Blue skin man

Avatar

In 2007 press reports described Paul Karason, an American man whose entire skin gradually turned blue after consuming what he believed was colloidal silver made by himself with distilled water, salt and silver, and using a silver salve on his face in an attempt to treat problems with his sinus, dermatitis, acid reflux and other issues.

Think before class:

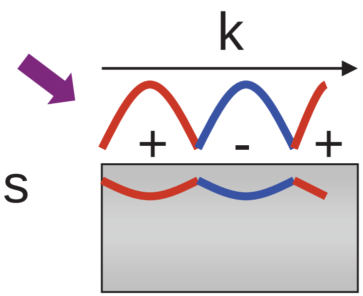
- What is the color of small (nm-size) gold?
- Why does it have these colors?

Content of this lecture

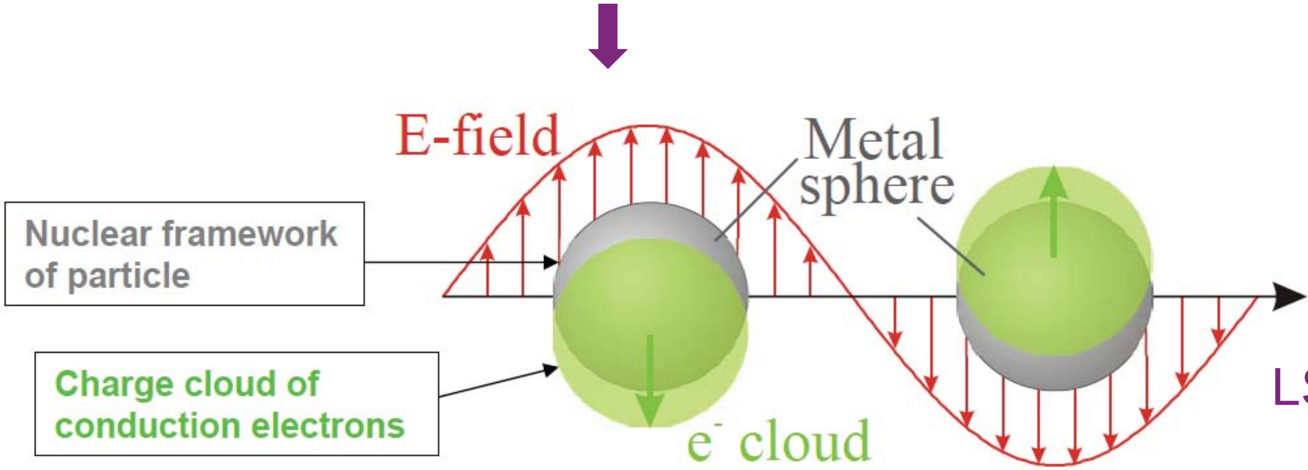
1. Localized surface plasmons (LSPs) on metal nanoparticles
   - Difference of LSPs with SPPs
   - Color effect of metal nanoparticles
   - Various metal nanoparticles
2. Resonance condition of LSPs
   - Review of dipole radiation
   - LSPs of nanoshperes (quasi-static approximation)
   - Size- and shape-dependence of LSPR (Mie theory)
   - LSPs of nanorods (Gans theory)
3. Coupling of LSPs between nanoparticles
4. LSPs of complex nanostructures – nanoshell
5. Comparison of volume plasmons, SPPs, and LSPs

1. LSPs of metal nanoparticles

- SPPs: propagating SPs (photons coupled to SPs) on an extended metal-dielectric interface.



- LSPs (localized surface plasmons): non-propagating SPs on a closed surface of metal nanoparticle/nanocavity.



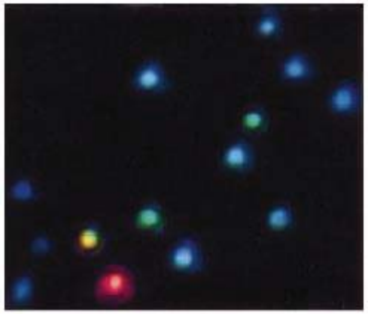
LSPs are confined on the particles

- The excitation of LSPs influences the extinction (i.e., absorption + scattering) of light from the nanoparticles → color effect

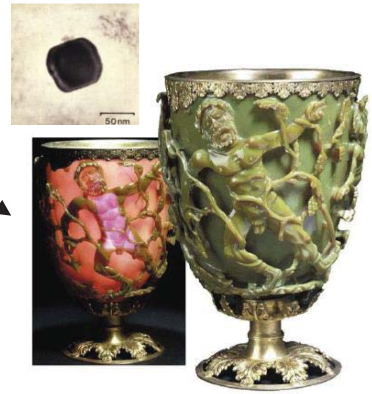
extinction: 消光比，absorption: 吸收，scattering: 散射

Color effect of metal nanoparticles

In the past:

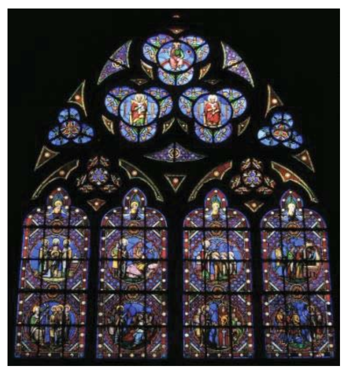


Different shapes & sizes
→ distinct colors



Lycurgus Cup

Au colloids in water
(M. Faraday ~1856)

