Optical absorption resonances of dye-coated silver-island films

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We have used Mie theory to account for the features of the transmission spectra of dye-coated silver-island films. The unusual behavior of the spectra arises from the effect of the dispersion and damping of the optical response of the absorbing coating on the structural resonances of the silver islands. Our modeling indicates that the power dissipation in the dye coating is enhanced compared with the dissipation of dye deposited on a nonresonant structure. These results help elucidate the excitation mechanisms of Raman and fluorescent emission of adsorbates at rough silver interfaces.

Stimulated initially by the observation of surface-enhanced Raman scattering (SERS),[1] recent studies have probed a variety of optical properties of rough silver interfaces.[2,3] Resonances between small silver particles and the incoming and outgoing electromagnetic waves are believed to play a crucial role in SERS.[4] The consequences of these resonances have been studied for many years, and, for isolated particles, they are well described by Mie theory.[5,6]

In this Letter, we examine the optical transmission of silver-island films overcoated with dye molecules. As first reported by Glass *et al.*,[2] the transmission of such films exhibits unusual spectra, which are not a simple superposition of the individual silver and dye transmissions. Similar unusual effects have been discussed for simple molecules adsorbed on a polycrystalline substrate.[7] We show that the application of Mie theory to calculate the absorption of a layer of isolated, coated silver spheroids qualitatively reproduces the observed spectra. Through this modeling, we are able to probe the power dissipation and find an enhanced absorption in the dye coating, with a corresponding reduction in the absorption in the silver. These results have direct application to elucidating the fundamental phenomena underlying SERS and other emissive processes of adsorbates at rough silver interfaces.

Island films[8] are prepared by a slow (0.5–1-Å/sec) thermal evaporation of mass thicknesses of 30–60 Å of silver on silica substrates. Varying thicknesses of dye coatings are deposited on the films by dipping the films into ethanolic solutions with different dye concentrations. A detailed study[9] shows that this dipping technique produces dye coverages that increase monotonically with solution concentration.

The variation of the transmission spectra of the coated films as the R6G layer thickness is increased is shown in Fig. 1. The transmission spectrum of the bare silver for each sample is identical with that of all other samples (Fig. 1a) and exhibits an absorption peak (at λ_{Ag}) caused by the structural resonance of the small silver particles in the film.[8] In none of the cases (Figs. 1b–1d) is the spectrum of the coated film a simple superposition of the individual silver spectrum and dye spectrum (Fig. 1e). For low coverages, the shape of the resonance of the silver is unaltered, but its amplitude is changed. For increasing coverages, an anomalous splitting appears and increases in severity with increasing dye thickness. The valleys in these spectra occur at approximately the wavelength of maximum dye absorption (λ_{dye}).

The shape of the transmission spectrum can also be changed as the relative spectral positions of λ_{Ag} and λ_{dye} are varied. The width and peak wavelength of the resonance of the bare silver are related to the shapes and sizes of the islands and the interparticle spacing[8] and can be varied by changing the deposition parameters of the film. The effect of varying λ_{Ag} relative to λ_{dye} is shown in Fig. 2. Qualitatively similar effects are observed when λ_{Ag} is held constant and λ_{dye} is varied by using different dye coatings.

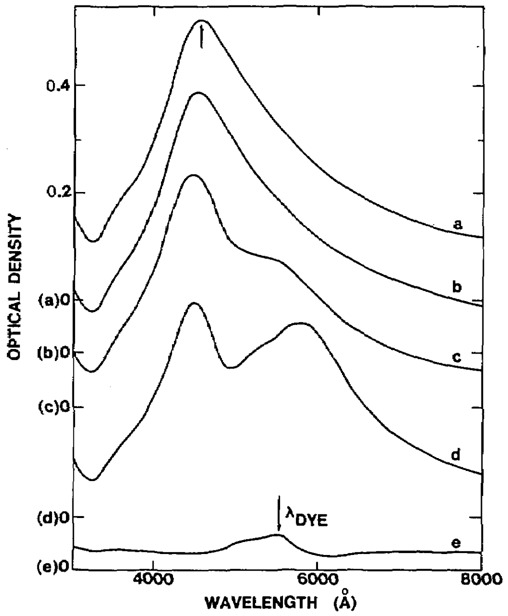

Fig. 1. Absorption spectra of 42-Å silver-island films with different thicknesses of R6G dye coatings. The solution concentrations of the R6G are (a) uncoated, (b) 2×10^{-5} M, (c) 2.8×10^{-4} M, (d) 10^{-3} M, and (e) 10^{-3} M on silica with no silver. The unlabeled arrow points to λ_{Ag}.

