

Lecture 10 – Light-Matter Interaction

Part 4

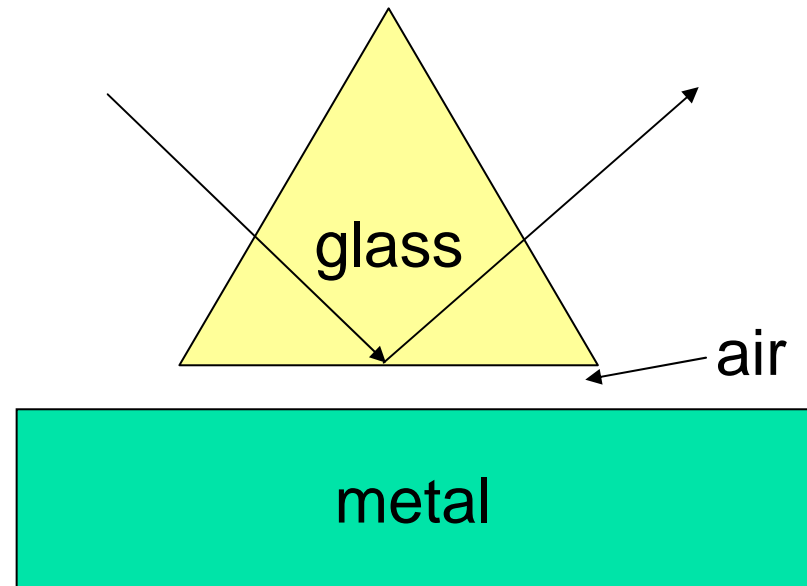
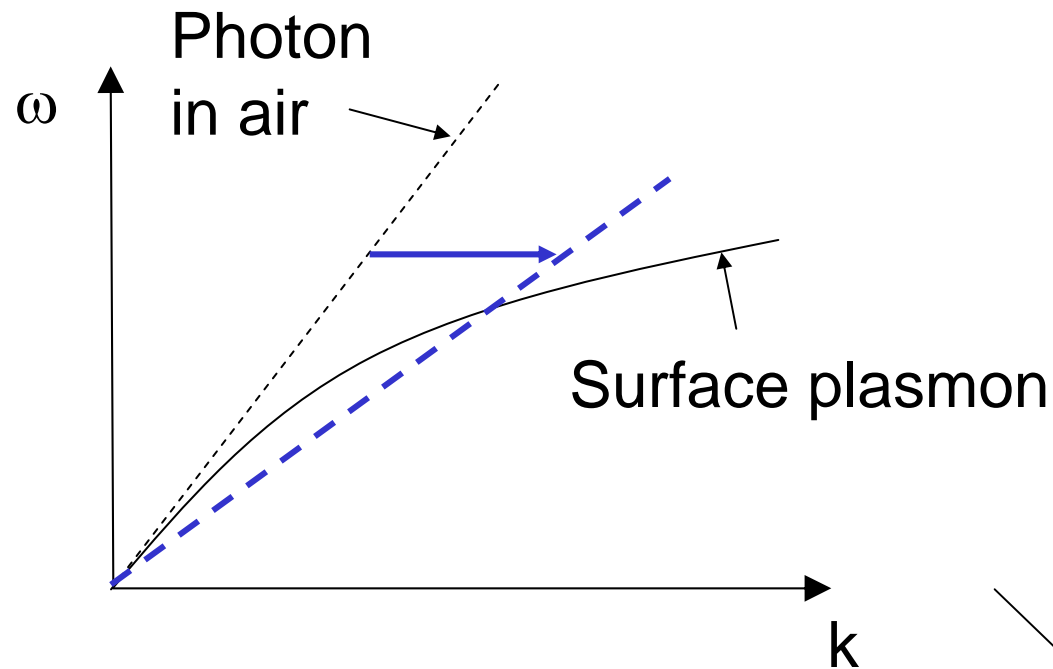
Surface Polaritons 2

EECS 598-002 Winter 2006
Nanophotonics and Nano-scale Fabrication
P.C.Ku

Schedule for the rest of the semester

- Introduction to light-matter interaction (1/26):
 - How to determine $\epsilon(r)$?
 - The relationship to basic excitations.
- Basic excitations and measurement of $\epsilon(r)$. (1/31)
- Structure dependence of $\epsilon(r)$ overview (2/2)
- Surface effects (2/7 & 2/9):
 - Surface EM wave
 - **Surface polaritons**
 - **Size dependence**
- Case studies (2/14 – 2/21):
 - Quantum wells, wires, and dots
 - Nanophotonics in microscopy
 - Nanophotonics in plasmonics
- Dispersion engineering (2/23 – 3/9):
 - Material dispersion
 - Waveguide dispersion (photonic crystals)