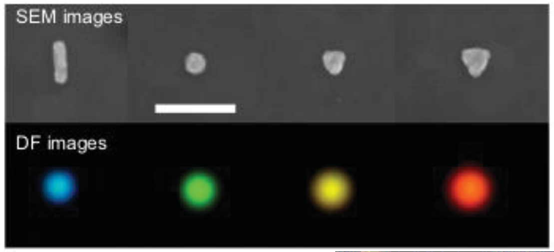


Stained glass in
church window

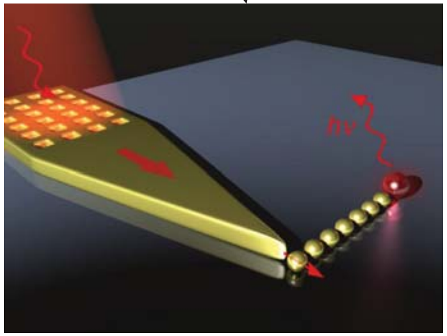
Nowadays (but the same principle):

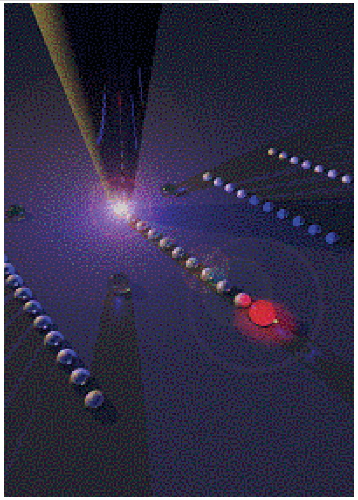
Colloid of metal
nanoparticles

Scale bar = 300 nm

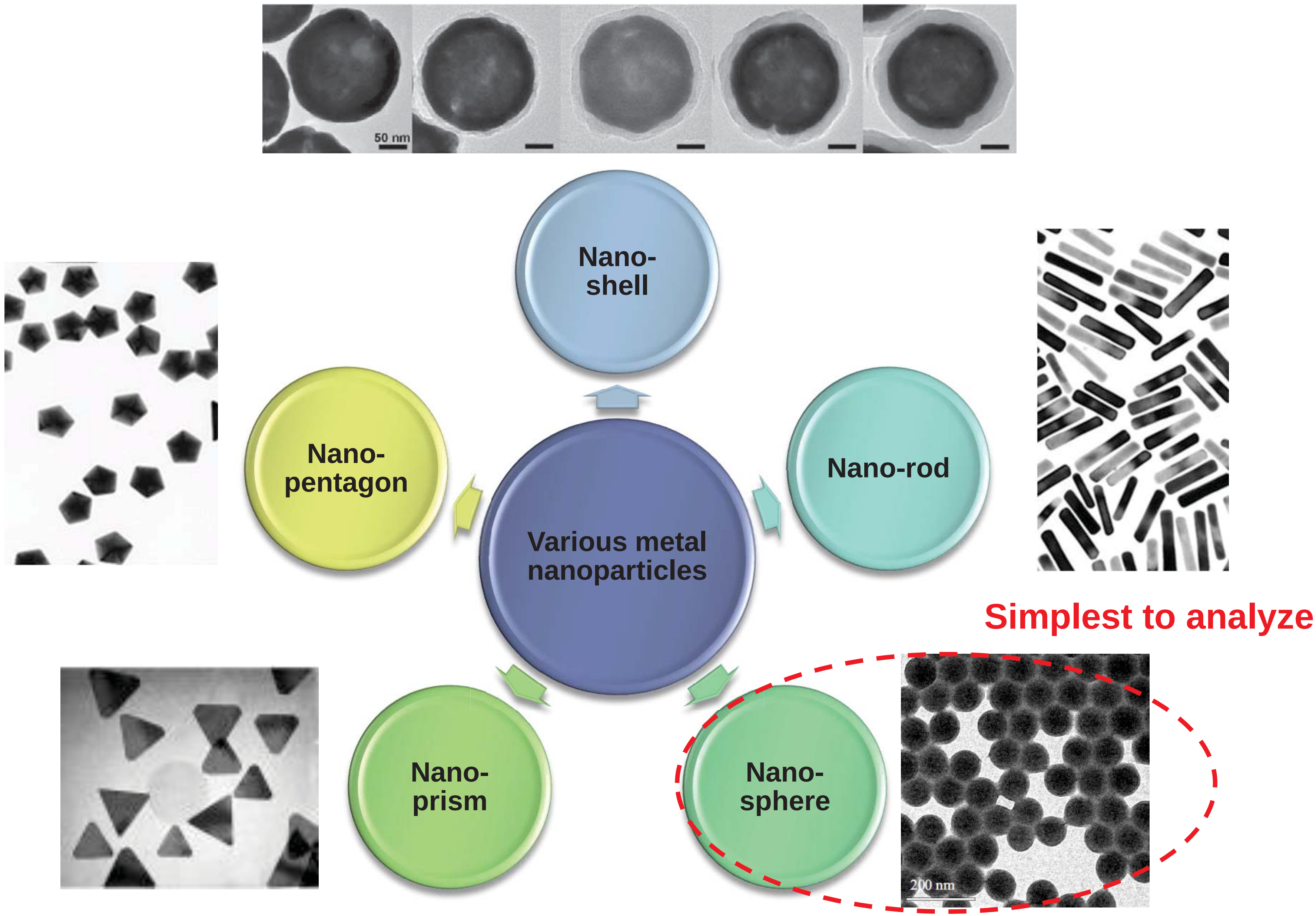


Focus and guide
light to nanoscale





colloid: 胶体， stained glass: 彩色玻璃

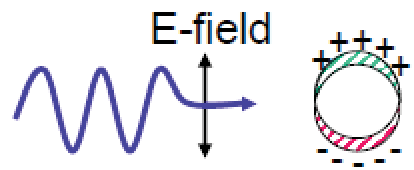


shell: 空壳， rod: 棒， sphere: 球， pentagon: 五边形

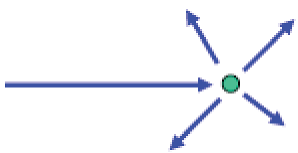
2. Resonance condition of LSPs

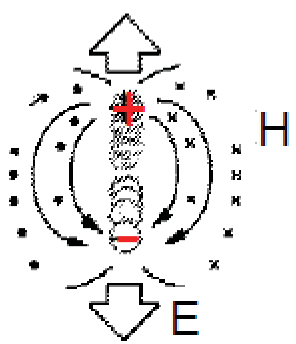
- When metal nanoshpere is small enough ($D \ll \lambda$), it can be regarded as an effective electric dipole.

Harmonic E field drives harmonic oscillation of free electrons

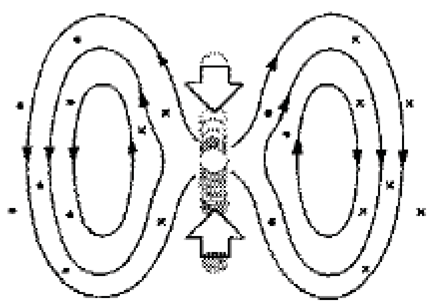


Oscillating dipole radiates (scattering of light)

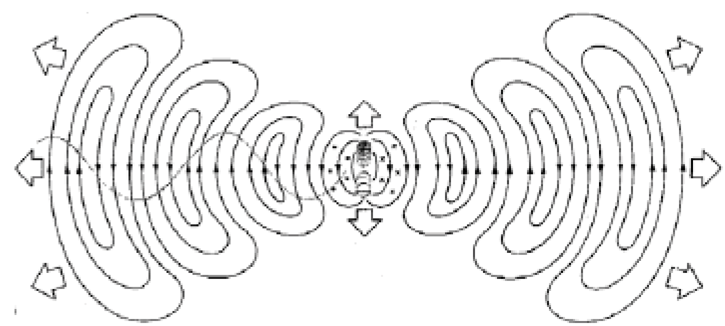




Start oscillation



