Light Interaction between Gold Nanoshells Plasmon Resonance and Planar Optical Waveguides

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We have studied the experimental and theoretical aspects of the interaction of gold nanoshells on a waveguiding structure. Gold nanoshells are core−shell particles consisting of a silica core surrounded by a thin gold shell. The waveguiding structure consists of a 2 μm thick layer of gold with a dielectric layer of varying thickness deposited on it. Light scattering experiments performed on gold nanoshells randomly deposited on the dielectric layer show a change in the scattering spectrum of the nanoshells because of coupling of light with the waveguide modes. Comparison of experimental data with theoretical calculations based on the classic theory of point dipoles placed over a conducting surface shows a significant shift in the dipole resonance position. A simple image charge calculation taking into consideration finite size effects explains the red shift observed in the experimental data for the smallest dielectric layer thickness. Observed deviations from the theoretical models are attributable to nanoshell aggregates.

1. Introduction

Noble metal nanoparticles are known for their ability to support resonant plasma oscillations. When these nanoparticles are placed on a waveguiding structure that can support optical guided modes within the spectral range of the nanoparticle resonance, there is a coupling of the scattered light from the nanoparticles to the waveguide modes. Stuart and Hall[1] have shown qualitative changes in the scattering spectra of silver nanoparticles randomly placed over a waveguiding structure. Linden et al.[2] have studied the change in the extinction spectra of an array of gold nanoparticles deposited over a waveguiding structure. Both groups have attributed the observed changes to light coupling to the modes supported by the underlying structure.

In this paper, we report on the interaction of gold nanoshells deposited on a waveguiding structure. Nanoshells are colloidal particles that consist of a small dielectric core covered by a thin metallic shell.[3,4] The wavelength of the plasmon resonance of the nanoshells can be tuned in the visible and near-infrared regions by varying the core/shell radii. This allows for the design of nanoshells with plasmon resonance across a spectral range from about 600 to 2500 nm.[5] Light scattering from nanoshells is explained by Mie scattering theory.[3−5]

2. Experimental Techniques

The nanoshells used in the following experiments consist of a silica core covered by a gold shell. The dipole resonance of the gold nanoshells was designed to be at 650 nm. The nanoshells used in the present experiment have a core radius $R_1 = 31$ nm and total particle radius $R_2 = 43$ nm. The average radius of the core is determined using transmission electron microscopy (TEM) and a statistical analysis of the TEM images. The total particle radius is determined by a theoretical curve fitting to the UV−visible spectrum of the nanoshells. The UV−visible spectrum of an aqueous solution of nanoshells is shown in Figure 1. In addition to the strong dipole resonance peak at 650 nm, a second broader peak at 900 nm is seen because of the presence of doublets and other low order aggregates present in the solution.[5] The theoretical cross section was calculated using Mie scattering theory.[3]

Figure 2a shows a schematic of our sample geometry. An approximately 200 nm thick layer of gold was sputter coated onto an indium−tin−oxide (ITO) coated glass slide. Self-assembled monolayers (SAMs) of a cationic polyelectrolyte PDDA (poly(diallyldimethylammonium chloride) and anionic sheets of an exfoliated synthetic clay (Laponite RD, a synthetic form of hectorite)[6] were deposited on the gold surface to control the spacing s to nominally nanometer precision between the gold surface and the gold nanoshells. The method of deposition and optical constants ($n = 1.50$, $k = 0$) were taken from ref 6.

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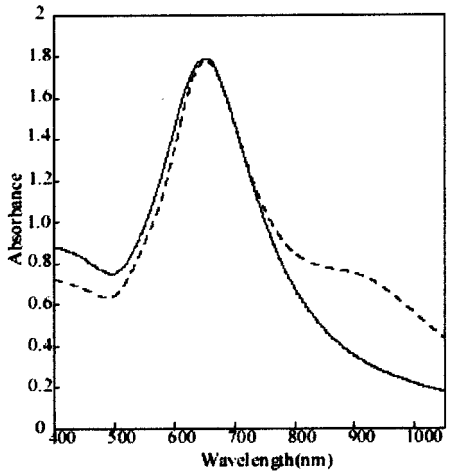

Figure 1. UV-visible spectrum (dashed line) and the calculated cross section (solid line) for an aqueous solution of gold nanoshells.

