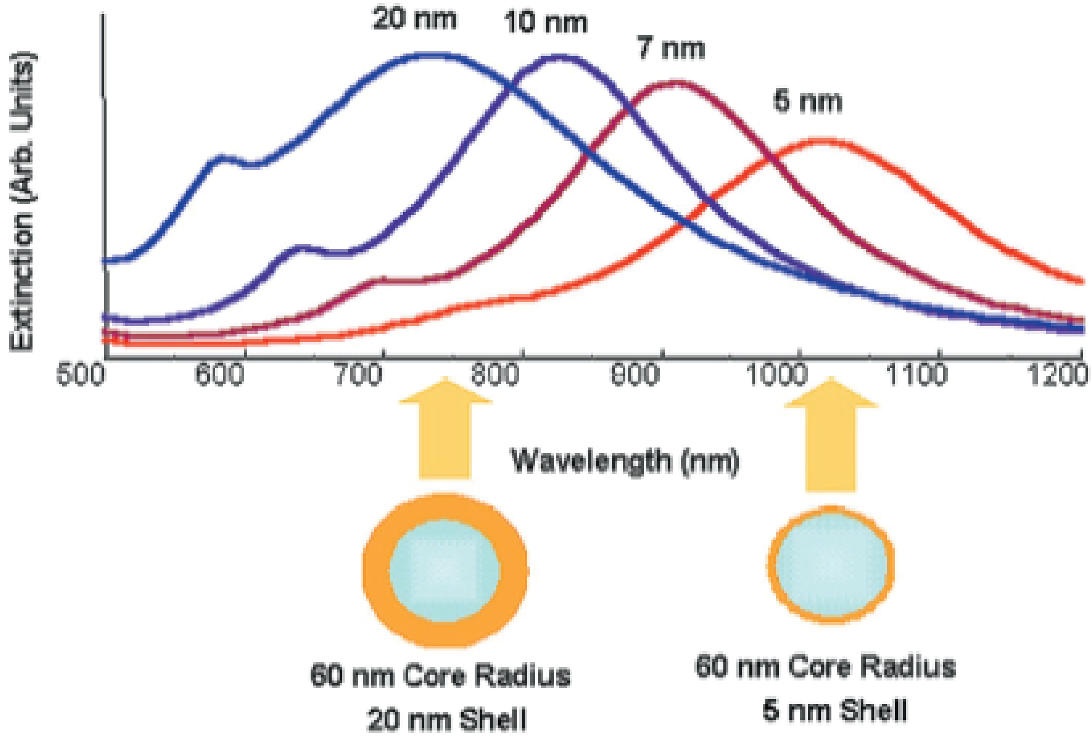
Lecture 19

Gold Nanoshells
Nanoshells – Electrostatic Approximation

Optical Resonances of Gold Nanoshells

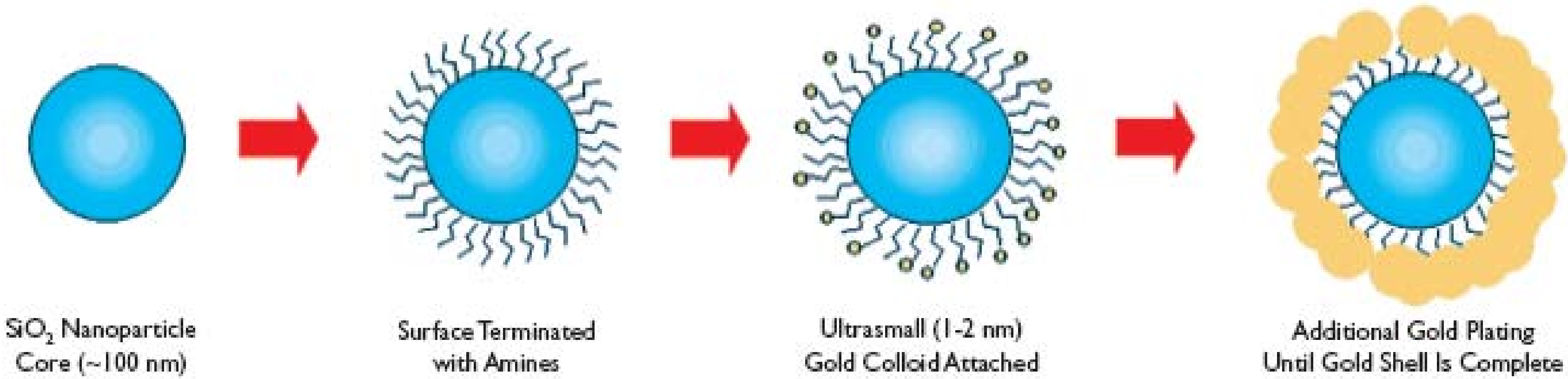
Calculated Optical Resonances of Silica Core, Gold Nanoshells