Generation of EM wave



After several periods

(radiation mainly ⊥oscillation direction)

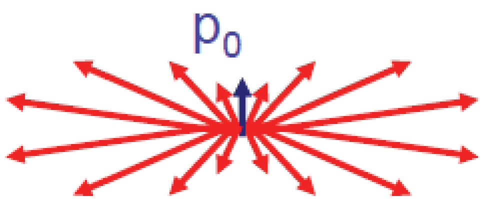
dipole: 电偶极子，conduction: 导电，radiate: 辐射，oscillation: 振荡

Review of dipole radiation

- Radiated intensity: $I = \dfrac{p^2\omega^4}{32\pi^2\varepsilon_0 c^3 r^2}\sin^2\theta$ (angle dependent)

Derivation: see any textbook on electromagnetism or electrodynamics

- Radiation pattern:



- Consider Lorentz model of the dipole moment: $\mathbf{p} = \dfrac{e^2}{m}\dfrac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}\mathbf{E}_L$

See Lecture 2

- We get: $$\boxed{I_S = \frac{e^4\omega^4}{32\pi^2 m^2\varepsilon_0 c^3 r^2}\left(\frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}\right)^2 E_L^2 \sin^2\theta}$$

Incoming intensity

- Conclusions:
  - Stronger scattering occurs at higher ω (shorter λ)
  - Scattering occurs in both forward and backward directions

