### Chapter 5

### PLASMONIC NANOMATERIALS

## Enhanced Optical Properties From Metal Nanoparticles and their Ensembles

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Abstract: The role of surface plasmons in the optical properties of noble metal nanoparticles is reviewed, with an emphasis on the dielectric function, size and shape effects, and interparticle coupling. Experimental and theoretical studies on the plasmonic responses of individual metal nanoparticles (spheres, rods, and prisms) and the collective behavior of nanoparticle ensembles will be discussed, as well as various photonic applications.

### **1. INTRODUCTION**

The first examples of nanotechnology, some historians might be inclined to argue, could very well be accredited to some glassblowers from the days of imperial Rome. Those ancient craftsmen were able to embed colloidal metal particles within their glassy works to enhance their lustrous qualities. Although they were most likely unaware of the nanoscopic nature of these inclusions, this did not prevent them from appreciating the enigmatic hues produced upon a change of incident light. One of the most striking examples of such Roman glasses is the famed Lycurgus cup, which dates back to the 4th century A.D. The chalice has a dark greenish tint under reflected lighting, but when illuminated from behind the goblet appears red (see Figure 1). These colors are attributed to the optical responses of colloidal gold particles dispersed throughout the glass. Similar phenomena are also featured in the stained-glass windows of many medieval cathedrals, most

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often from colloidal particles of coinage metals such as copper and gold (red) or silver (yellow).



*Figure 1.* The Lycurgus cup (4<sup>th</sup> century A.D.) appears green when viewed with reflected light (*left*), but red when illuminated from behind (*right*). Printed with permission from the National British Museum of History.

Although the technology for producing metal-stained glass had been practiced for centuries, the source of their brilliant colors remained shrouded in mystery until the mid-nineteenth century, when Faraday published his seminal experiments ascertaining the colloidal nature of "red gold."<sup>1</sup> Faraday's work, followed by contributions from Tyndall, Mie, and many others, provided the foundations for understanding the physical behavior and optical responses of metal nanoparticles.

The purpose of this chapter is to review both basic concepts and current developments in the optical properties of metal nanoparticles, particularly gold and silver, and to highlight opportunities for applying such materials to applications which can benefit from their sensitive and tunable electromagnetic responses. Chemical sensing, biomedical imaging, highthroughput screening analysis, and nanoscale photonics are some of the many prospects which have sparked a resurgence of interest in this venerable class of nanomaterials. These activities have been further motivated by recent advances in metal nanoparticle synthesis, nanoscale self-assembly and lithography, and by a growing appreciation for the collective optical responses of metal nanoparticles in ensemble states.

#### 2. Surface plasmons in spherical metal nanoparticles

The strong optical extinctions of conductive metal nanoparticles arise from an electrodynamic phenomenon known as surface plasmons. These are generated by the collective excitation of free electrons in response to a characteristic electromagnetic frequency, very much similar to the function of a radio antenna. The physical nature of surface plasmons will be discussed here in sufficient detail for making useful connections between metal nanostructures and their optical properties; for a more comprehensive treatise on the physics of surface plasmons, the reader is directed to the monographs by Raether<sup>2</sup> and by Kreibig and Vollmer.<sup>3</sup>

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 (see Figure 2). The former are important for generating local field factors, which enhance linear and nonlinear optical effects near the metal surface. However, metal nanostructures often support both types of plasmons simultaneously; in fact, it can be difficult to decouple one from the other, resulting in a confusion of terms. Nevertheless, the plasmonic coupling of metal nanoparticles with light enhances a broad range of useful optical phenomena, such as resonant light scattering (RLS), surface plasmon resonance (SPR), and surfaceenhanced Raman scattering (SERS), all of which have tremendous potential for ultrasensitive chemical and biomolecular detection and analysis.



*Figure 2.* Incident light on nanostructured metal surfaces can generate localized (standing) plasmon resonances (*left*) as well as surface plasmon waves (*right*). Excitation of conduction electrons (red) produces local electromagnetic fields (pink) near the metal surfaces.

#### 2.1 Surface plasmons: theoretical considerations

In the simplified case of a metal nanosphere with radius *R* much smaller than the incident wavelength (a condition commonly referred to as the quasistatic approximation), the plasmon response is essentially dipolar in nature. The strength and frequency of this resonance is related to the total number of electrons in the oscillating dipole (defined essentially by the particle volume, or  $R^3$ ), the complex dielectric function  $\varepsilon(\omega)$ , and the dielectric constant of the local medium  $\varepsilon_d$ . The plasmonic response is directly measureable by optical extinction and can be quite intense; for example, the molar extinction coefficient ( $\varepsilon$ ) for 30-nm Ag particles in water at plasmon resonance ( $\omega_{SP} = 3.25 \text{ eV}$ , or  $\lambda_{SP} = 380 \text{ nm}$ ) is on the order of  $10^{10} \text{ M}^{-1} \text{ cm}^{-1}$ . Extinction includes both absorption and scattering components, which have different scaling relationships with nanoparticle size. The absorption cross section (a theoretical area value used to quantify the number of photons interacting within that region) increases linearly with particle volume, whereas the scattering cross section is relatively smaller but scales with volume squared. Such power functions are approximate and deviate significantly for particles above the quasi-static size limit.