•Resonant wavelength tunability is useful: for example gold nanoshells could be an alternative to IR absorbing dyes which are limited by thermal stability, toxicity, and lightfastness

From: Halas, Optics & Photonics News, pp. 26-30, August 2002

Optical Resonances of Gold Nanoshells



- Nanoparticles chemically modified so that gold colloids will attach to their surface

- Nanoparticles coated with gold colloid (1-2 nm), covering ~25% of the surface

- Nanoparticle then immersed in electroless plating solution

- Minimum metal thickness achievable is ~ 5nm

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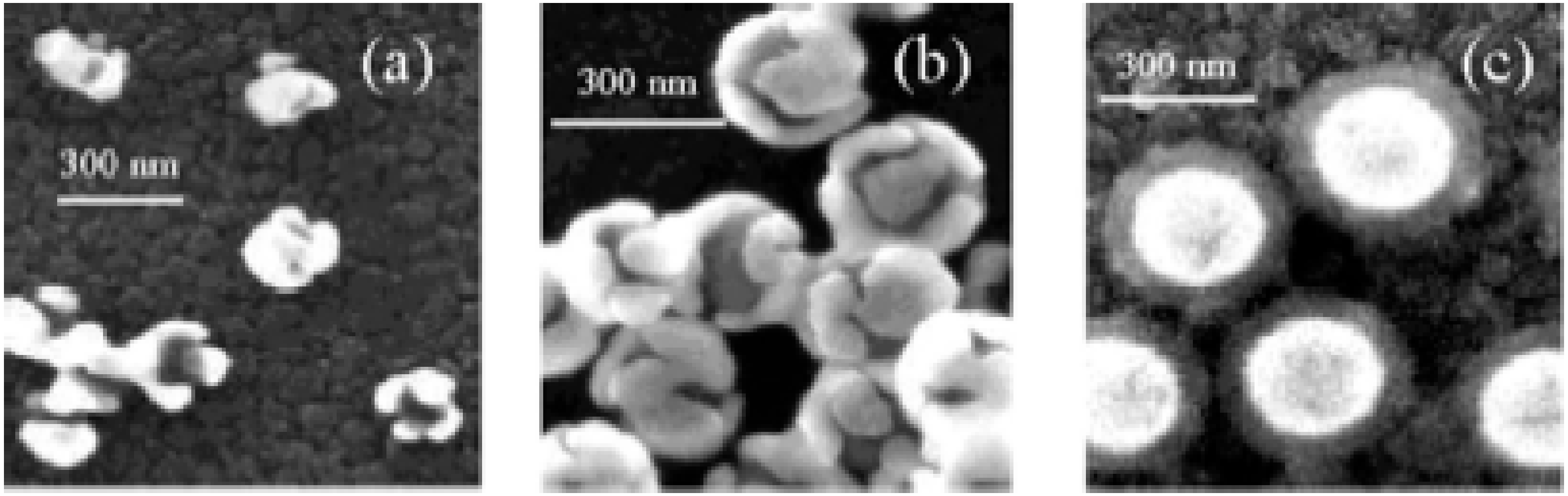
Optical Resonances of Gold Nanoshells