Optical excitation of surface plasmons

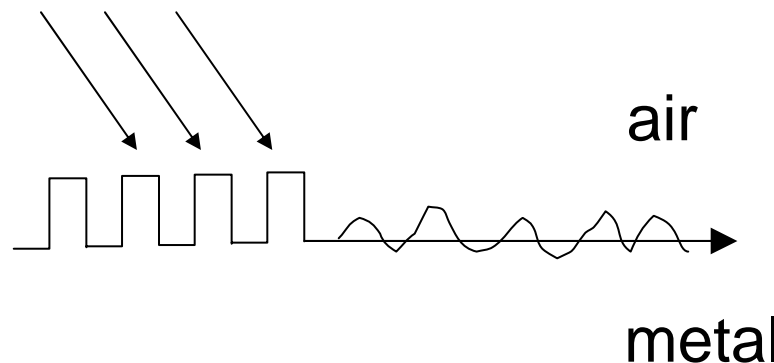


Excitation of surface plasmons via gratings

- The TM solution in a 1-D periodic structure (grating) is:

$$H_{k_x}(z) = \sum_{m=-\infty}^{\infty} H_m \left(k_x - \frac{2\pi m}{\Lambda} \right) e^{i(k_x - 2\pi m/\Lambda)z}$$

The grating couples different k_x components together.



$$\frac{\omega}{c} \sqrt{\epsilon_1} \sin \theta + \frac{2\pi m}{\Lambda} = k_x$$

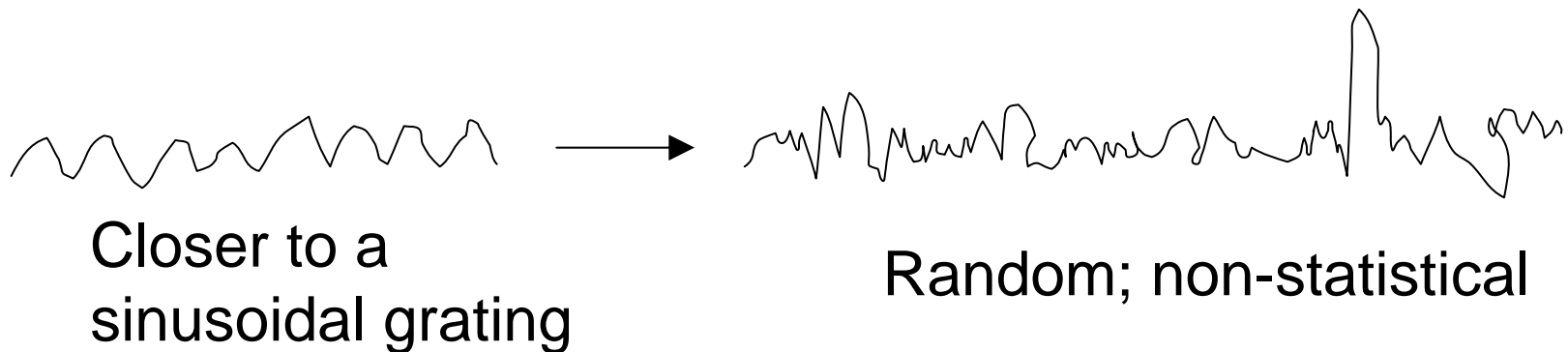
Excitation of surface plasmons via rough surface

- The surface profile can be decomposed into a set of gratings with different periods.