The dipolar plasmon response (oscillator strength) of the nanoparticle is often defined by its polarizability, which can be expressed in terms of the parameters above by the electrostatic Clausius–Mossotti equation (also known as the Lorentz-Lorenz equation):

$$\alpha = 4\pi\varepsilon_0 R^3 \left| \frac{\varepsilon - \varepsilon_d}{\varepsilon + 2\varepsilon_d} \right| \tag{1}$$

The resonance condition leading to maximum polarization is  $|\varepsilon + 2\varepsilon_d| = 0$ , requiring  $\varepsilon(\omega)$  to be negative. However, the complex dielectric function must be divided into real and imaginary components  $\varepsilon'(\omega)$  and  $\varepsilon''(\omega)$  in order to remove the phase-dependent term from the equation; resonance is thus achieved when  $\varepsilon'(\omega) = -2\varepsilon_d$  and  $\varepsilon''(\omega) << 1$ . The dielectric function is negative when  $\omega$  is below some threshold frequency  $\omega_p$ , known also as the plasma frequency. The relationship between  $\varepsilon(\omega)$  and  $\omega_p$  can be illustrated by the Drude model, a conceptually useful description of free-electron behavior in metals. Here  $\varepsilon'(\omega)$  and  $\varepsilon''(\omega)$  can be approximated in terms of  $\omega_p$ and  $\Gamma$ , the plasmon relaxation frequency:

$$\varepsilon'(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} \tag{2}$$

$$\varepsilon''(\omega) \approx \frac{\omega_p^2 \Gamma}{\omega(\omega^2 + \Gamma^2)} \tag{3}$$

Applying these relations to Eq. (1) yields a Drude resonance frequency  $\omega_D = \omega_p / \sqrt{2\varepsilon_d + 1}$  when  $\varepsilon''(\omega)$  is small. The plasma frequency  $\omega_p$  is a bulk material property and is scale-invariant within the quasi-static limit. However, the Drude free-electron response varies with geometric shape, which suggests a useful theoretical handle for predicting characteristic resonance frequencies of ellipsoids (nanorods) and other anisotropic particles as a function of aspect ratio.

Unfortunately the free-electron model cannot be directly applied toward calculating the plasmonic response of most metals of interest, because of the additional electric susceptibility introduced by interband transitions between the outermost *d* and *s* orbitals at optical frequencies (threshold excitation energies for Ag(4*d*→5*s*) and Au(5*d*→6*s*) are close to 3.9 and 1.8 eV, respectively). These electronic excitations couple strongly with the free-electron response, resulting in large changes to  $\varepsilon'(\omega)$  and  $\varepsilon''(\omega)$ ; in addition, they can provide a significant relaxation (damping) mechanism for plasmon decay, reducing the quality of the optical resonance. In the case of Ag, interband transitions are responsible for changes in the resonance condition and the subsequent frequency difference between the theoretical Drude response ( $\omega_D = 5.6 \text{ eV}$ ) and the observed plasmon resonance ( $\omega_{SP} = 3.6 \text{ eV}$ ). In the case of other metals such as Au and Cu,  $\varepsilon''(\omega)$  cannot be neglected at optical frequencies so the resonance condition derived from Eq. (1) is no longer strictly applicable.

Exact solutions for the optical properties of metal nanostructures can be obtained instead using electrodynamic Mie theory, whose formulations are derived from Maxwell's equations. Application of Mie theory requires the input of  $\varepsilon_d$  and  $\varepsilon(\omega)$  as a function of frequency for a given particle size, either as experimental values or as numerical approximations. Various optical functions can be calculated with great accuracy; for example, extinction and optical conductivity ( $\varepsilon''/\lambda$ ) spectra of Cu, Ag, and Au particles in the quasi-static limit were calculated using Eq. (4), with the effect of  $\varepsilon''$  on the resonance band plainly visible (see Figure 3).<sup>3</sup> The calculated extinctions reproduce the experimental spectra with a high degree of fidelity, although the effect of certain physical parameters cannot be accounted for, such as surface charge from the electrostatic double layer.



*Figure 3.* Optical conductivity ( $\varepsilon''/\lambda$ , in red) and extinction spectra (in black) of Cu, Ag, and Au nanoparticles calculated as a function of photon energy (2R = 10 nm,  $\varepsilon_d = 1$ ). The relative intensity of absorption by Ag is much higher than that of Au or Cu (adapted from Ref. 3).

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$$\sigma_{ext}(\omega) = \frac{12\pi\varepsilon_d^{3/2}R^3\omega}{c} \left| \frac{\varepsilon''}{(\varepsilon'+2\varepsilon_d)^2 + (\varepsilon'')^2} \right|$$
(4)

Mie theory has been used to estimate variations in the electrodynamic response due to particle size, anisotropy, and other extrinsic parameters, independently from changes in the optical material function. This includes metal nanoparticles beyond the quasi-static limit ( $2R/\lambda > 0.05$ ), whose plasmon resonances are redshifted by phase retardation and broadened by radiation damping (*vide infra*). Higher-order plasmon modes also become significant; for example, quadrupole resonances in Ag and Au particles can be observed in optical extinction spectra starting from ~60 nm.

Another important transition takes place in the mid-nanometer size regime: scattering supersedes absorption as the dominant optical response, at about 60 nm for Ag and 80 nm for Au. Dipole ( $S_1$ ) scattering typically provides the largest contribution, followed by quadrupole ( $S_2$ ) scattering.<sup>4</sup> As particles continue to increase in size, the various absorption and scattering modes reach a maximum, then fade away until only the bulk optical properties for Ag and Au particles of various size in water have been calculated by Yguerabide,<sup>5</sup> and are reproduced here to illustrate the dramatic effect of size on plasmonic response (see Figures 4–5 and Tables 1–2).



*Figure 4*. Mie extinction properties of spherical Ag nanoparticles in water, calculated as a function of diameter (adapted from Ref. 5).

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2R (nm)	$\lambda_{\max} (nm)^a$	$\epsilon (M^{-1} cm^{-1})^b$	$C_{sca} (\mathrm{cm}^2)^c$	$\varphi \left( C_{sca} / C_{ext} \right)^d$
20	390	$4.16 \times 10^{9}$	$6.42 \times 10^{-13}$	0.041
40	400	$2.87 \times 10^{10}$	$2.78 \times 10^{-11}$	0.255
60	420	$6.75 \times 10^{10}$	$1.41 \times 10^{-10}$	.0550
80	445 [380]	$1.04 \times 10^{11}$	$2.92 \times 10^{-10}$	0.741
100	485 [390]	$1.35 \times 10^{11}$	$4.28 \times 10^{-10}$	0.835
120	530 [400]	$1.66 \times 10^{11}$	$5.57 \times 10^{-10}$	0.844
140	580 [415]	$1.98 \times 10^{11}$	$6.88 \times 10^{-10}$	0.913
160	640 [445] [390]	$2.97 \times 10^{11}$	$8.97 \times 10^{-10}$	0.819
180	[460] [400]	$3.41 \times 10^{11}$	$1.13 \times 10^{-9}$	0.848
200	[485] [405]	$4.04 \times 10^{11}$	$1.35 \times 10^{-9}$	0.876
300	[490] [420]	$8.0 \times 10^{11}$	$2.7 \times 10^{-9}$	0.877

*Table 1.* Mie extinction properties for Ag nanoparticles as a function of size (adapted from Ref. 5).  ${}^{a}\lambda_{max}$  values are calculated for dipolar, quadrupolar and higher-order plasmon resonances [latter two in brackets].  ${}^{b}$ Coefficients are calculated at maximum extinction.  ${}^{c}C_{sca}$  = scattering cross section.  ${}^{d}\varphi$  = relative scattering efficiency.