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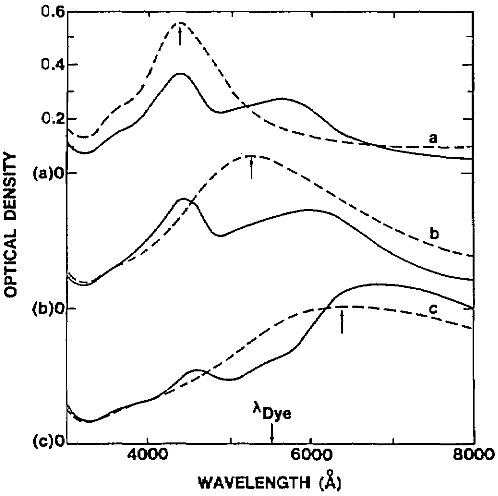

Fig. 2. Absorption spectra of bare (dashed lines) and coated (solid lines) silver-island films with increasing λ_{Ag} (arrows). The concentration of the R6G ethanolic dip was 10^{-3} M.

To account for the observed spectra, we use a simple model that still retains the essential physics. We apply Mie theory to calculate the absorption of a dilute collection of optically isolated, oblate spheroids with the incident field polarized along the semimajor axis (A). The dielectric function of the silver ($\epsilon_{Ag} = \epsilon'_{Ag} + \epsilon''_{Ag}$) is assumed to be the same as in bulk,[10] whereas the dye is assumed to respond to the optical wave like a damped, harmonic oscillator.[11] The amplitude of the dye response is chosen such that a 5-Å layer of dye has an optical density of 0.002 [$\epsilon''_{dye}(\max) \approx 2.6$]. However, the spectral halfwidth of ϵ''_{dye} and λ_{dye} of the model response are chosen to be 480 and 4400 Å, respectively, and are meant merely to illustrate physical principles rather than to model a particular dye. We assume that the particles are sufficiently small that they respond to the optical field as dipoles. Then their effect on the incident field is only absorptive and their extinction efficiency (absorption cross section/geometric cross section) is $Q = 8\pi B\alpha''/\lambda$, where B is the semiminor axis of the spheroid, λ is the optical wavelength in the external medium, and α'' is the imaginary part of the polarizability of the spheroid. The polarizability is determined by (1) solving Laplace's equation for the field potential in three regions of space: in the silver particle core, in the coating, and external to the particle, (2) matching the boundary conditions on the potential at the interfaces, and (3) enforcing regularity of the solution at infinite distance from the particle. We use Sheng's solution to this problem [Ref. 12, Eqs. (3a) and (3b)] with dielectric and geometric parameters appropriate to our problem. The optical density of a dilute collection of particles is proportional to the Q of a single particle.[5]

Calculated transmission spectra for a silver spheroid with a 3:1 aspect ratio and core major axis of 75 Å and varying thicknesses of dye coating are shown in Fig. 3. The simple model qualitatively accounts for all the features observed in the dye-thickness dependence of the transmission spectra. Initially, the dye coating broadens and damps the silver resonance while, for thicker coatings, a splitting develops. We note that both the valley and the small peak in the valley are predicted (Fig. 3d) and observed (Fig. 1d).

Within this simple model, the predicted silver absorption peaks are much narrower than observed and λ_{Ag} is determined solely by the ellipticity. Variations in island shape and size, boundary scattering of conduction electrons, and the effect of fields from neighboring islands have been ignored but would all broaden the resonance and shift λ_{Ag}. Mean-field models based on the Maxwell–Garnett formulation and incorporating additional parameters to describe these effects have been used successfully to account for the optical properties of the bare silver films.[8] Spectra calculated with mean-field models also show similar effects caused by the dye coating.[13] However, since the essential physics underlying the effects of the coating is reflected in the simple model, the additional parameters involved in the mean-field models add unnecessary complications and are not considered here.

Figure 4 shows the calculated absorption spectra as the ellipticity is varied to move λ_{Ag} relative to λ_{dye}. Again, all the features of the observed spectra are qualitatively reproduced. When λ_{Ag} is shorter than λ_{dye}, the short-wavelength peak of the spectrum is larger; as λ_{Ag} moves to larger wavelengths beyond λ_{dye}, the long-wavelength peak of the spectrum moves to longer wavelengths and becomes larger. More-elaborate models give a better account[13] of the width and position of the resonance but show a similar effect of the coating.

We also calculated the power deposited in the dye and the silver when the coated particle is excited by the

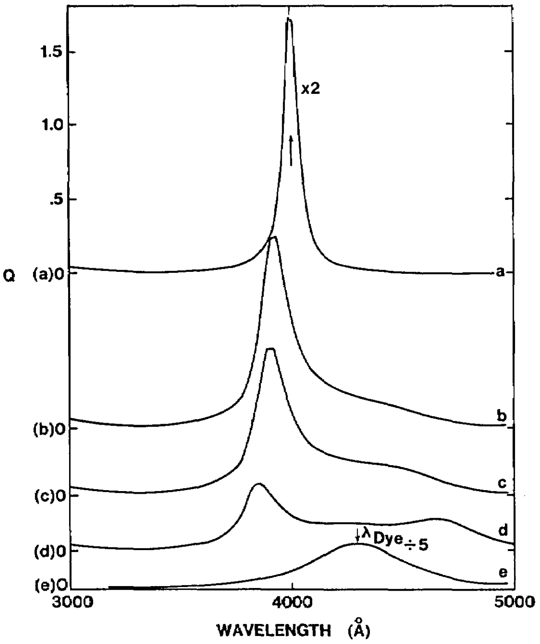

Fig. 3. Calculated absorption of silver spheroids for increasing thicknesses of absorbing dielectric coatings. The 3:1 aspect ratio and the core major axis of 75-Å are held constant, and the fractional increases in the major axis that are due to the coatings are (a) 0, (b) 0.04, (c) 0.07, and (d) 0.27. The absorption of the dye coating of case (d) but with a hollow core is shown in (e).