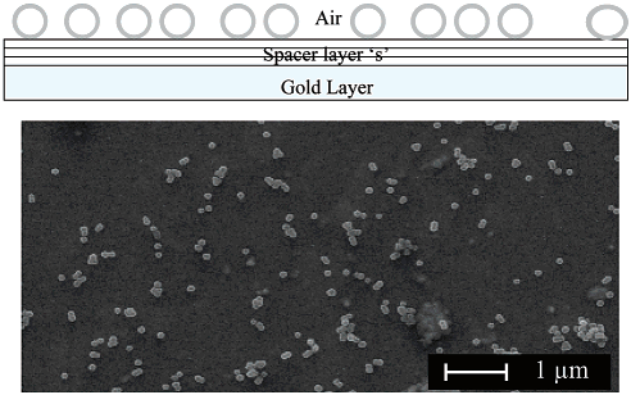

Figure 2. (Top) Schematic diagram of sample geometry. (Bottom) SEM micrograph showing a typical distribution of nanoshells on the dielectric surface.

A submonolayer of gold nanoshells (Figure 2b), with an average spacing of 200 nm and approximately 27% coverage (as determined by scanning electron microscopy), was deposited on the SAMs by evaporating 10−20 μL of concentrated aqueous solution containing nanoshells. Figure 2b also shows the presence of doublets and low order aggregates.

For light scattering experiments, the samples were illuminated at normal incidence by light from a tungsten−halogen lamp passed through a monochromator. The elastically scattered light was collected using a lens positioned at 45° and a Hammamatsu S1336−44BQ photodiode detector. All experimental data are shown to scale as acquired and have been reproduced on similar samples with the same percentage of nanoshell coverage to ensure consistency.

3. Results and Discussion

Figure 3 shows the modification in the nanoshell scattering spectrum because of interaction of the nanoshell resonance with the surface plasmon (SP) of the nearby gold surface. We can divide the surface plasmon−nanoshell plasmon interaction into three regimes depending upon the separation *s*. In spectra 3 parts a and b for the smallest separations, there is a significant overlap of the near field of the nanoshell with the surface plasmon mode. Here we observe the strong dipole peak that has shifted from 650 nm in water to 760 nm for $s = 3.4$ nm and to 694 nm for $s = 17$ nm. As well, there is an enhancement of the quadrupole peak at about 580 nm. As the thickness of the spacer layer increases (spectra 3 parts c and d), we observe less enhancement

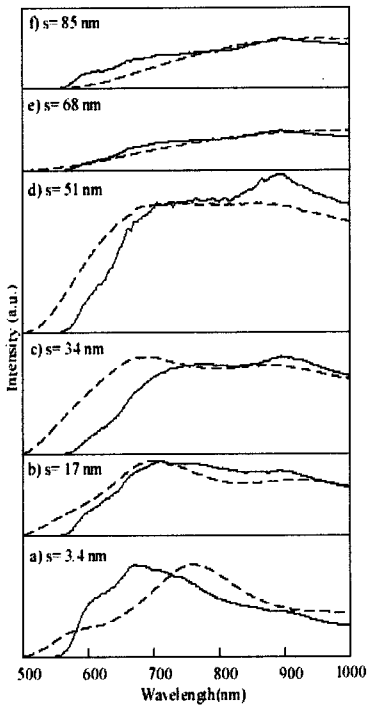

Figure 3. Light scattering spectra for various thickness of spacer layer. The dashed lines are the experimental data, and the solid lines are the calculated theoretical spectra.

of the dipole and quadrupole peaks, but the peak at 900 nm because of interparticle effects dominates. This enhancement of the peak because of interparticle interactions suggests that the surface plasmon mode mediate the interaction between nanoshells over a much longer distance, governed by the surface plasmon attenuation length. In the last two spectra for large separations, as the overlap between the nanoshell near field and the surface plasmon mode decreases, the broad peak because of the dipole and interparticle effects decreases and red shifts to longer wavelengths.