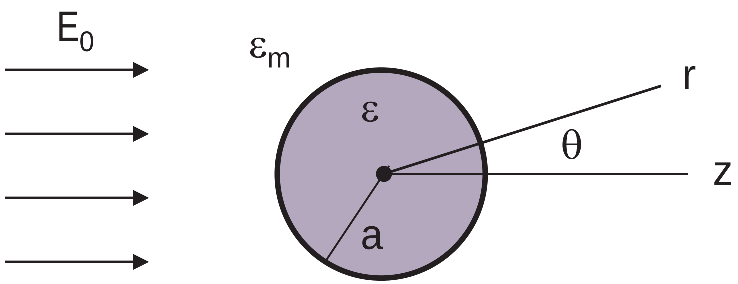
Rayleigh scattering

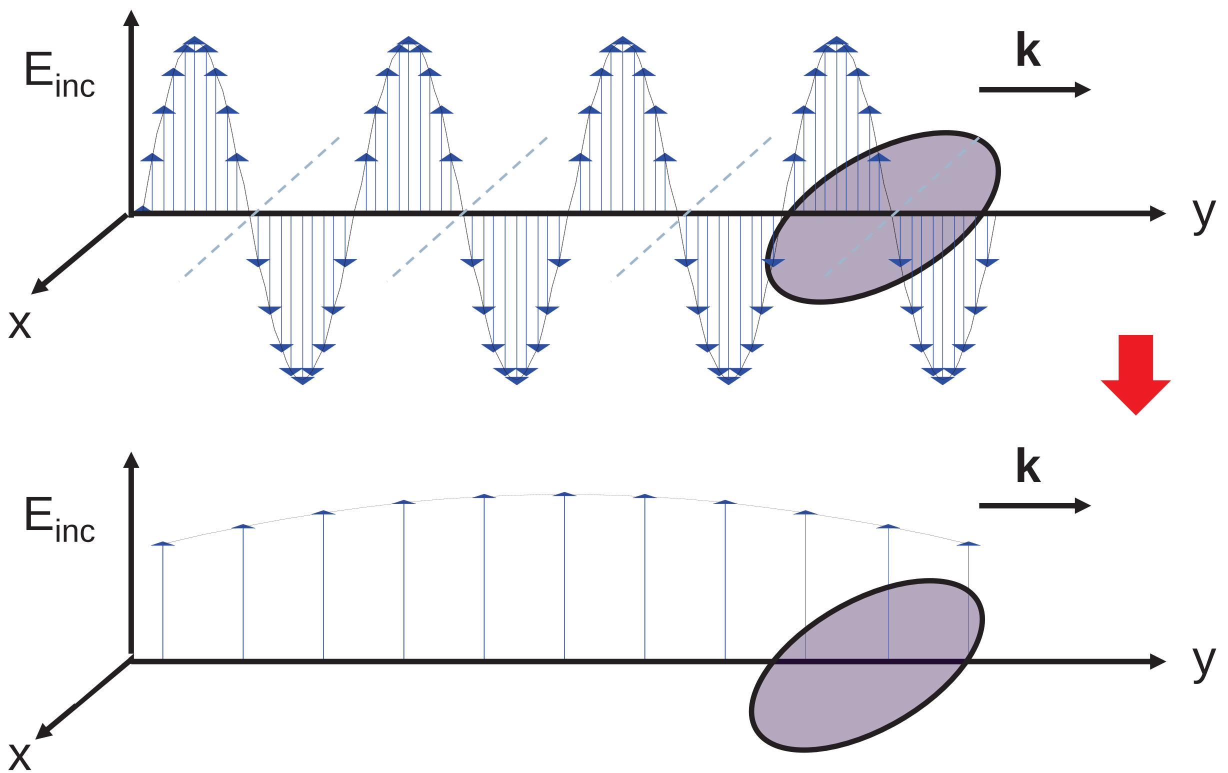
electromagnetism: 电磁学， electrodynamics: 电动力学， polarizability: 极化率

LSPs of nanospheres

- If particle small enough ($2a << \lambda$)
  $\rightarrow$ treated as an electric dipole

- quasi-static approximation:
  constant phase over the particle volume





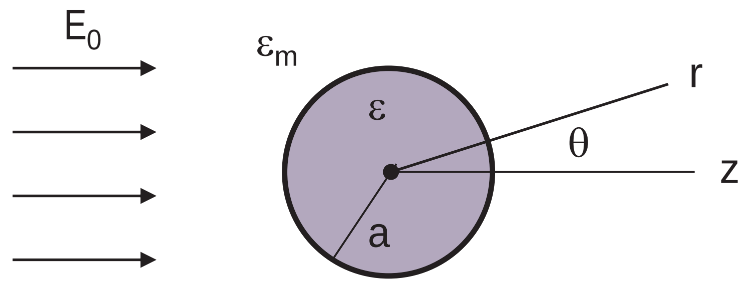
$$\mathbf{E}_{\text{inc}}(\mathbf{r},t)=\mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$$

$$\mathbf{E}_{\text{inc}}(\mathbf{r},t)=\mathbf{E}_0 e^{-i\omega t}$$

quasi-static approximation: 准静态近似， constant: 常数

- Incidence: uniform static electric field

$$\mathbf{E}_{\text{inc}} = E_0 \hat{\mathbf{z}}$$



- The electric fields inside ($\mathbf{E}_1$) and outside ($\mathbf{E}_2$) the sphere may be found from the scalar potentials $\mathbf{E}_{1,2} = -\nabla \Phi_{1,2}$
- The scalar potentials satisfy Laplace's equation:

$$\nabla^2 \Phi_1 = 0 \quad (r < a), \quad \nabla^2 \Phi_2 = 0 \quad (r > a)$$

- Boundary conditions:

$$\Phi_1 = \Phi_2 \quad (r = a), \quad \varepsilon \frac{\partial \Phi_1}{\partial r} = \varepsilon_m \frac{\partial \Phi_2}{\partial r} \quad (r = a), \quad \lim_{r \to \infty} \Phi_2 = -E_0 z$$

- The following solutions satisfy the above equations:

$$\Phi_1 = -\left(\frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} \right) E_0 r \cos\theta, \quad \Phi_2 = \underbrace{-E_0 r \cos\theta}_{\text{applied field}} + \underbrace{a^3 \left(\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right) E_0 \frac{\cos\theta}{r^2}}_{\text{Effective dipole at the sphere center}}$$

applied field

Effective dipole at the sphere center

(electric) potential: 电势

- Introduce the dipole moment **p** as:

$$\Phi_{\text{out}} = -E_0 r \cos\theta + \frac{\mathbf{p}\cdot\mathbf{r}}{4\pi\varepsilon_0\varepsilon_m r^3} \qquad \mathbf{p} = 4\pi\varepsilon_0\varepsilon_m a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}\mathbf{E}_0$$

- Therefore, the polarizability (defined via $\mathbf{p} = \varepsilon_0\varepsilon_m\alpha\mathbf{E}_0$):

$$\alpha = 4\pi a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$$

$\varepsilon = \varepsilon_1(\omega)+i\varepsilon_2(\omega)$
permittivity of metal

ε_m, real permittivity of the embedding dielectric

- Resonant enhancement under the condition:

$$\left|\varepsilon(\omega)+2\varepsilon_m\right| = \text{minimum}$$

← called "Fröhlich condition"

