission events such as SERS, metal nanoparticle superlattices may also be capable of blocking electromagnetic radiation at select frequencies, i.e., a photonic band gap. Highly monodisperse particles on the order of an optical wavelength are well known to crystallize into 3-D superlattices, and often produce opalescent Bragg reflections. Colloidal crystals may also exhibit photonic band gaps in the visible to NIR range, and have been highly sought after as a way to manipulate the flow of light.^[60] In principle, a photonic band gap can be engineered from nearly any type of material by periodically modulating its dielectric properties. However, lattices with relatively low dielectric contrast are not optimal materials for designing photonic band gaps at optical wavelengths. Periodic metal–dielectric nanostructures are capable of much stronger optical modulation; “inverse-opal” metal-coated colloidal crystals have recently been fabricated and have some promise as photonic band-gap materials.^[61]

Theoretical studies by Moroz indicate that plasmonic colloidal crystals can support a complete photonic band gap in the visible and even the near-UV range.^[62] Close-packed, face-centered cubic (FCC) crystals of colloidal Ag particles were calculated to possess tunable band gaps, at frequencies defined by the particle radius and plasma wavelength (R/λ_p) and with relative gap widths between 5% and 10% as defined by $(\Delta\omega/\omega_c)$, the gap width to mid-gap frequency ratio. The photonic band gaps were predicted to be greatest for colloidal crystals with $R/\lambda_p > 0.9$; for Ag, 3-D arrays of large, submicron-sized

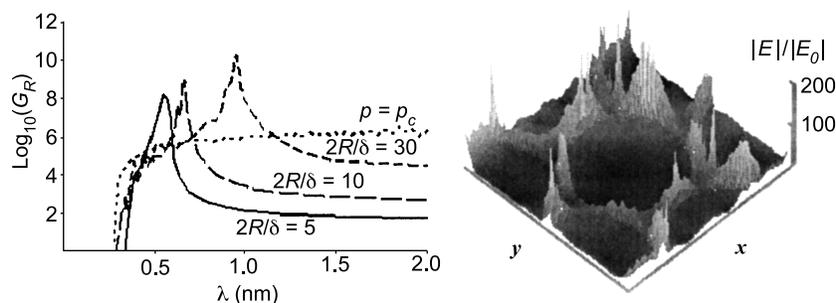


Fig. 8 Left: numerical calculations of surface-averaged field enhancements (G_R) from 2-D hexagonal superlattices, with diameter–spacing ratios of 5, 10 and 30, vs. a random metal–dielectric film at the percolation threshold ($p=p_c$). (From Ref. [59].) (Copyright 2003, American Chemical Society.) Right: local field distribution within a hexagonal lattice produced by p -polarized light ($\lambda=600$ nm, $2R/\delta=10$).



particles would be needed to produce band gaps for visible wavelengths.

A related study by Zhang et al. suggests that tunable photonic band gaps can also be made using metal-coated, core-shell nanoparticles as 3-D array elements.^[63] The band gaps of these materials are predicted to be less dependent on long-range order, a critical and challenging issue in the self-assembly of colloidal crystals. Photonic band gaps have been calculated for FCC lattices of SiO₂/Ag core-shell nanoparticles of different sizes and packing densities: 500/50-nm core-shell particles at 45% packing density are expected to have a robust band gap centered at $\lambda=1.5$ μm , whereas 160/50-nm core-shell particles at 42% packing density are expected to have a band gap across the visible spectrum. Graf and van Blaaderen have recently reported a closely related core-shell colloidal crystal, in which a second dielectric shell has been grown around the metal-coated nanoparticle.^[64] The outermost SiO₂ shell reduces the van der Waals interactions considerably, and permits their self-organization into colloidal crystals with fractional densities close to that proposed by Zhang et al.^[63]

CONCLUSION

In closing, the controlled assembly of metal nanoparticles into well-defined structures can yield novel collective electromagnetic behavior, with excellent potential for function and application. Chemical and bioanalytical nanosensors have already reached a remarkably advanced stage of development, with detection and analysis bordering on the single-molecule limit, and the emerging area of nanophotonics may have long-term impact on telecommunications and device integration.

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