*Figure 5*. Mie extinction properties of spherical Au nanoparticles in water, calculated as a function of diameter (adapted from Ref. 5).

2R (nm)	$\lambda_{\max} (nm)^a$	$\epsilon (M^{-1} cm^{-1})^b$	$C_{sca} (\mathrm{cm}^2)^c$	$\varphi \left( C_{sca} / C_{ext} \right)^d$
20	535	$1.57 \times 10^{9}$	$8.36 \times 10^{-14}$	0.014
40	535	$1.63 \times 10^{10}$	$6.05 \times 10^{-12}$	0.100
60	545	$5.32 \times 10^{10}$	$6.33 \times 10^{-11}$	0.313
80	555	$1.14 \times 10^{11}$	$2.31 \times 10^{-10}$	0.546
100	575	$1.62 \times 10^{11}$	$4.56 \times 10^{-10}$	0.739
120	605	$2.07 \times 10^{11}$	$6.90 \times 10^{-10}$	0.876
140	635 [535]	$2.46 \times 10^{11}$	$8.79 \times 10^{-10}$	0.940
160	665 [540]	$2.80 \times 10^{11}$	$1.02 \times 10^{-9}$	0.963
180	720 [550]	$3.14 \times 10^{11}$	$1.16 \times 10^{-9}$	0.974
200	780 [560]	$4.51 \times 10^{11}$	$1.38 \times 10^{-9}$	0.788
300	[660] [555]	$7.98 \times 10^{11}$	$2.94 \times 10^{-9}$	0.968

*Table 2.* Mie extinction properties for Au nanoparticles as a function of size (adapted from Ref. 5).  ${}^{a}\lambda_{max}$  values are calculated for dipolar, quadrupolar and higher-order plasmon resonances [latter two in brackets].  ${}^{b}$ Coefficients are calculated at maximum extinction.  ${}^{c}C_{sca}$  = scattering cross section.  ${}^{d}\varphi$  = relative scattering efficiency.

#### 2.2 Surface plasmons and the material function

We have touched on the fact that the free-electron plasmon response can be strongly influenced by interband transitions, a property of the bulk metal. Several other material factors also have an influential role on surface plasmons and  $\varepsilon(\omega)$ : (a) the electron mean free path, (b) the skin depth, and (c) local medium effects, including surface adsorption. These are discussed in some detail below for the case of spherical, crystalline metal nanoclusters.

2.2.a. Size confinement effects on the plasmon band. Metal nanoparticles exhibit peak broadening when their diameters are much less than the electron mean free path  $L_e$ , a material-dependent property describing the quasi-elastic scattering of conduction electrons ( $L_e$  in bulk Ag and Au are about 50 and 40 nm, respectively). The effective path length  $L_r$  decreases almost linearly with 2R, corresponding with a change in  $\varepsilon(\omega)$  from the bulk dielectric function. Broadening of the plasmon band in Ag and Au nanoparticles becomes evident for 2R < 10 nm; the plasmon resonance frequency is not affected, but the relaxation rate  $\Gamma$  increases with a 1/Rrelationship due to the greater electron scattering by the particle surface (see Figure 6).<sup>6</sup> In the case of the very smallest nanoclusters (2R < 2 nm), it has been argued that the local density of states may be reduced to the extent that they no longer form a continuous band structure. Experimental evidence for quantum size effects has recently been obtained in the form of electrochemical "Coulomb staircase" measurements on single gold nanoclusters, with redox-like behavior observed for particles with diameters well below 2 nm.<sup>7</sup> Quantum-mechanical effects of a different sort have also been established in the ensemble electronic states of metal nanoparticle superlattices, as shall be discussed in a later section (cf. Section 4.2a).



*Figure 6*. Size confinement effects on the plasmon resonance band for Ag nanoparticles, calculated using bulk dieclectric constants (adapted from Ref. 3).

**2.2.b. Skin depth.** The incident lightwave on a bulk metal surface has a fairly low penetration depth, with an exponential attenuation of electric field strength below the surface (see Figure 2, *right*). The electric field within the metal can be expressed as a function of depth *z*:

$$\left| \mathbf{E}(z) \right| = \left| E_0 \right| e^{-z/\delta} \tag{5}$$

Here the skin depth  $\delta$  is defined as

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$$\delta = \frac{c}{\omega k} = \frac{\lambda}{2\pi k} \tag{6}$$

where *k* is the absorption coefficient of the metal. The bulk refractive index *n* and the absorption coefficient *k* are related to the complex dielectric function by  $n + ik = \sqrt{\varepsilon' + i\varepsilon''}$ , so *k* can be expressed solely in terms of the dielectric function as

$$k = \sqrt{\frac{\sqrt{\left(\varepsilon'\right)^2 + \left(\varepsilon''\right)^2} - \varepsilon'}{2}}$$
(7)

Calculations of  $\delta$  using Eqs. (6) and (7) at different optical wavelengths suggest an average value of ~30 nm for both Ag and Au, with an exceptionally large value of ~80 nm near the plasmon resonance in the case of Ag. This reaffirms the dipolar nature of localized plasmon resonances for nanoparticles with diameters on the order of  $L_e$ , and suggests the onset of multimodal plasmon modes in larger metal nanoparticles. A low skin depth also promotes the propagation of surface plasmon polaritons in anisotropic metal nanostructures such as nanorods, with intriguing consequences for their optical emissions.