For Drude metal located in lossless dielectric: ➡

$$\omega_{lsp} = \frac{\omega_p}{\sqrt{1+2\varepsilon_m}}$$

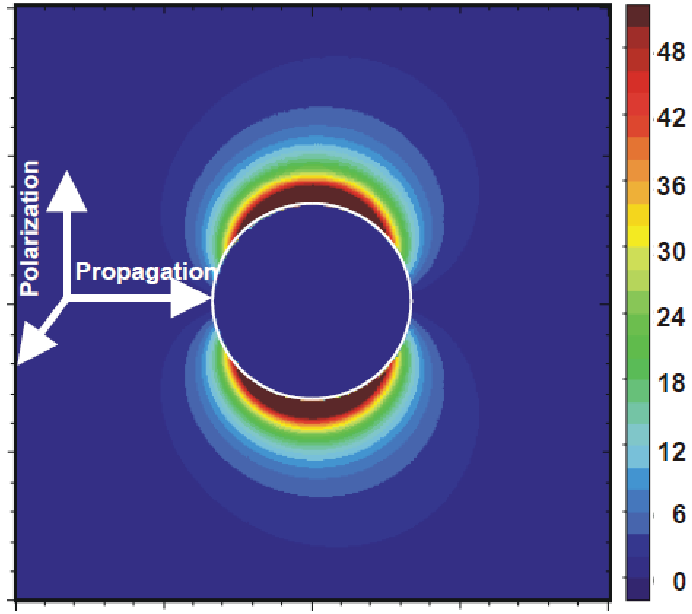
can be used for sensing

dipole momentum: 电偶极矩

- The electric field can be obtained by $\mathbf{E} = -\nabla\Phi$:

$$\mathbf{E}_{\text{in}} = \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m}\mathbf{E}_0 \qquad \mathbf{E}_{\text{out}} = \mathbf{E}_0 + \frac{3\mathbf{n}(\mathbf{n}\cdot\mathbf{p}) - \mathbf{p}}{4\pi\varepsilon_0\varepsilon_m}\frac{1}{r^3}$$

Calculated **E** Field:
20 nm Ag nanosphere
in vacuum



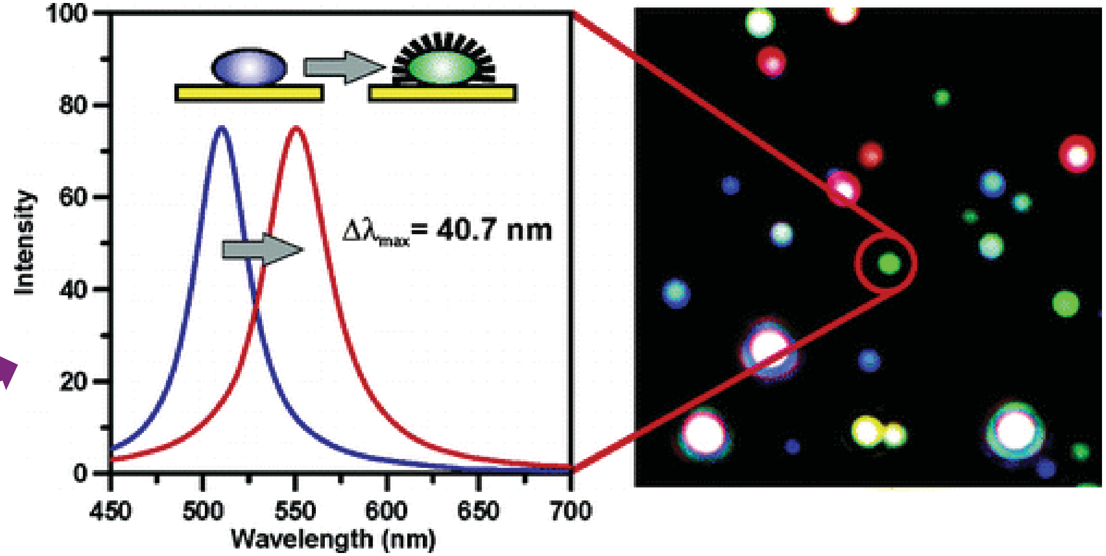
- At resonance, the extinction (scattering + absorption) is large
- Near field enhancement → many prominent applications such as sensing, SERS, enhanced nonlinearity, data storage, …

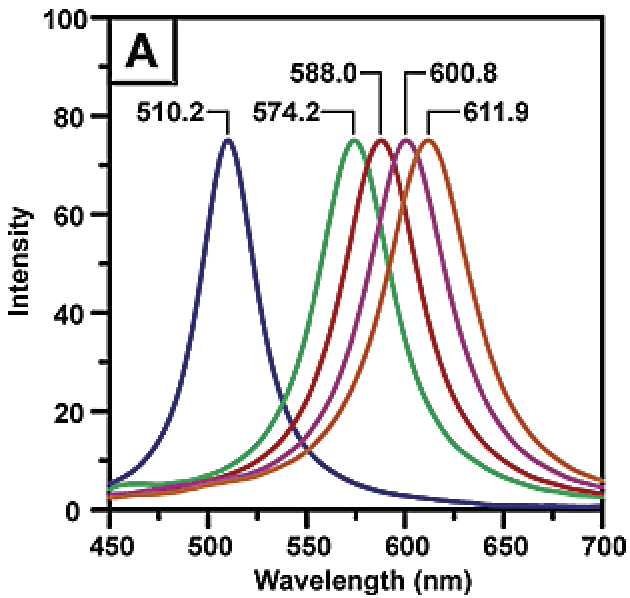
For full derivation, see J. D. Jackson, *Classical Electrodynamics* (Wiley, NY, 1999) and S. A. Maier, *Plasmonics: Fundamentals and Applications* (Springer, NY, 2007).