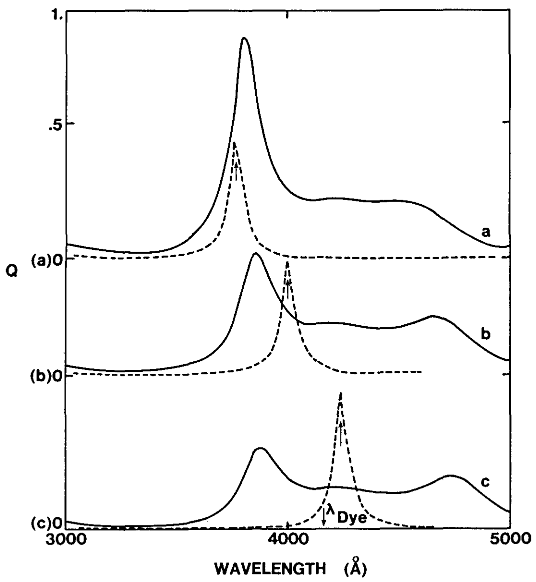

Fig. 4. Calculated absorption of bare (dashed lines) and coated (solid lines) silver spheroids with varying λ_{Ag} (arrows). The aspect ratios are (a) 2:1, (b) 3:1, and (c) 4:1. The fractional increase in the major axis that is due to the coating is 0.27, and the core major axis is 75-Å. The curves for bare silver have been reduced by a factor of 8.

optical wave. If the incident intensity is I_0, the power absorbed by the composite spheroid is $P_C = Q\pi A^2 I_0$,[5] whereas the power absorbed in the silver core is $P_{Ag} = \omega\epsilon''_{Ag}|E|^2V/8\pi$, where ω is the optical frequency, V is the core volume, and E is the uniform field inside the core.[14] E is related to the incident field by a complicated expression involving geometric factors and all the dielectric functions in the problem and is obtained from the potential found in the boundary-matching solution of Laplace's equation.[15] The power absorbed in the dye coating is then $P_{dye} = P_C - P_{Ag}$. The following results are obtained: (1) More power is deposited in the dye on the silver core than is deposited in dye on a similar nonresonant structure. (2) Less power is deposited in a silver core coated with dye than in uncoated silver. (3) More power is dissipated in the dye than in the silver, even for coatings as thin as a fractional increase of 0.04 in the spheroid axes. (4) The spectral dependence of the power absorbed in the composite particle, the silver core, and the dye coating is essentially the same.

From the experiments and modeling described above, we can derive a physical picture of the mechanisms causing the observed spectra of the dye-coated, silver-island films. For a certain set of wavelengths near λ_{Ag}, the silver particles in the film act as antennas, draw radiation from an area larger than their geometric size (as evidenced by $Q > 1$), and concentrate the field inside the particles. The field intensification occurs because of a structural resonance of the in-phase response of the conduction electrons to the incident and depolarization fields and causes the absorption resulting from ϵ''_{Ag} to increase. However, the nonzero value of ϵ''_{Ag} tends to damp the electronic oscillations that set up the resonance and therefore to decrease the strength of the resonance. The dispersion of ϵ'_{dye} alters the detailed boundary conditions and causes modifications in the spectral shape of the structural resonance of the composite and can cause the anomalous splitting. Further, since $\epsilon''_{dye} > \epsilon''_{Ag}$, the power absorbed in the coated silver core is less than the power absorbed in a similar uncoated core, and most of the absorption occurs in the dye.

The enhanced absorption of the coating can also enhance inelastic light-scattering processes from the molecules, and we do indeed observe intense Raman scattering from dye molecules on silver-island films, in contrast to the case of dyes in solution or on bare silica. However, we do not observe Raman scattering from the acoustic vibrations[3] of the dye-coated silver islands, illustrating that the absorptive coating actually reduces the power dissipated in the silver core. Whereas the use of strongly absorbing coatings allows us to probe the absorption process experimentally, we expect similar phenomena to occur for coatings with smaller ϵ''. For example, if λ_{dye} is shifted into the UV to model coatings consisting of organic molecules, such as benzene, we find that the silver resonance is broadened somewhat and causes the power absorbed in the coating to be substantially increased. Thus we believe that the understanding of the absorption process of coated silver spheroids developed in this Letter may aid in elucidating the detailed mechanisms involved in SERS and other optical processes at rough interfaces.

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