**2.2.c. Local dielectric and surface effects.** Coupling between the Drude free-electron response and interband excitations can be weakened by modulating  $\varepsilon_d$ , such that the Drude frequency is shifted away from the electronic transition threshold (see Section 2.1). An especially dramatic effect can be expected in the case of Cu, which has a significant  $\varepsilon''(\omega)$  at plasmon frequencies above 2 eV (see Figure 3). By embedding Cu nanoparticles in transparent media with  $\varepsilon_d > 5$ , the plasmon resonance frequency of Cu nanoparticles can be lowered to below 2 eV, resulting in a large enhancement in optical extinction (see Figure 7).<sup>8</sup> Metal nanoparticles are also solvatochromic; polymer-stabilized Au particles dispersed in organic solvents of varying refractive indices (n = 1.33-1.60) demonstrated a

shift in absorption from red to purple ( $\lambda_{SP} = 520-545$  nm), accompanied by an increase in extinction intensity.<sup>9</sup> The experimental data was found to be in excellent agreement with Mie theory, based on the changes in  $\varepsilon_d$ .



*Figure 7.* Extinction peaks of Cu nanoparticles embedded in various dielectric media  $(\varepsilon_d)$ .<sup>3</sup>

Surface adsorbates (ligands) can also influence the optical properties of metal nanoparticles. Strongly adsorbing anions and chemisorptive surfactants such as thiols accelerate plasmon relaxation, resulting in peak broadening (*vide supra*). This effect has been attributed to a reduction in conduction electron mobility, due to electronic coupling between the plasmon and charge-transfer bands formed by the metal–adsorbate complex.<sup>10</sup> Strong optical resonance can be restored in some cases by cathodic (negative) charging, which induces ligand desorption.

#### 2.3 Plasmon decay and radiative damping

The quality of the dipolar plasmon response depends both on the intensity of polarizability and the coherence lifetime of the collective oscillations. The latter is determined by the dephasing (or decay) of the collective dipole, which is characterized by the relaxation constant  $T_2 = 2\hbar/\Gamma$ . Plasmon relaxation occurs by radiative damping and also by nonradiative electronic mechanisms such as interband transitions (*vide supra*). Radiative damping of an oscillating electronic dipole is the electromagnetic equivalent of mechanical damping in a vibrating system, with the conduction electrons providing an effective mass.

Both radiative damping and polarizability increase with particle volume, such that the increased dipole oscillator strength is accompanied by broadening of the optical response. Radiative damping also scales with  $1/\lambda^3$ , with a consequently reduced effect on plasmons at lower frequencies. Radiative damping in single metal nanoparticles has recently been measured by Klar *et al.* using near-field scanning optical microscopy, which permitted

quantitative determination of plasmon linewidths (I) from individual nanoparticles.<sup>11</sup> These were narrower than that produced by bulk measurements, and yielded an excellent correlation between experiment and Mie theory.

As a practical rule of thumb, damping and phase-retardation effects in spherical nanoparticles will have a compromising effect on optical emission and field-enhanced applications such as SERS when  $2R/\lambda > 1/\pi\sqrt{\varepsilon_d}$  (approximately 0.24 in water).<sup>12,13</sup> However, it is important to mention that radiative damping is not necessarily dependent on the overall particle volume, but rather on those portions which define an 'optical domain.' This point will become clear when discussing the optical properties of anisotropic structures such as nanorods and nanowires.

#### 3. Anisotropic metal nanoparticles

An important feature of dipolar plasmon resonance is its high sensitivity to shape anisotropy: isolated spherical nanoparticles typically support a single resonance frequency, whereas anisotropic particles such as rods and triangles will exhibit at least one additional plasmon mode, as well as large redshifts in plasmon resonance. Electric birefringence is also enhanced by structural anisotropy, and can be used in conjunction with optical extinction to estimate particle eccentricity.<sup>14</sup> Modifications to the original Mie theory (by Gans) have permitted the optical response of anisotropic nanoparticles to be calculated and compared with analytical measurements. Both theoretical and experimental investigations of anisotropic metal nanoparticles indicate several important differences in their enhanced optical properties when compared with those of spherical nanoparticles.

#### 3.1 Surface plasmons in metal nanorods and nanowires

According to Mie–Gans theory, cylindrical nanorods support two distinct plasmon modes: a transverse mode oscillating perpendicular to the principal axis, and a longitudinal resonance with a coaxial polarization. Several groups have shown that both frequencies are determined by the particle's aspect ratio.<sup>15,16</sup> The longitudinal plasmon mode can be strongly redshifted into the NIR: for example, Au nanorods dispersed in water with aspect ratios of ~4:1 exhibit longitudinal plasmon resonances centered at 800 nm, whereas nanorods with aspect ratios of ~9:1 exhibit resonance shifts toward shorter wavelengths with increasing aspect ratio, until an asymptotic value is reached (~500 nm).

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*Figure 8.* Longitudinal plasmon resonances calculated for Au nanorods in water with different aspect ratios, based on electrodynamic Mie–Gans theory (adapted from Ref. 15).

Methodologies for synthesizing metal nanorods are now well established. Nanoparticle-seeded growth mediated by cationic surfactants can produce cylindrically symmetric nanorods with aspect ratios as high as 20:1, with diameters on the order of 10–20 nm.<sup>17,18</sup> For thicker nanorods (> 20 nm), pulsed electrodeposition into metallized nanoporous membranes has been demonstrated to produce nanorods of any aspect ratio.<sup>19,20</sup> The latter synthetic method offers excellent control over nanorod dimensions: rod thickness is predetermined by pore diameter, whereas rod length is a direct function of deposition time or coulombs (current × time). In addition, the electroplating solution can be interchanged to enable the preparation of bi-, tri-, or multimetallic nanorods. This has been recently demonstrated in the production of submicron "nano-barcodes," in which several different metals can be incorporated into the nanorod, with each segment producing its own characteristic plasmonic response.<sup>21,22</sup> These are currently being marketed as single-particle optical labels for various bioanalytical applications.<sup>23</sup>



*Figure 9.* Optical micrograph (160×, N.A. = 1.4,  $\lambda$  = 405 nm) of bimetallic 'striped' Ag–Au nanorods, approximately 300 nm × 6  $\mu$ m.<sup>23</sup>

