

Metal nanoparticle plasmonics inside reflecting metal films

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Abstract

Oxide coated metal nanoparticles buried within a thin metal layer support a surface plasmon resonance. A local dip occurs in spectral reflectance along with a switching off of the film's plasmonic response. Models are introduced in which these resonances are tunable by altering the ratio of oxide thickness to core particle radius. The optical response of two experimental examples is presented and modeled using effective medium theory. Beyond the resonance zone the doped layer switches back to the plasmonic response of a nano-porous version of the host metal whose effective plasma frequency arises only from the percolating component.

Plasmon resonant absorption in conducting nanoparticles is widely used to add absorption bands to transparent materials. If the added particles are small enough relative to wavelength there can be negligible scattering¹ and the composite material is in effect optically homogeneous. A similar means of adding controlled absorption bands to reflecting materials would create new opportunities in spectral control, plasmonic technology and thin film physics. A simple approach is presented to achieve this with conducting nanoparticles if coated with thin enough dielectric and embedded in reflecting metal. If the coated particles are small enough optical homogeneity occurs and specular reflectance is retained. Particles larger than ~50 to 80 nm across would introduce resonant scattering and hence diffuse reflectance. The particles in this study are under 15 nm across and no evidence was observed for a diffuse component in reflectance. This is a new class of composite effective medium, with a very wide range of controllable optical response. It can be a two phase composite if particle and host conductor are the same metal, or three phase if they are different. As with bare metal particles in transparent matter resonant shifts occur if particle shape changes, but they can also occur in this case if the ratio of coated particle total volume to core particle volume changes.

Core-shell nanoparticle resonators, in which a dielectric core with a thin layer of metal is embedded in an insulator² are also tunable by altering this ratio. Surface plasmon resonances on the two adjacent metal surfaces in such particles hybridise³. The resultant low energy resonance shifts in location with changes in the ratio f of core insulator volume to total particle volume. Nano-circular cylinders have $f = (r/R)^2$ and nanospheres $f = (r/R)^3$, with r core radius, and R combined core-shell radius. The predominantly metal nanostructure of interest here is their counterpart in which metal replaces insulator and vice versa. Such a relationship between two structures is referred to as Babinet's Principle. Evidence for such resonant entities⁴ with 2-dimensional character has been recently reported in two different types of porous metal films which grew via diffusion^{5,6}. Resonance broadening arose from the natural distribution of f .

The insulating shell in that study was a void or dielectric filled void. Here it is a thin dielectric coating on an isolated metal nanoparticle. From a practical perspective both elements in this composite particle, the core metal and the shell, can in principle be independently controlled in size to control f . Considerable scope for engineering the resonance structure and location follows. If f has a range of values in the composite then the model following gives a set of overlapping resonances leading to one broadened resonance. If instead core particle size and coating thickness do not vary much, a quite narrow resonance will result.

Small composite nanoparticles plus host metal film act as a quasi-static effective medium with complex effective dielectric constants $\epsilon^* = \epsilon_1^* + i\epsilon_2^*$ and complex indices $(n^* + ik^*) = \sqrt{\epsilon^*}$. Our experimental data involves metal nanoparticles formed on a glass substrate, then coated thinly with Al_2O_3 , and finally buried under metal. Normal incidence optical data has electric fields perpendicular to each particle's vertical axis. The effective dielectric constant of such a composite if a single f value applies to all N_{cs} particles in volume V is given by equations (1) and (2). $q = (N_{cs}/V)v_{cs}$ is the volume fraction within the metal host of core-shell entities of volume v_{cs} . Allowance for particle shape is made using a depolarization parameter L . The constituent dielectric constants are ϵ_{hm} for the host metal, ϵ_h for the insulator coating each particle, and ϵ_{mp} for the metal nanoparticle.

$$\epsilon^* = \epsilon_{mh} \left\{ 1 + (q/L) \frac{\alpha(f, L)}{1 - q\alpha(f, L)} \right\} \quad (1)$$

with

$$\alpha(f, L) = \frac{\epsilon_{MG}(f) - \epsilon_{hm}}{\epsilon_{MG}(f) + (1/L - 1)\epsilon_{hm}} \quad \text{and} \quad \epsilon_{MG}(f) = \epsilon_h \left\{ \frac{\epsilon_{mp} + \epsilon_h \left(\frac{1}{L} - 1 \right) + f \left(\frac{1}{L} - 1 \right) (\epsilon_{mp} - \epsilon_h)}{\epsilon_{mp} (1 - f) + \epsilon_h \left[\frac{1}{L} - 1 + f \right]} \right\} \quad (2)$$

The core-shell particle behaves optically like a uniform particle with $\epsilon = \epsilon_{MG}$, which is formally the Maxwell-Garnett effective dielectric constant of a metal in insulator⁷. Only homo-structures are treated in this letter, but it is still necessary to distinguish between ϵ_{hm} and ϵ_{mp} because the nanoparticle's Drude term may involve a higher scattering rate than that of the continuous metal.