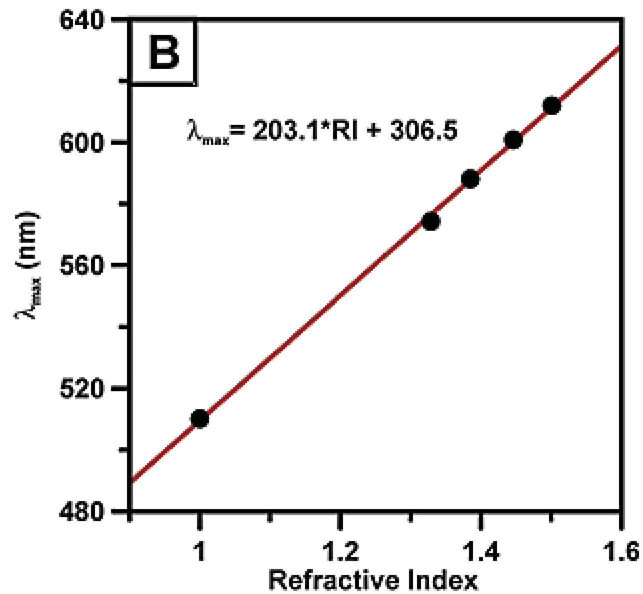
Application example 1:

Sensing with 35 nm Ag nanospheres

a monolayer of small-molecule adsorbates on the Ag nanoparticle







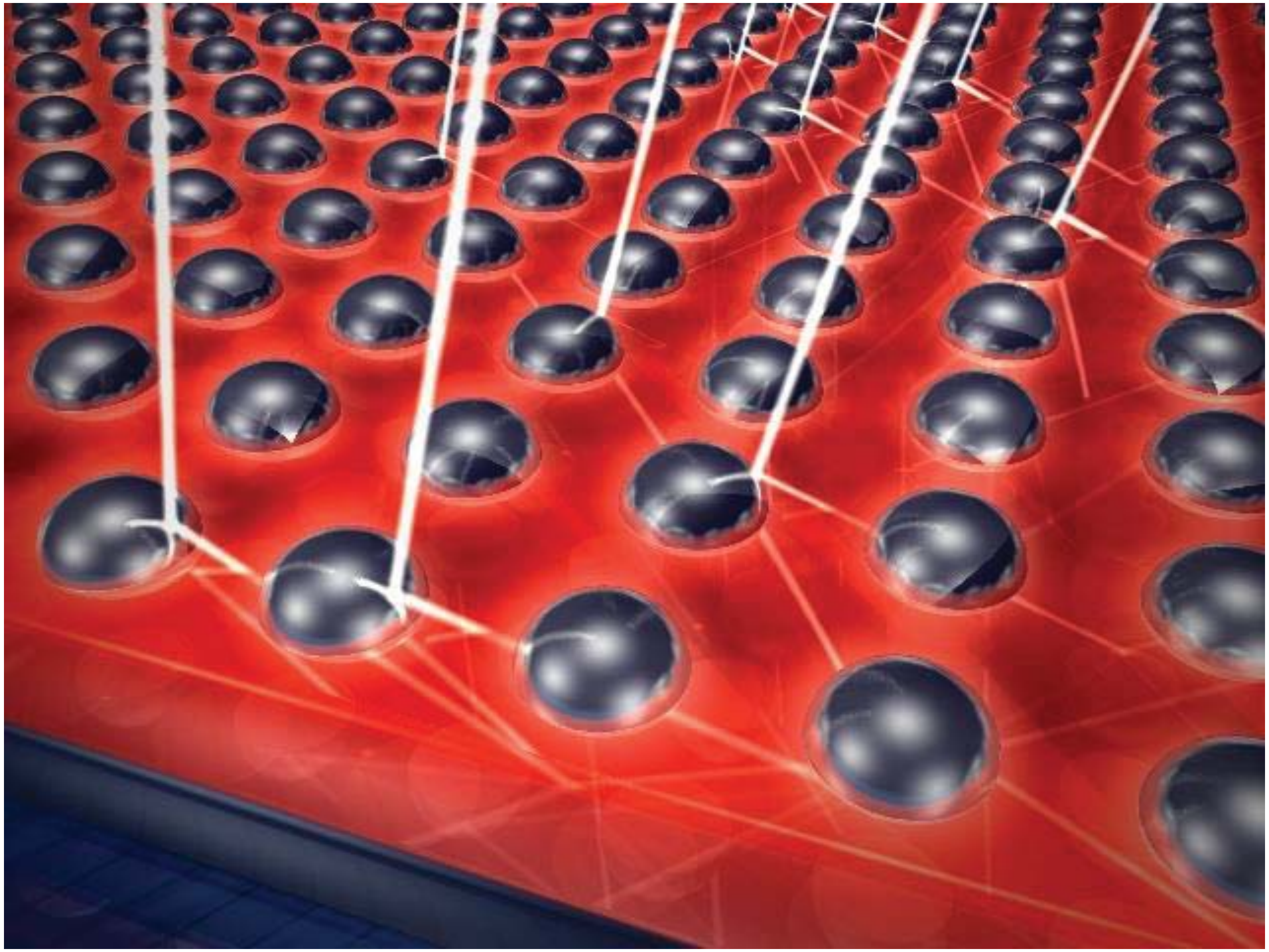
Resonance shift with respect to refractive index (RI) change of surrounding medium