A very important optical quality of Au nanorods is their low rate of plasmon decay, which reduces the linewidth of their optical response. A recent single-particle scattering study by Sönnichson et al. provided FWHM linewidths of individual Au nanospheres and nanorods, with the latter producing higher quality resonances due to reduced radiative damping effects.<sup>24</sup> Spherical nanoparticles with plasmon resonances centered at 800 nm produced emissions with broad linewidths ( $\Gamma = 0.9$  eV, or ~500 nm), whereas nanorods at the same resonance frequency produced much narrower emission peaks ( $\Gamma$ = 0.1 eV, or ~50 nm). The plasmon linewidths are limited by nonradiative damping effects caused by the intraband transitions in gold  $(\Gamma \sim \hbar/T_l^{\text{IB}})$  but remain narrow even at longer wavelengths, and are only slightly broader than those derived from electrodynamic calculations (cf. Figure 8). It is interesting to note that even very long metal nanowires (~30  $nm \times 6 \mu m$ ) retain high optical scattering efficiency without significant line broadening ( $\lambda_{SP}$  = 520 nm).<sup>22</sup> The nanowires' transverse plasmon resonances are evidently unperturbed by radiative damping, which suggests that the plasmon relaxation rate is unaffected by dimensional changes normal to the direction of polarization.

The distinction of transverse and longitudinal modes in plasmonic nanowires gives rise to an interesting dichotomy: electric polarizations in the transverse direction can propagate as surface plasmon waves along the nanowire's principal axis. Optical input energy can be transported as surface-bound plasmon waves and be re-emitted as light at the far end of the nanowire, provided that propagation is favored over absorption or emission. This suggests possible applications in the emerging area of nanophotonics, in which electromagnetic information can be processed and directed at nanometer length scales.

An elegant study by Dickson and Lyon demonstrates the critical role of the dielectric function in plasmon propagation, using 20-nm Au and Ag nanowires coupled to an evanescent light source (see Figure 10).<sup>25</sup> In both cases, irradiation of 820-nm light at one end (input) produces scattered light at the other (output), but when 532-nm light is used only the Ag nanowire supports plasmon propagation. Efficient optical energy transport is not observed in Au nanowires presumably because of their significant absorption at that wavelength. Very interestingly, a bimetallic Au–Ag nanowire exhibits *unidirectional* plasmon propagation at 820 nm, with efficient transport only in the Au $\rightarrow$ Ag direction— in other words, a nanophotonic diode. The full potential of plasmonic nanowires and nanostructured heterojunctions as components in photonic circuits and devices remains to be discovered.



*Figure 10.* Optical image of 20 nm × 4.7  $\mu$ m Au nanorod, with the lower end exposed to evanescent illumination at (*a*) 532 nm and (*b*) 820 nm.<sup>25</sup> A dotted outline of the nanorod has been drawn as a visual aid. Scattering is only observed from the input end in (*a*) whereas both ends emit light in (*b*), indicating plasmon propagation at 820 nm. Scale bar = 1  $\mu$ m.

## **3.2** Surface plasmons in metal nanoprisms and polyhedra

Electrodynamic calculations can also be extended to nanoparticles with anisotropy in three dimensions (nanoprisms and polyhedra). Schatz and coworkers have used numerical methods such as discrete dipole approximation (DDA) to calculate the extinction properties and local field factors of Ag trigonal prisms and truncated tetrahedra under polarized light.<sup>26</sup> As in the case of the nanorods, shape plays a critical role in the dipolar resonance frequencies of the plasmon modes. The lowest-energy plasmon peak is largely determined by the tip-to-tip distance on the triangular nanoparticles, but even a slight truncation of the vertices will result in a sizable shift to shorter wavelengths (see Figure 11). The DDA calculations also reveal a significant quadrupolar resonance at higher frequencies, a plasmon mode often obscured in isolated spherical particles of comparable size.



*Figure 11.* Calculated extinction spectra for 100-nm Ag trigonal prisms with truncations (see inset) of 0 nm (*green*), 5 nm (*red*), and 10 nm (*blue*).<sup>26b</sup> Prism thickness is 16 nm.

A comparison of experiment and theory reveals similar trends with respect to dielectric effects on plasmon resonances in triangular nanoprisms, although discrepancies due to surface oxidation and other environmental factors prevent complete convergence. Other polyhedra with less pronounced anisotropies exhibit smaller shifts in plasmon resonance: single-particle scattering studies of spheroidal, pentagonal, and triangular Ag nanoparticles have demonstrated a shape-dependent trend in optical response, with the latter experiencing the greatest average shift toward longer wavelengths.<sup>27</sup>

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Methodologies for synthesizing metal nanoprisms with controlled dimensions are presently under development. One of the first reliable methods for fabricating triangular nanoprisms was developed by Van Duyne and coworkers, in which a hexagonally close-packed monolayer of colloidal spheres served as a template for metal vapor deposition.<sup>28</sup> The "nanosphere lithography" approach provides access to truncated tetrahedral metal islands with in-plane diameters ranging from ~20 nm to hundreds of nanometers depending on the size of the particles in the colloidal mask, and heights of 5–50 nm as a function of the metal evaporation rate (see Figure 12). The plasmon resonances of triangular Ag particles are size-tunable and have reasonably narrow linewidths, with primary extinction maxima ranging from 550 nm to 6.0  $\mu$ m, well into the mid-infrared range.<sup>29</sup>



*Figure 12.* Nanosphere lithography.<sup>28</sup> A monolayer of close-packed microspheres (*left*) is exposed to thermally evaporated metal (Ag), then removed by sonication in organic solvent to reveal a periodic array of truncated tetrahedrons.