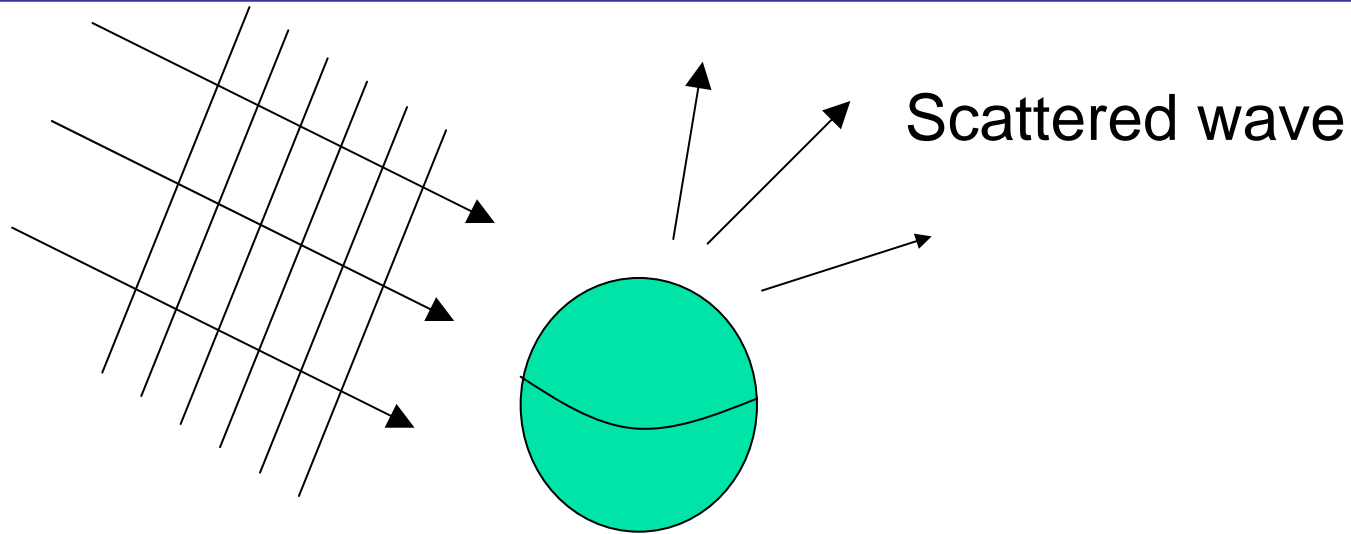
$$\varepsilon(x) = \int_G \tilde{\varepsilon}(G) e^{iGx} dG$$

Localization of surface plasmons

- When the surface becomes rather rough, the scattering of the surface plasmons is strong enough that the propagation of surface plasmons along the interface approaches a diffusion process → surface plasmons become localized.



Surface plasmons on the sphere surface

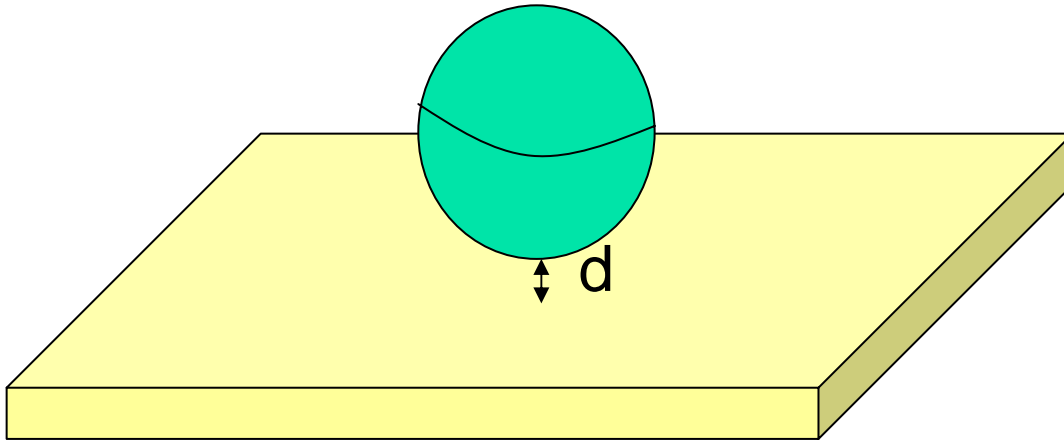


The scattering cross section from a small particle is proportional to $\frac{\epsilon_s - \epsilon}{\epsilon_s + 2\epsilon}$

When $\epsilon_s = -2\epsilon$, the scattering cross section \rightarrow infinity \rightarrow surface EM wave can be supported.

Modulation of the plasmon resonance

- If we put another object very close to the metal sphere, the effective dielectric constant of the metal is modified.
→ The plasmon resonance position is shifted.