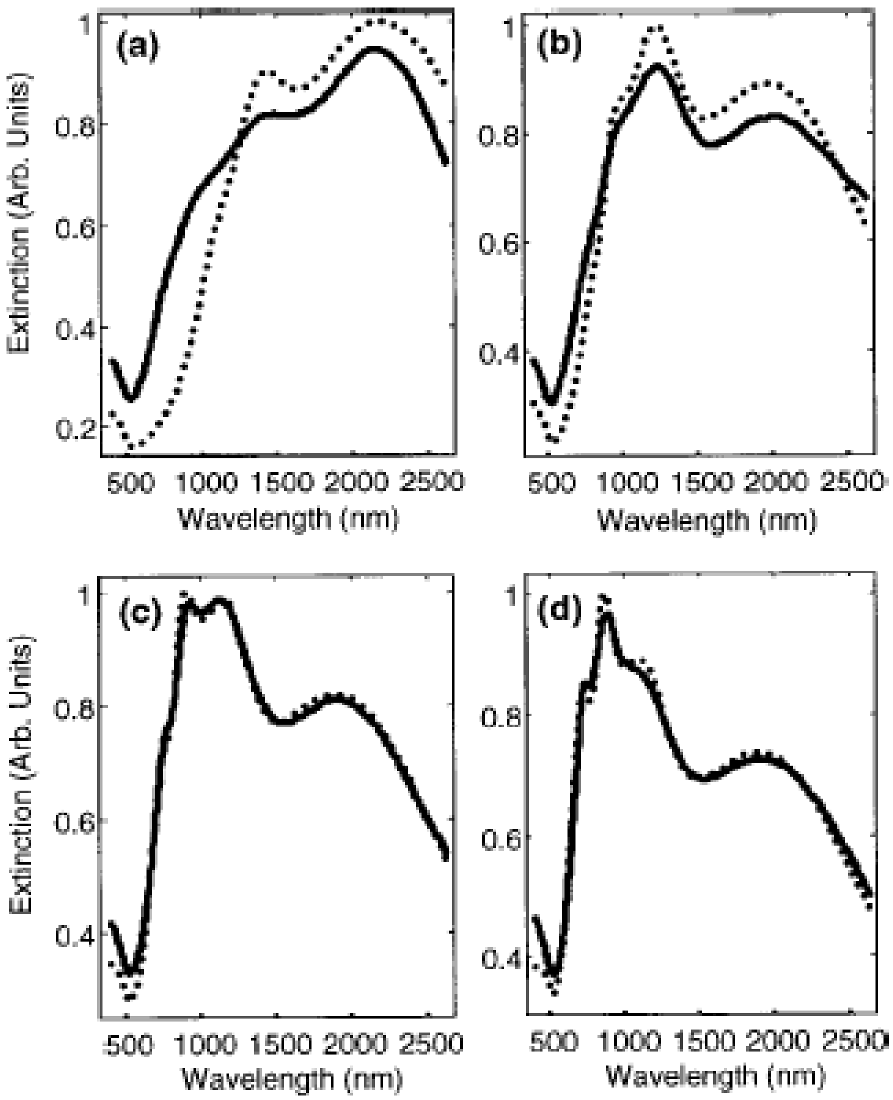
•The melting temperature of metallic nanostructures are typically lower than that of the bulk material

•Silica encapsulation layers of 60-70 nm raise the effective melting temp. from 325 deg. C to greater than 625 deg. C

•In these SEMs, silica core, gold nanoshells have been heated to 325 deg C:
(a). Uncoated nanoshell
(b). Coated with 5nm silica
(c). Coated with 50nm silica

From: Halas, Optics & Photonics News, pp. 26-30, August 2002

Infrared Extinction Properties of Gold Nanoshells



- With gold nanoshells, the optical resonance can be tuned from 2.3 eV to < 0.45 eV

- Spectra are of gold nanoshells with silica cores

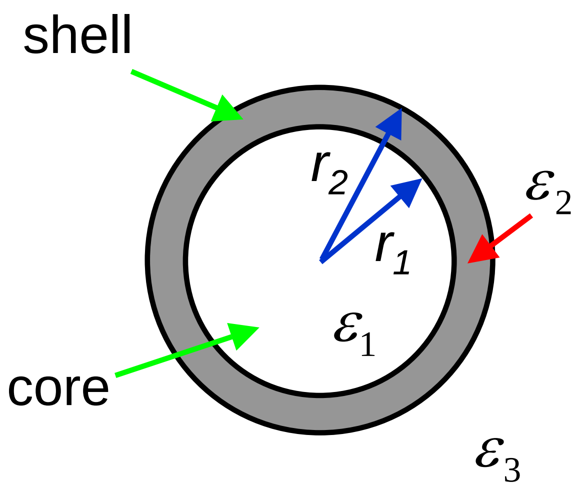
Solid line: experimental data
Dotted line: theory

- Theoretical spectra calculated for 210 nm radius silica core with:

(a). 6 nm gold shell
(b). 10.5 nm gold shell
(c). 15.0 nm gold shell
(d). 20.0 nm gold shell

From: Oldenburg et al, Applied Physics Letters, volume 75, pp. 2897-2899 (1999)

Nanoshells – Electrostatics Approximation



- It is assumed that the particle diameter is much smaller than the wavelength

- The electrostatic solution is obtained by solution of Laplace's equation for the potential

- General solution for potential in each region is given by:

$$\Phi_i(r,\theta) = [A_i r + (B_i / r^2)]\cos\theta \qquad (19.1)$$

where A_i and B_i are constants multiplying the monopole and dipole terms

& *i = 1, 2, or 3* for the core, shell and medium, respectively

Nanoshells – Electrostatic Approximation

•Recall that Laplace's Equation in spherical coordinates is given by:

$$\nabla^2\Phi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Phi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Phi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}$$

$$= 0 \qquad (19.2)$$

•It may be shown that (19.1) satisfies Laplace's equation (19.2)

•How do we find the potential in the core, shell, and embedding medium ?