Solution syntheses of metal polyhedra have recently been achieved with some degree of control. A report by Jin *et al.* demonstrates a novel photoinduced method of converting spherical Ag nanoparticles into triangular prisms with variable in-plane diameters but nearly uniform thicknesses.<sup>30</sup> Also worth mentioning is the synthesis of metal nanoparticle cubes by Sun and Xia, whose anisotropic growth is surfactant-mediated.<sup>31</sup>

With respect to applications, the plasmonic responses of triangular nanoparticles have demonstrated a remarkably high sensitivity to changes in their local environment. For example, shifts in the surface plasmon resonance (SPR) wavelength due to alkanethiol adsorption were sufficiently sensitive that a difference of two carbons (e.g., C10 vs. C12 thiol) gave a differential response of ~8 nm in the extinction maxima.<sup>32</sup> These SPR shifts have proven to be useful for biomolecular sensing: functionalizing the nanoprisms' surfaces with biotinylated ligands enabled them to detect streptavidin binding events at very low concentrations, with saturation adsorption at 100 pM and limits of detection in the low picomolar range ( $\Delta\lambda$  ~4 nm).<sup>33</sup> By comparison, nonspecific protein adsorption induced only a 2-nm redshift in the resonance peak. Additional peakshifting could be induced by adding biotinylated Au nanoparticles as secondary labels, whose near-field coupling with the metal substrate provides a mechanism for enhancing SPR sensitivity.<sup>34</sup> In fact, electromagnetic coupling plays a key role in the plasmonic responses of metal nanoparticle ensembles, and can enhance their optical properties by many orders of magnitude.

#### 4. Metal nanoparticle ensembles

Up to this point we have focused on the optical properties of isolated metal nanostructures, with minimal interactions between particles. However, some of the highest signal amplifications have been achieved using nanoparticles with strong electromagnetic coupling. For example, many of the early SERS observations in the late 1970's and early 1980's were performed using kinetic aggregates of Ag and Au nanoparticles.<sup>35</sup> Unfortunately, reproducible activities from such substrates has been poor; although there is strong evidence that aggregated nanoparticles contain "hot spots" which produce the great majority of the enhanced Raman intensities, they vary widely from sample to sample and often disappear after a few days' aging. This variability is made all the more frustrating by several fairly recent reports of single-molecule SERS spectroscopy;<sup>36</sup> while the detection of individual molecules is possible, the conditions which enable reproducible single-molecule analysis have not yet been established.

It is not terribly surprising that the complexity of disordered aggregates have been slow to yield the secrets of these elusive but potentially enormous optical enhancements. In the last few years significant progress has been made in the electromagnetic theory of metal–dielectric interfaces, both for periodic nanostructures<sup>37</sup> and for fractal aggregates.<sup>38</sup> There have also been several important advances in the self-assembly of discrete or periodically ordered metal nanostructures, and continued progress along both of these lines can be expected to produce some concrete answers. Here we shall review several recent studies on discrete nanoparticle aggregates (clusters), two-dimensional (2D) arrays, and three-dimensional (3D) aggregate structures. It will become evident that in addition to particle size and shape,

interparticle spacing  $(\delta)$  is a critical parameter to the collective optical properties of nanoparticle ensembles.

#### 4.1 Discrete metal nanoparticle clusters

Nanoparticles separated by a few diameters begin to experience significant electromagnetic dipole coupling, which gives rise to additional plasmon modes. Effective-medium theories such as the Maxwell-Garnett formula have been used to approximate the optical responses of coupled nanoparticles up to a certain point, but these lose their accuracy if the spacing is much less than one particle diameter ( $\delta < 1.5R$ ). Simulations based on generalized Mie theory  $\frac{3}{39}$  or numerical approaches such as DDA<sup>26</sup> appear to provide more consistent models of collective optical properties, for N-particle systems of discrete size. These have been used to predict the extinction and absorption cross sections of specific aggregate structures, such as chained particles in linear or bent conformations (see Figure 13). Overall, the calculated optical responses are quite similar to those determined for anisotropic particles; linear chains (resembling nanorods) produce longitudinal plasmon resonances at strongly redshifted wavelengths, whereas close-packed aggregates (resembling prisms) exhibit less pronounced shifts in their collective plasmon resonance frequencies.



*Figure 13.* Extinction spectra of 20-nm Ag particle aggregates in different geometries, as calculated by generalized Mie theory (adapted from Ref. 3).

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 function of  $|E/E_0|$ ) for a given frequency  $\omega$ . 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  $\omega$  and  $\omega'$  are the incident and Stokes-shifted frequencies, respectively.<sup>40</sup> In the simplest case of a two-sphere system, it is well known that local field factors are greatest when the two particles are almost touching. Käll and coworkers have performed electrodynamics calculations on pairs of Au and Ag particles (10–90 nm) separated by as little as 1 nm, and suggested  $G_{EM}$  values in excess of 10<sup>11</sup> for the best cases.<sup>41</sup> These "hot spots" are exquisitely sensitive to interparticle spacing; changes in  $\delta$  by just a few nanometers can cause the local enhancements to drop by several orders of magnitude (see Figure 14). The calculations imply that nanoparticle dimers may have potential as substrates for routine singlemolecule SERS, given a reliable method for localizing analytes in regions of high field.



*Figure 14.* Electrodynamics simulation of local field enhancements ( $G_{EM}$ ) between two 90-nm Ag particles ( $\varepsilon_d = 1$ ) at different interparticle separations ( $\delta = 5.5$  and 1.0 nm).<sup>41</sup>

So far, successful methods of organizing nanoparticles into ensembles of well-defined size and shape have mostly relied on lithographically defined surfaces<sup>42</sup> or on serially directed assembly using scanning probe microscopy tips.<sup>43</sup> Surprisingly, there are few reports for producing even dimers of metal nanoparticles in a controlled fashion by self-assembly. A recent contribution to this area from Feldheim and coworkers uses a tectonic approach, in which the aggregation of metal nanoparticles is coordinated by a rigid, multivalent organic ligand.<sup>44</sup> Dimers, trimers, and tetrahedral clusters of colloidal Ag and Au nanoparticles could be prepared and partially separated by gradient centrifugation.<sup>45</sup> The reduced symmetry of the nanoparticle trimers enhances their nonlinear optical properties; for example, the hyper-Raman scattering efficiency per unit nanoparticle (8 nm) was shown to be nearly an order of magnitude higher for noncentrosymmetric trimers versus dimers or monomers.<sup>46</sup>

#### 4.2 Periodic metal nanoparticle 2D arrays

5.