The first step was sputter coating a substrate held at 220 °C with silver or gold mass thicknesses in the range 6 nm to 8 nm, then continuing to heat in vacuum for another 90 minutes at 235 °C. Isolated metal nanoparticles form with sufficient spacing to coat with thin Al₂O₃ at thicknesses from 1.5 nm to 5.0 nm. Finally a dense layer of the same metal as the particle was coated to a mass thickness of 40 nm. A schematic of the film structure is in figure 1. The two layer optical model has base layer relative permittivity ϵ^* and thickness t^* , and top layer with ϵ_{hm} and thickness t_{hm} . $\epsilon^*(\lambda)$, t^* and t_{hm} are found by fitting normal incidence reflectance spectra from the glass side and transmittance spectra together. SEM images and particle height estimates from AFM data on particles before burying set the starting values of t^* and t_{hm} .

Two samples on glass are analyzed with coating sequences (a) 8nm Ag-heated/3nm Al₂O₃/40 nm Ag (b) 6nm Au-heated/2nm Al₂O₃/40 nm Au. Figure 2 shows the reflectance spectra of the composite gold sample from the glass side compared with that with no embedded core-shell particles. The reflectance minimum is at 780 nm. Silver has similar behavior with minimum at 745 nm. The values of n^* , k^* found experimentally are plotted in figure 3(a) and (b) with dashed/dotted lines. These effective optical constants are quite interesting, not just at resonance. For $\lambda > 1500$ nm Drude response occurs, but with a lower effective plasma frequency (7.3 eV for Ag or 7.7 eV for Au) compared to the measured uniform film values (8.9 eV for Ag and 9.4 eV for Au). The electrically

isolated nanoparticles thus do not contribute to the effective Drude term and the composite high metal content film acts at these wavelengths like a nanoporous metal⁸.

A distribution of individual f values and hence multiple overlapping peaks is present since observed particle cross-sections in our SEM images vary. The experimental resonant peaks in figures 2 and 3 result. Figure 3(c) indicates theoretically for $f = 0.62$ in equations (1) and (2) what is expected in the limit when each particle has the same size and oxide coating thickness, namely a narrower and stronger absorptance peak. The theoretical fit (solid lines) to the observed indices n^* , k^* in figures 3(a) and 3(b) thus required the use of a weighted sum of individual f terms in equations (1) and (2). The two f -distributions used are plotted in figure 4 and correlate reasonably well with imaged particle cross sections and estimated particle heights with oxide coating thickness fixed in all particles. Resonances are very weak for $f < 0.3$ and can be ignored. The component metal indices used were as measured on dense thin films for the upper layer, but in the composite layer a modification of Drude relaxation time was needed due to reduced mean free paths in the nanostructure. The best fit $q_{\text{Ag}} = 0.35$ and $q_{\text{Au}} = 0.40$. These values were consistent with images and the average L values of 0.45 for Ag and 0.40 for Au.

The same metal nanoparticles used above in 40 nm of Al_2O_3 under a 40 nm metal over-layer were made, to check they behaved quite differently. An interesting new feature is the ability to switch from a plasmonic ($k^* > n^*$) to a non-plasmonic effective medium ($k^* < n^*$) then back again as wavelength increases as seen in fig. 3. While the particles do not contribute to the effective plasma frequency at long wavelengths the inter-band metal terms from particles and host are both present. In conclusion we note that Babinet's type structures are of growing interest in plasmonics, for example for enhanced transmittance through nanovoids⁹ and plasmonic antennas¹⁰ but these studies are largely two-dimensional. Three-dimensional Babinet's systems represent a new paradigm with much scope.

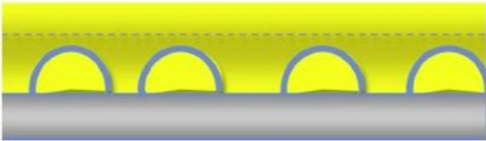
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Figure captions

1. Schematic of experimental coating structure being analyzed showing thin insulator shell on gold nanoparticle all embedded in gold.
2. Glass side reflectance of (a) 40 nm dense gold layer (b) Al₂O₃ coated Au nanoparticles over-coated with a 40 nm gold layer.
3. Experimental (dashed/dotted lines) and modeled (solid lines) optical constants of sputtered metal core-insulator shell composite particles in metal (a) silver (b) gold (c) silver - model only for with $f = 0.62$. (a) and (b) used a distribution of f values.
4. Distribution of core-shell volume ratios f required to fit the resonant peaks in fig. 3 for the Ag (triangles) and Au (squares) nanostructures.

t^*



t_{hm}