•Use boundaries conditions at the core/shell and shell/medium interfaces

•Continuity of tangential component of the electric field:

$$\left.\frac{\partial\Phi_i}{\partial\theta}\right|_{r=r_i} = \left.\frac{\partial\Phi_{i+1}}{\partial\theta}\right|_{r=r_i} \qquad (19.3)$$

Nanoshells – Electrostatic Approximation

- Continuity of normal component of displacement field:

$$\varepsilon_i \frac{\partial \Phi_i}{\partial r}\bigg|_{r=r_i} = \varepsilon_{i+1} \frac{\partial \Phi_{i+1}}{\partial r}\bigg|_{r=r_i} \qquad (19.4)$$

- In region 1 (the core), $B_1 = 0$

- In region 3 (surrounding medium), far from the shell we have:

$$\Phi_3 = -E_0 r \cos\theta \qquad (19.5)$$

- Therefore, we have $A_3 = -E_0$

- Therefore, the remaining unknowns are A_1, A_2, B_2 and B_3

Nanoshells – Electrostatic Approximation

•Once the potential is found, the electric field in reach region may be found using the definition of the potential:

$$E_i = -\nabla\Phi_i(r,\theta) \qquad (19.6)$$

•This gives us the electric field in the core as:

$$E_1 = \frac{9\varepsilon_2\varepsilon_3}{\varepsilon_2\varepsilon_a + 2\varepsilon_3\varepsilon_b} E_0(\cos\theta\,\hat{r} - \sin\theta\,\hat{\theta}) \qquad (19.7)$$

•Similarly, the field in the shell is given by:

$$E_2 = \frac{3\varepsilon_3}{\varepsilon_2\varepsilon_a + 2\varepsilon_3\varepsilon_b}\{[(\varepsilon_1 + 2\varepsilon_2) + 2(\varepsilon_1 - \varepsilon_2)(\frac{r_1}{r})^3]E_0\cos\theta\,\hat{r}$$

$$-[(\varepsilon_1 + 2\varepsilon_2) - (\varepsilon_1 - \varepsilon_2)(\frac{r_1}{r})^3]E_0\sin\theta\,\hat{\theta}\} \qquad (19.8)$$

Nanoshells – Electrostatic Approximation

- The electric field in the surrounding medium is then given by:

$$E_3 = \left(2\frac{\varepsilon_2\varepsilon_a - \varepsilon_3\varepsilon_b}{\varepsilon_2\varepsilon_a + 2\varepsilon_3\varepsilon_b}\frac{r_2^3}{r^3} + 1\right)E_0\cos\theta\,\hat{r} + \left(\frac{\varepsilon_2\varepsilon_a - \varepsilon_3\varepsilon_b}{\varepsilon_2\varepsilon_a + 2\varepsilon_3\varepsilon_b}\frac{r_2^3}{r^3} - 1\right)E_0\sin\theta\,\hat{\theta} \qquad (19.9)$$

- In equations (19.7), (19.8) & (19.9) we have:

$$\varepsilon_a = \varepsilon_1(3 - 2P) + 2\varepsilon_2 P \qquad (19.10)$$

$$\varepsilon_b = \varepsilon_1 P + \varepsilon_2(3 - P) \qquad (19.11)$$

$$P = 1 - (r_1 / r_2)^3 \qquad (19.12)$$

Nanoshells – Electrostatic Approximation

•Examination of (19.9) shows us that the field in the surrounding medium is the same as a dipole with an effective dipole moment given by:

$$\boldsymbol{p} = \varepsilon_3 \alpha\, \boldsymbol{E}_{ind} \qquad (19.13)$$

•The polarizability is given by:

$$\alpha = 4\pi\varepsilon_0 r_2^3 [\frac{\varepsilon_2\varepsilon_a - \varepsilon_3\varepsilon_b}{\varepsilon_2\varepsilon_a + 2\varepsilon_3\varepsilon_b}] \qquad (19.14)$$

•Therefore, resonance is obtained when the real portion of the denominator of (19.14) goes to zero:

$$\mathrm{Re}\{\varepsilon_2\varepsilon_a + 2\varepsilon_3\varepsilon_b\} = 0 \qquad (19.15)$$

Nanoshells – Electrostatic Approximation

•Let us assume that the core and embedding medium are dielectrics

•Therefore, the resonance condition as a function of wavelength is:

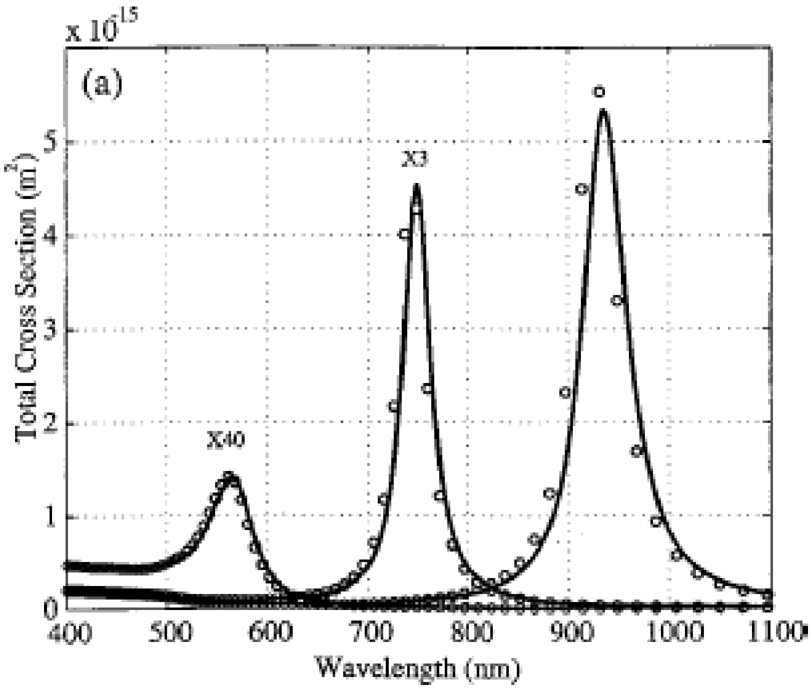
$$\frac{r_1}{r_2}=[1+\frac{3}{2}\frac{\varepsilon_2^{'}(\lambda)(\varepsilon_1+2\varepsilon_3)}{[\varepsilon_2^{'}(\lambda)]^2-\varepsilon_2^{'}(\lambda)(\varepsilon_1+\varepsilon_3)+\{\varepsilon_1\varepsilon_3-[\varepsilon_2^{''}(\lambda)]^2\}}]^{1/3} \quad (19.16)$$

•This expression gives the ratio of the core radius to the total radius needed to obtain a resonant condition at a particular wavelength

•This expression demonstrates that metallic nanoshells possess geometric tunability of the resonance wavelength

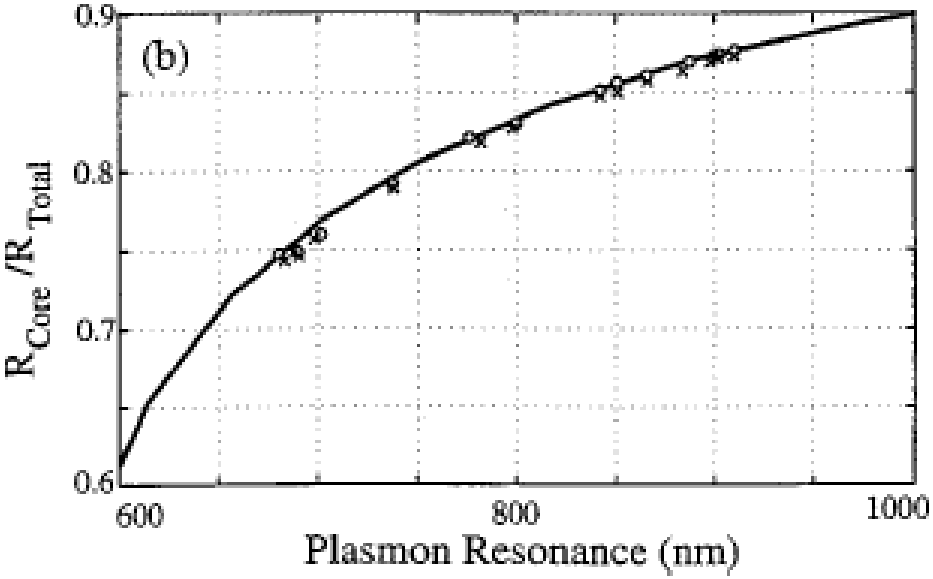
Nanoshells – Electrostatic Approximation

Total Cross-section vs Wavelength



•In going from shorter to longer wavelengths, the total radii are: 4.0, 10.0, 17.0 nm

Ratio of Core Radius to Total Radius Required to Give Plasmon Resonance at a Particular Wavelength



•Au-coated Au_2S nanoshells

From: Averitt et al, Journal of Optical Society of America B, vol. 16, pp. 1824-1832 (1999)