Theoretically, the energy transfer process can be explained using arguments similar to those used by Stuart and Hall[1] to explain the change in the scattering spectra of silver island films deposited on a silicon on insulator (SOI) structure. These arguments are based on the classic theory of a point dipole over a metal surface proposed by Chance, Prock, and Silbey (CPS)[7] and further developed by Weber and Ford.[8] The CPS theory provides an energy transfer mechanism between an excited point dipole and the surface plasmon (and other propagating modes) that falls within the near field of the dipole. Stuart and Hall[1] carry the arguments further by considering an energy transfer path mediated by the propagating waveguide modes.

The incident white light is scattered by the nanoshells and couples to the surface plasmon mode. This interaction is thus proportional to $\sigma_s f_m$, where σ_s is the scattering cross section of the nanoshells and f_m is the fraction of scattered energy that couples to the SP mode. Because of the reciprocity of light, the energy in the SP can couple out to the nanoshells via the same mechanism and thus is proportional to the same term $\sigma_s f_m$. The guided mode has a propagation length of L_m, and thus, all of the nanoshells within an area proportional to L_m^2 can act as channels for the energy transfer from the SP to the nanoshells. Finally, a fraction of this energy is scattered into air as f_{air}. Thus, we can write the wavelength dependence of the total interaction as

$$\eta_m(\lambda) = (\sigma_s(\lambda)\, f_m(\lambda))^2\, L_m{}^2(\lambda)\, f_{air}(\lambda) \quad (1)$$

Theoretical fits are done by using eq 1. To calculate $L_m(\lambda)$, the form of the electric fields for guided modes in each layer are written down and then continuity equations applied. This results in a transcendental equation for the propagation constant of the *m*th mode, which can be numerically solved. Because the propagation constant is directly related to the effective indices of the mode, n_{eff}, the attenuation length is obtained by noting that $L_m(\lambda) = \lambda/(4p\ Im(n_{eff}))$. The energy coupling fractions, $f_m(\lambda)$ and $f_{air}(\lambda)$, are determined numerically from the equations for modified damping rates of dipoles near interfaces.[7,8] Figure 3 shows the comparison of the theoretical and experimental spectra for dielectric layer thickness from 3.4 to 85 nm. The theoretical data are scaled to the maximum of the experimental data. The theory does not take into account modifications in the nanoshell spectra because of interparticle interactions that may occur either because of aggregation on the spacer layer or because of interactions between the nanoshell and its image. Interparticle effects and the interaction distance over which they occur are currently under investigation.

On comparison, we observe that for the smallest dielectric layer (spectrum 3a), the observed dipole peak is red shifted by about 65 nm with respect to the theoretically predicted peak. The quadropole peak observed at 580 nm is not well fit by this theory, as it assumes that a pure point dipole and no higher order multipoles participate in the energy transfer process. As the dielectric spacer layer thickness increases (spectra 3 parts b−d), we observe a blue shift in the position of the dipole resonance peak, which shifts to wavelengths smaller than those predicted by theory. By shifting the theoretical curves, one can achieve a reasonable agreement with the experimental data. In Figure 4, we show a comparison of the experimental data with the shifted theoretical curves. These shifts are listed in Table 1. A number of theoretical investigations of point dipoles interacting with conducting surfaces have shown surface induced shifts in the dipole resonance frequency.[9−12]