**4.2.a.** Collective optical properties of small nanoparticle arrays. There have been numerous studies on the self-assembly and collective properties of 2D nanoparticle superlattices, the great majority of which have been prepared from metal particles in the 2–10 nanometer size range. Such ensembles have been reviewed elsewhere;<sup>47</sup> in brief, while several important advances have been made in correlating physical properties with 2D periodic structure, many more relationships remain to be elucidated. An important challenge to this effort is the development of reliable methods for fabricating arrays with excellent long-range order, a subject which has remained an active area of investigation.<sup>48</sup>

With respect to optical properties, Heath and coworkers have established quantitative relationships between the periodic structure and the dielectric function of 2D metal nanoparticle ensembles.<sup>49,50</sup> Hexagonally close-packed (hcp) arrays of Ag nanocrystals (2–6 nm) were self-assembled on air–water interfaces and subjected to gradual changes in surface pressure in a Langmuir trough (see Figure 15). Compression of the monolayer films increased their nonlinear optical responses as well as their reflectance. These could be parameterized in terms of D/2R, a ratio between the average center-to-center distance ( $2R + \delta$ ) and the unit particle diameter.



*Figure 15.* Close-packed monolayer of butanethiol-coated 3.5-nm Ag particles (red) in a Langmuir trough.<sup>50</sup> *Left*, Ag nanoparticle film under low surface compression; *right*, same film under slightly greater compression, but with a substantially higher reflectance.

For D/2R values between 1.7 and 1.2, it was determined that quantummechanical exchange interactions play a significant role in the collective optical properties of the nanoparticle arrays, particularly in their nonlinear optical responses. Second-harmonic generation (SHG) was observed to have an exponential dependence on D with a maximum response at  $D/2R \sim 1.2$ , whereas local field factors provided only a minor contribution to SHG enhancement.<sup>51</sup> In addition, the linewidth of optical reflectance narrowed as D/2R approached 1.2, due to greater electronic delocalization and less scattering from the particle surface (cf. Section 2.2a). Further decreases in interparticle spacing resulted in an abrupt loss of reflectance and SHG, signifying the onset of a quasi-continuous metallic state. The insulator-to-metal transition was observed to be reversible, as decompression of the monolayer films to D/2R > 1.2 restored the strong optical response. The complex dielectric function  $\varepsilon(\omega)$  could be derived from constants *n* and *k*, which in turn were obtained from bulk optical measurements at different stages of compression. It was determined that the free-electron (Drude-like) behavior of the metallic phase shifts  $\varepsilon'(\omega)$  toward negative values, whereas  $\varepsilon''(\omega)$  is relatively unaffected by changes in spacing.<sup>52</sup> A decrease in  $\varepsilon'(\omega)$  corresponds to a higher absorption coefficient *k* especially when  $\varepsilon'(\omega) < 0$  (cf. Eq. (7)), and is thus largely responsible for the significant loss in linear optical response at low values of D/2R.

It is worth mentioning that long-range order can also be a significant factor in the arrays' collective properties. This has been demonstrated to be an important parameter for electronic transport: the current–voltage relationship of highly crystalline nanoparticle arrays varies as a simple power function,<sup>53</sup> whereas disorder introduces nonlinear scaling behavior.<sup>54</sup> With regard to optical properties, nonlinear effects are also promoted by lattice disorder; small (~10%) fluctuations are sufficient to break the symmetry within the superlattice, enhancing second-order polarizability ( $\chi^2$ ) and the subsequent SHG.<sup>55</sup> However, at very small interparticle distances the effects of local disorder are dominated by exchange coupling, and thus have only a minor effect on SHG intensity.

**4.2.b.** Collective optical properties of large nanoparticle arrays. Metal particles in the mid-nanometer size range (20–200 nm) are also important candidates for self-assembly because of their size-dependent optical properties, but their strong interaction potentials can promote kinetic aggregation, resulting in poorly organized structures. This can be viewed as a problem in dispersion control; if repulsive interactions can offset particle self-attraction at close range, one should be able to achieve conditions for thermodynamically controlled self-organization. Earlier demonstrations by Schmid<sup>56</sup> and by Giersig and Mulvaney<sup>57</sup> have indicated that colloidal Au particles can be assembled into 2D domains with local order. Beyond that however, there have been relatively few studies in which large (>20 nm) metal nanoparticles are organized into periodic superlattices.

A general method for organizing metal nanoparticles into self-assembled 2D arrays has recently been developed by Wei and coworkers, using multivalent macrocyclic surfactants known as resorcinarenes.<sup>58</sup> These compounds are capable of extracting colloidal Au particles from aqueous suspensions and dispersing them into organic solvents or at air–water interfaces.<sup>59</sup> In the latter case, resorcinarene-stabilized nanoparticles as large

as 170 nm could spontaneously organize into monoparticulate films with long-range order (see Figure 16).<sup>60</sup> Careful inspection of the TEM images reveals an inverse correlation between array periodicity and interparticle spacing, most likely as a result of greater van der Waals attraction with unit particle size. The particle diameter-to-spacing  $(2R/\delta)$  ratios range from about 15 to well over 100, well beyond the metal–insulator threshold defined by the Heath group.<sup>49</sup>

5.



*Figure 16.* Self-organized 2D arrays of large Au nanoparticles.<sup>60</sup> Unit particle sizes: (a) 16 nm; (b) 34 nm; (c) 87 nm.

The 2D arrays exhibit size-dependent optical extinction and reflectance at visible and NIR wavelengths, and have been found to be excellent substrates for SERS.<sup>61</sup> Surface-averaged Raman signals generated from the adsorbed resorcinarenes could be optimized as a function of periodicity and excitation wavelength, with cross sections enhanced by as much as 10<sup>7</sup>. The observed trends are in accord with theoretical calculations describing electromagnetic SERS,<sup>62</sup> and also with earlier SERS studies on disordered metal colloid aggregates.<sup>63</sup> 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 surface plasmon polaritons in the Au nanoparticle films contribute significantly to the SERS effect.