Field enhancement

- Because of the “incredibly large” scattering cross section, the electric field on the surface is greatly enhanced.

$$\vec{E}_i = \hat{z}E_i e^{ikx} \approx \hat{z}E_i \text{ as } kx \ll 1$$

$$\vec{E}_s(\vec{r}) = \left[\hat{r}2 \cos \theta + \hat{\theta} \sin \theta \right] \left(\frac{a}{r} \right)^3 E_s$$

At the surface along the z direction:

$$E_{total}(a) = 2 \frac{\epsilon_s - \epsilon}{\epsilon_s + 2\epsilon} E_i + E_i = \frac{3\epsilon_s}{\epsilon_s + 2\epsilon} E_i$$

The enhancement is:

$$\left| \frac{E_{total}(a)}{E_i} \right|^2 \approx \left| \frac{3\epsilon_s}{\epsilon_s + 2\epsilon} \right|^2$$

Enhanced Raman scattering

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The Chemical Laboratory

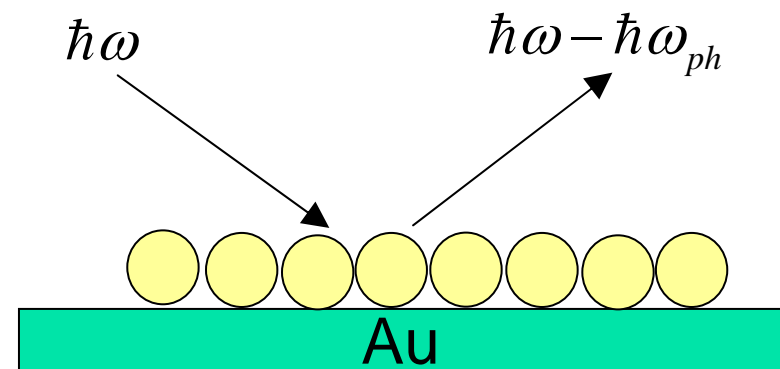
University of Kent at Canterbury, Kent, England

Anomalously Intense Raman Spectra of Pyridine at a Silver Electrode

Sir:

Raman spectra of pyridine adsorbed at a silver electrode which had previously been roughened by repeated electrochemical cycling have already been reported by Hendra and coworkers.^{1,2} The purpose of this communication is to report that the Raman spectra of pyridine at a silver electrode, after a single oxidation-reduction cycle and particularly when recorded during and immediately after the cycle, are remarkably and anomalously intense. As an indication of the extent of this intensity enhancement the Raman signals that we observed from the ring-stretching modes of surface pyridine were

that scattered light is collected from roughly 4×10^5 times as many molecules in the pure liquid pyridine sample than at the electrode surface. We are thus led to conclude that there is a considerable enhancement ($\sim \times 10^5$) in the spectra of the adsorbed pyridine by a surface effect which greatly increases the molecular Raman scattering cross sections. It has been suggested by Philpott⁶ that broadening of the electronic energy levels of molecules at roughened metal surfaces may induce resonant Raman scattering from molecules adsorbed on metals through interaction with surface plasmons. Resonant Raman



Surface plasmon induced Raman enhancement

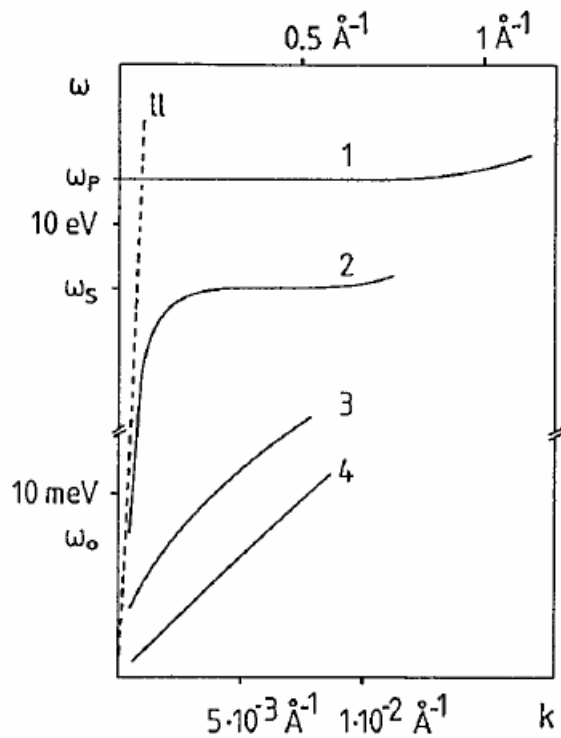
2.3 Surface-Enhanced Raman Scattering

In the mid-1970s, opticians were surprised by the high-intensity Raman scattering from certain adsorbates on rough surfaces of copper, silver, or gold [13,14]. It was soon found that field enhancement by SPP excitation plays an important role (see, for example, the review articles of *Chang* and *Laube* [15], *Otto* [16], and *Wokaun* [17]). The SPPs are localized at small protrusions and crevices of the rough surface.