The basic trends of these shifts can be understood by considering the reflected field (E_{ref}) incident at the position of the dipole. For purposes of this analysis, the nanoshell is approximated by a point dipole. CPS[9] derived an approximate expression for the frequency shift of the dipole resonance, $\Delta\omega$, because of E_{ref}

$$\frac{\Delta\omega}{b_\infty} \approx -\frac{3}{4}\gamma\, Re\left(\frac{\epsilon_1 E_{ref}}{k^3 \mu_0}\right) \quad (2)$$

Here, b_∞ is the decay rate (the lifetime of the resonance) in the absence of an interface, ϵ_1 is the dielectric constant of the medium in which the dipole (the nanoshell) is embedded, k_1 is the wave-vector in that region, γ is the quantum yield of the emitting state, and μ_0 is the dipole moment. For the current discussion, γ is taken to be 1. Both the magnitude and the sign of the frequency shift depend critically on the reflected field at the position of the dipole. Therefore, it is important to know how E_{ref} behaves with change in dielectric layer thickness. The use of appropriate Fresnel coefficients at both interfaces gives the net reflected field at the dipole position.

E_{ref} changes sign as the spacer layer thickness changes. This is true for both the parallel and perpendicular polarization of light. For normal incidence of light, E_{ref} goes from a positive to a negative value with increasing value of *s*, suggesting a transition from red to blue shifts in the dipole resonance position. Similar results are obtained for the case of parallel polarization.

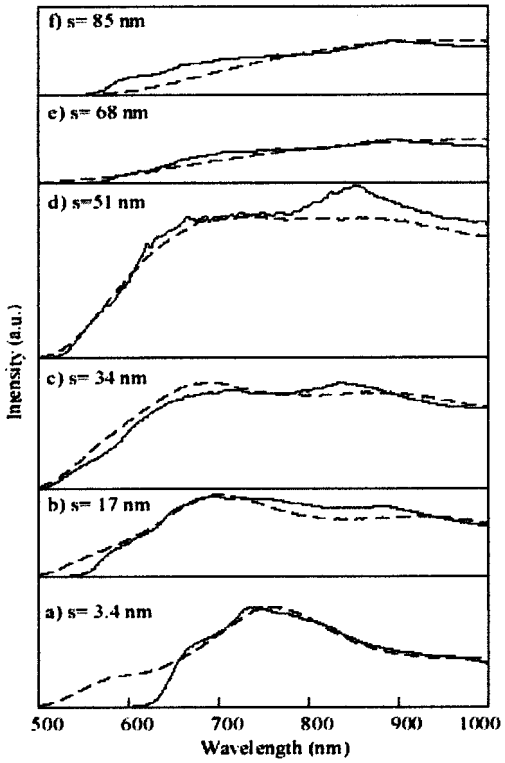

Figure 4. Comparison of the experimental light scattering spectra and the shifted theoretical curves. The dashed lines are the experimental data and the solid lines are the calculated theoretical spectra, shifted by amount shown in Table 1.

TABLE 1: Experimental and Theoretical Shift in Dipole Peak Position for Different Spacer Layer Thickness

spacer layer thickness	shift in peak position	CPS theory	image charge theory
3.4 nm	+ 65 nm	+2.4 nm	+26 nm
17 nm	−15 nm	−25 nm	+11 nm
34 nm	−60 nm	−32.7 nm	+4.9 nm
51 nm	−40 nm	−26 nm	+2.6 nm
68 nm	0	−18 nm	+1.6 nm
85 nm	0	−14.2 nm	+1.0 nm

The shifts calculated using eq 2 for the spacer layer thickness in the experiment are listed in Table 1. These shifts are in qualitative agreement with shifts used in Figure 4.

The large red shift observed for the thinnest dielectric films cannot be explained using CPS theory. The CPS theory treats the dipoles as point dipoles. A physical effect absent from the CPS theory is the effect of the image interaction of a finite dipole with a conducting surface.