The large Au nanoparticle arrays are capable of detecting exogenous analytes by SERS and thus have potential as spectroscopic chemical sensors.<sup>61</sup> Volatile organic compounds adsorbed onto the array surface produce a detectable signal within seconds; however, theoretical calculations indicate that detection limits can be further lowered by adjusting the interparticle spacing. Incremental changes in  $\delta$  will delocalize field intensities, but at the same time increase 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  $2R/\delta$ .<sup>64</sup> The resonant  $G_R$  values can

surpass those produced by disordered metal-dielectric films by several orders of magnitude (see Figure 17).



*Figure 17. Left*, numerical calculations of surface-averaged field enhancements ( $G_R$ ) from 2D hexagonal superlattices with diameter–spacing ratios of 5, 10, and 30, versus a random metal–dielectric film at the percolation threshold ( $p = p_c$ ). *Right*, local field distribution within a hexagonal lattice produced by *p*-polarized light ( $\lambda = 600 \text{ nm}$ ,  $2R/\delta = 10$ ,  $E_{\theta} = E_{v}$ ).<sup>64</sup>

# 4.3 Metal and metal-dielectric nanoparticles in 3D superlattices

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. possess a photonic band gap. Photonic crystals with band gaps in the visible to NIR range have been highly sought after as a way to manipulate the flow of light.<sup>65</sup> 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. Metal–dielectric periodic 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.<sup>66</sup>

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.<sup>67</sup> Close-packed, face-centered cubic (FCC) crystals of colloidal Ag particles were calculated to have tunable band gaps, at frequencies defined by the particle radius and plasma wavelength  $(R/\lambda_p)$  and with gap widths  $(\Delta \omega / \omega_c)$  between 5 and 10%. The photonic band gaps were predicted to be greatest for colloidal crystals with  $R/\lambda_p > 0.9$ ; in the case of Ag, 3D arrays of large, submicron-sized particles would be needed to produce band gaps for visible wavelengths. A related study by Zhang *et al.* suggest that tunable photonic band gaps can also be made using metal-coated, core–shell nanoparticles as 3D array elements.<sup>68</sup> 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 SiO<sub>2</sub>/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  $\lambda = 1.5 \ \mu$ m, whereas 160/50-nm core–shell particles at 42% packing density are expected to have a band gap across the visible spectrum.

A number of reports have recently been published on the preparation and optical properties of nanoparticles with dielectric cores and metallic shells. Halas and coworkers have fabricated semicontinuous Au and Ag nanoshells by electroless deposition onto submicron silica particles.<sup>69</sup> Extinctions could be tuned as a function of shell thickness and core diameter, from the visible to the mid-IR range; the latter were produced by nanoparticles with high core–shell aspect ratios.<sup>70</sup> Highly monodisperse core–shell nanoparticles can be crystallized into 3D arrays with colorful Bragg reflections (see Figure 18). An interesting variant reported by Graf and van Blaaderen involves the growth of a second dielectric shell around the metal-coated nanoparticle.<sup>71</sup> The outermost SiO<sub>2</sub> 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.*<sup>68</sup>



*Figure 18.* Colloidal crystals of core–shell nanoparticles formed in aqueous solution.<sup>71</sup> Left, photograph of crystal comprised of SiO<sub>2</sub>/Au core–shell nanoparticles (core = 205 nm, shell = 31 nm); *right*, top layer of SiO<sub>2</sub>/Au nanoparticle superlattice.

#### 4.4 Nonperiodic nanoparticle ensembles

Many of the structure–property relationships which have been defined for 2D and 3D arrays are also qualitatively observed in disordered metal nanoparticle ensembles. Large changes in optical extinction and scattering are readily achieved by ligand-induced aggregation, with direct applications

toward chemical and biomolecular sensing.<sup>72</sup> One of the best-known examples is the colorimetric detection of DNA polynucleotides by Mirkin and coworkers.<sup>73</sup> The technology is remarkably simple: 13-nm Au particles functionalized with two different oligonucleotide probes undergo hybridization with complementary (target) DNA strands, turning the solution from red to blue. The colorimetric "spot test" assay is capable of detecting antisense oligonucleotides in femtomole quantities (nanomolar concentrations), and can differentiate single-nucleotide mismatches as a function of a characteristic melting temperature. The magnitude of the color change (due to the increased electromagnetic coupling within the DNAnanoparticle network) is dependent both on the effective interparticle distance between nanoparticles and on aggregate size. Hybridization with antisense oligonucleotides of different lengths revealed marked differences in the kinetics of aggregate formation, with gradual increases in average cluster size correlating with changes in optical extinction.<sup>74</sup>

As mentioned earlier, nonperiodic nanoparticle ensembles can also enhance spontaneous emission events such as SERS,<sup>63</sup> albeit with some degree of variability. One practical method of preparing SERS substrates with fairly reliable and stable enhancements is to adsorb metal nanoparticles onto amine or thiol-functionalized substrates. Submonolayer ensembles of colloidal metal particles can be prepared with packing densities of up to 30% (see Figure 19, *left*), which is well below the close-packing limit (~90%) but sufficient to produce significant electromagnetic coupling and SERS.<sup>75,76</sup> Electrostatic self-assembly of Au nanoparticles on spherical submicron particles has also been reported recently;<sup>77</sup> 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 (see Figure 19, *right*).



*Figure 19. Left,* planar ensemble of ~40-nm Au particles adsorbed onto thiol-functionalized  $SiO_2$ .<sup>75</sup> *Right,* spherical core–shell ensembles of 30-nm particles adsorbed onto amine-functionalized  $SiO_2$  particles (390 nm).<sup>77</sup> Scale bar = 200 nm in both cases.

In closing, the sundry topics described in this chapter represent only a fraction of the areas in which plasmonic nanomaterials have found

application. There is a strong need for further developments in theory and computational methods to predict collective electromagnetic behavior, and also for new methods of anisotropic nanoparticle synthesis and their controlled assembly into novel plasmonic nanostructures. As nanotechnology continues to evolve, these directions will become increasingly defined by their near- or long-term 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. Biomedical optics also promises to be a fruitful field for plasmonic applications, given the biological inertness of gold and the relative transparency of human tissue to NIR wavelengths. Lastly, the emerging area of nano-photonics is anticipated to have long-term impact on telecommunications and device integration, with possible added benefits for the first two application areas.

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