An individual protrusion can be modeled as a semi-ellipsoid on a plane. Laplace's equation can be solved analytically for this geometry [18,19]. As a general result, several plasmon resonances of approximately equal strength were found, but the field enhancement due to SPP excitation is not sufficient to explain the immense enhancement factors experimentally observed.

Ref: S. Kawata, Near-Field Optics and Surface Plasmon Polaritons, Springer (2001) ch.1.

Plasmons in reduced dimensional structures

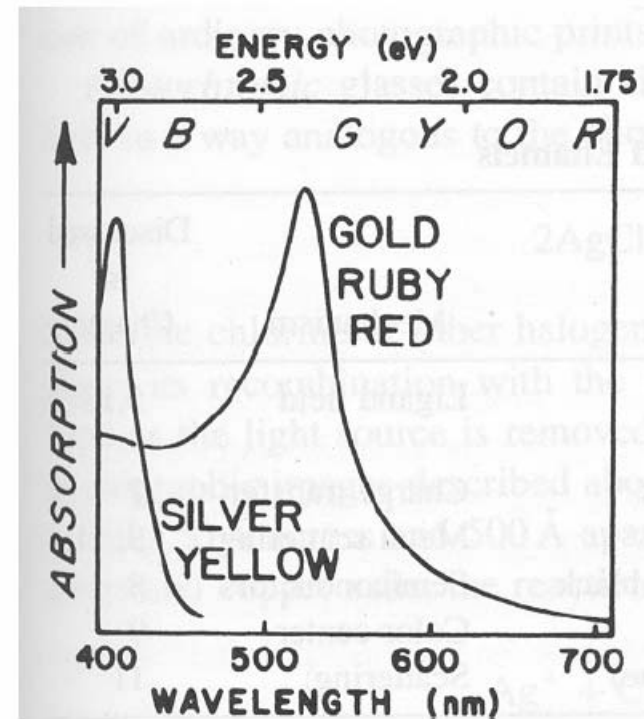


1. Plasmons
2. Surface plasmons
3. Plasmons in 2D structures
4. Plasmons in 1D structures

Ref: H. Raether, Surface Plasmons, Springer-Verlag (1986).

$\epsilon(r)$ at small size

- The absorption spectrum for metal nanoparticles is different from that of a bulk metal piece.



Ref: S. Link and M. A. El-Sayed, J. Phys. Chem. B **103** (1999) 8410.

Surface-plasmons near surface

Plasmon dispersion relation: $\frac{\varepsilon(\omega)}{\varepsilon_0} = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$

Near surface: $\gamma \rightarrow \gamma(r) = \gamma_0 + \frac{Av_F}{r}$

where v_F is the velocity of electrons at the Fermi's energy.

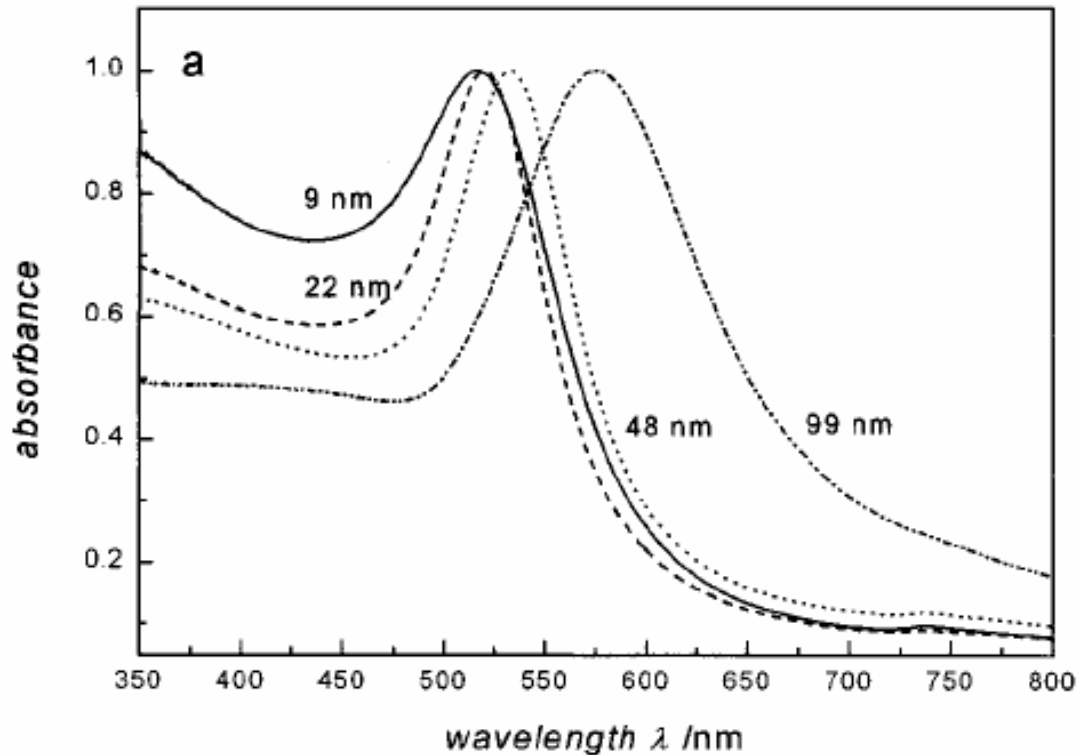
For surface-plasmons near the surface:

The resonance is at $\varepsilon_s' + i\varepsilon_s'' = -2\varepsilon$

The spectral width of the resonance absorption $\sim \varepsilon_s''$

Both depend on r .

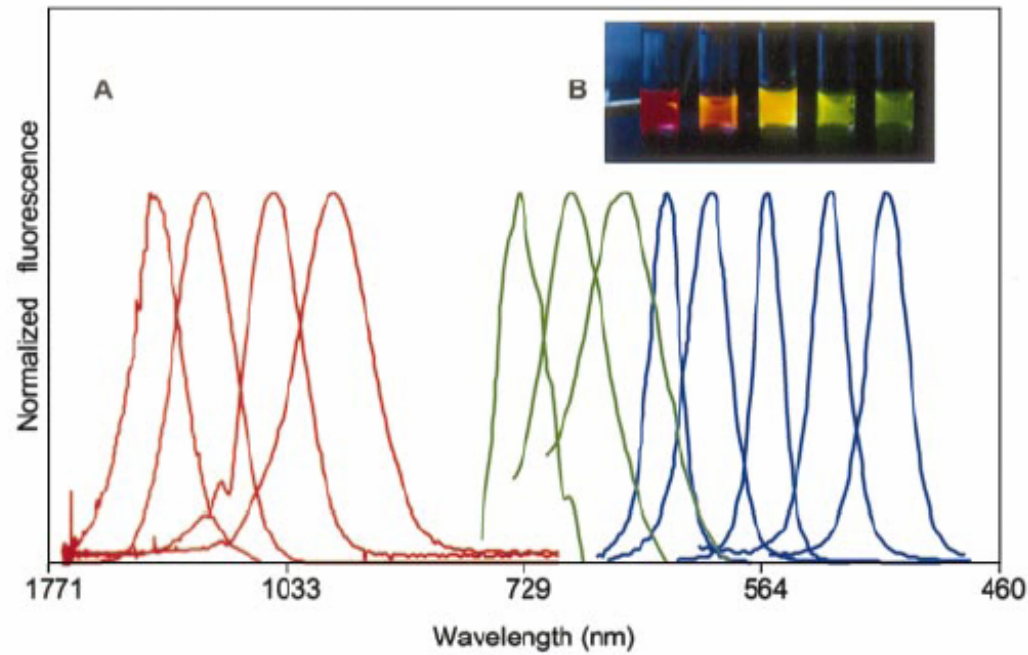
Au particles resonance shift



Ref: S. Link and M. A. El-Sayed, J. Phys. Chem. B **103** (1999) 4212.

Size-dependent emission wavelength

Fig. 2. (A) Size- and material-dependent emission spectra of several surfactant-coated semiconductor nanocrystals in a variety of sizes. The blue series represents different sizes of CdSe nanocrystals (16) with diameters of 2.1, 2.4, 3.1, 3.6, and 4.6 nm (from right to left). The green series is of InP nanocrystals (26) with diameters of 3.0, 3.5, and 4.6 nm. The red series is of InAs nanocrystals (16) with diameters of 2.8, 3.6, 4.6, and 6.0 nm.



(B) A true-color image of a series of silica-coated core (CdSe)-shell (ZnS or CdS) nanocrystal probes in aqueous buffer, all illuminated simultaneously with a handheld ultraviolet lamp.

Ref: M. Bruchez Jr. et al, Science **281** (1998) 2013.

Reading

- Kawata, chapter 1 by P. W. Pohl.