A simple approach to modeling the plasmon oscillations of the conduction electrons of the nanoshell as a rigid translation of spherical charge distribution with respect to its positive background has been developed. The image interaction between the finite dipole and the conducting surface results in a red shift of the dipole plasmon frequency. For horizontal polarization, the image charge model predicts

$$\Delta\omega_p^H(z, R) = \omega_p^0\left\{1 - \sqrt{1 - \left[9\left(\frac{z}{R}\right)^2 + 1\right]^{-3/2}}\right\} \quad (3)$$

and for vertical polarization the shift in frequency is

$$\Delta\omega_p^V(z, R) = \omega_p^0\left\{1 - \sqrt{1 - 6\frac{z}{R}\left[9\left(\frac{z}{R}\right)^2 - 1\right]^{-2}}\right\} \quad (4)$$

where $\Delta\omega_p$ is the theoretical dipole resonance frequency shift from the experimentally observed resonance frequency ω_p^0, z is the distance of the center of the spherical particle from the conducting surface, and R is its radius. The calculated shifts for the vertical polarization are included in Table 1. As can be seen, the model predicts a relatively strong red shift for the thinnest dielectric layer, and subsequently smaller red shifts for larger spacer layer thickness.

4. Conclusion

In conclusion, the light scattering spectrum of the nanoshells is modified because of the presence of an underlying waveguiding structure. We have measured the shifts in the scattering spectra as a function of the gold−nanoshell−gold surface separation. The nanoshell-surface plasmon interaction is strongly dependent on overlap of the gold nanoshell near field and the surface plasmon mode and thus on the gold−nanoshell−gold surface separation. The classical CPS theory does not take into consideration the finite size of the nanoshell and thus fails to explain the large red shifts observed for the smallest spacer layer thickness. We have developed a simple model considering the nanoshell as a finite sized dipole and the forces exerted on it because of the presence of its image charge. The image charge theory shows similar trends to those observed and gives much better agreement with the large red shift for the smallest separations. Nanoshell−nanoshell interactions are not included in this theory and could contribute to deviations from the experimental values obtained. Investigations are currently underway to explore further the near field of low aggregate nanoshells and their effect on waveguide structures. The tunable plasmon resonant scattering of metal nanoshells provides an additional "tool" for the coupling of light in to and out of optical waveguide structures. This property should lead to further applications in optical waveguide structures and waveguide-based photonic devices.

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References and Notes

(1) Stuart, H. R.; Hall, D. G. *Phys. Rev. Lett.* **1998**, *80*, 5663−5666.
(2) Linden, S.; Kuhl, J.; Gissen, H. *Phys. Rev. Lett.* **2001**, *86*, 4688−4691.
(3) Oldenburg, S. J.; Averitt, R. D.; Westcott, S. L. *Chem. Phys. Lett.* **1998**, *288*, 243.
(4) Jackson, J. B.; Halas, N. J. *J. Phys. Chem. B* **2001**, *105*, 2743.
(5) Oldenburg, S. J.; Jackson, J. B.; Westcott, S. L.; Halas, N. J. *Appl. Phys. Lett.* **1999**, *75*, 2897−2899.
(6) Klienfeld, E. R.; Ferguson, G. S. *Science* **1994**, *265*, 370−373.
(7) Chance, R. R.; Prock, A.; Silbey, R. In *Advances in Chemical Physics*; Prigigine, I., Rice, S. A., Eds; Wiley: New York, 1978; Vol. 37, pp 1−65.
(8) Ford, G. W.; Weber, W. H. *Phys. Rep.* **1984**, *113*, 195−287.
(9) Chance, R. R.; Prock, A.; Silbey, R. *Phys. Rev. A* **1975**, *12*, 1448−1452.
(10) Morawitz, H. *Phys. Rev.* **1969**, *187*, 1792−6.
(11) Kuhn, H. *J. Chem. Phys.* **1970**, *53*, 101−8.
(12) Aravind, P. K.; Metiu, H. *Surf. Sci.* **1983**, *124*, 506.