McFarland and Duyne, Nano Lett. **3**, 1057 (2003).

monolayer: 单层，adsorbate: 被吸附物

Application example 2:

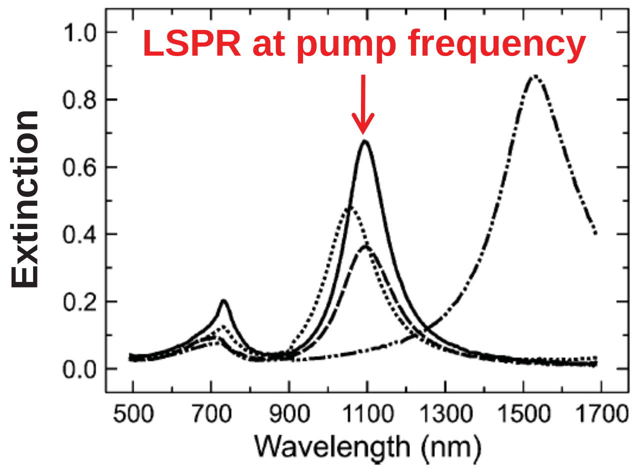
Light trapping in solar cells by metallic nanoparticles

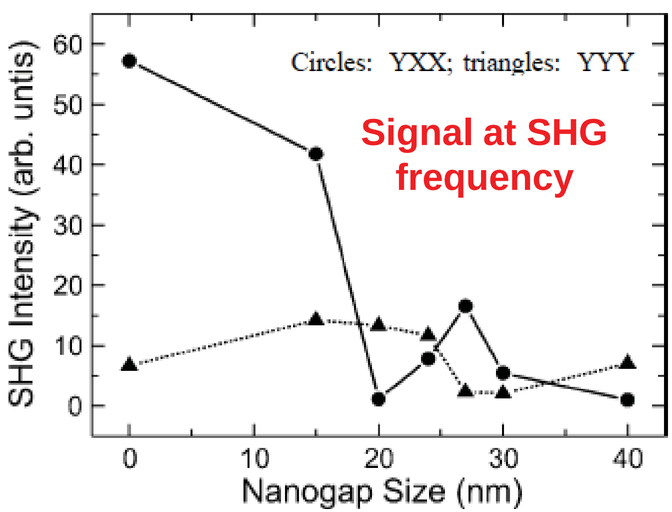


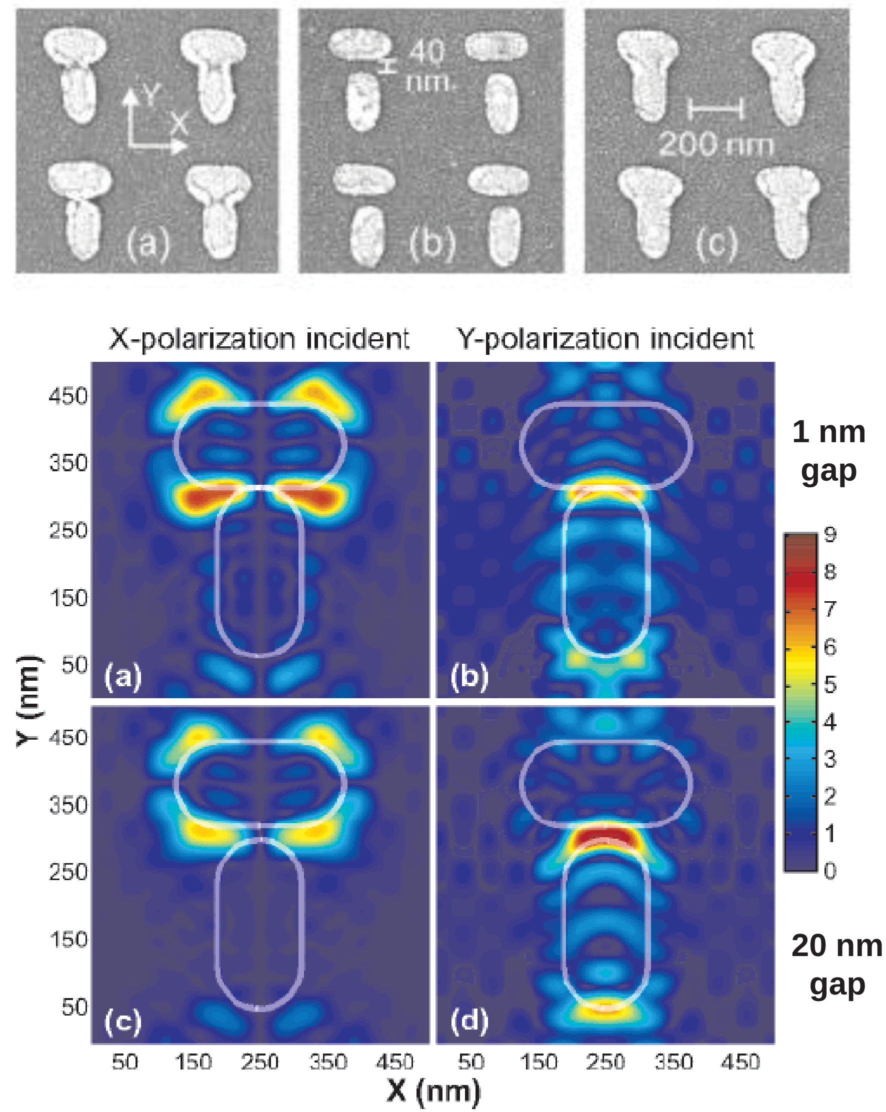
light trapping: 集光，solar cell: 太阳能电池

Application example 3:

Enhanced second-harmonic generation in metal nanoparticle array





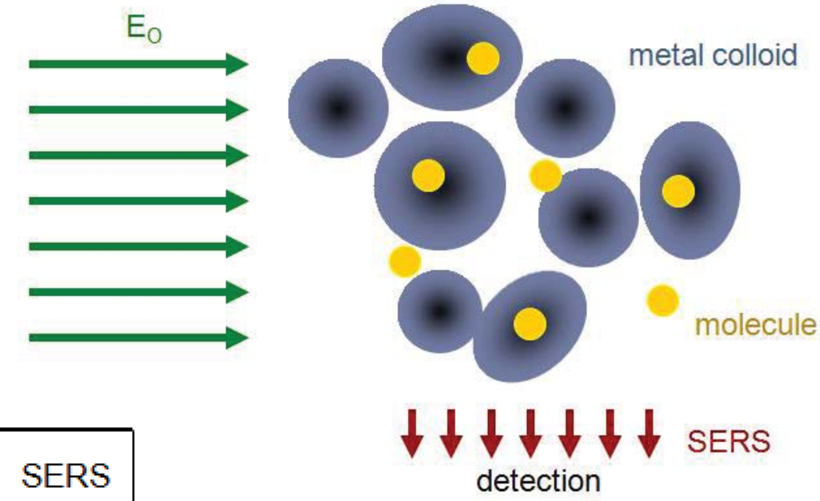


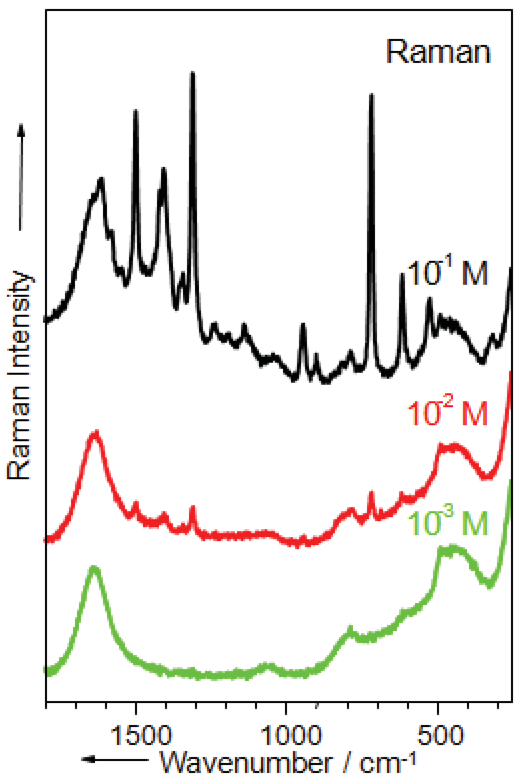
Canfield et al., Nano Lett. **7**, 1251 (2007)

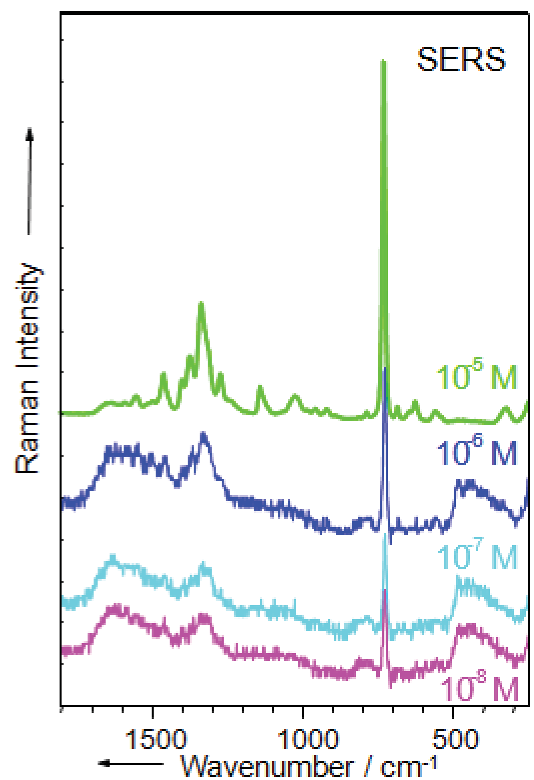
nonlinear effect: 非线性效应， second-harmonic generation: 二次谐波激发

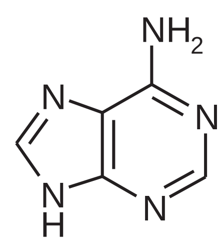
Application example 4:

Surface enhanced Raman spectroscopy (SERS)









Adenine

SERS improves the detection limit

adenine: 腺嘌呤

Size- and shape-dependence of LSPR

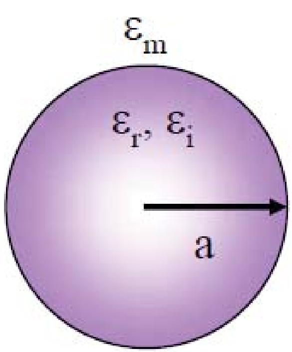
- Quasi-static approximation is valid only for nanoparticles < 100 nm at visible and near-infrared frequencies; size-dependence is not captured.
- For rigorous analysis of nanosphere – Mie theory

Mie theory (1908):

size dependence

shape dependence

$$E(\lambda) = \frac{24\pi^2 N a^3 \varepsilon_m^{3/2}}{\lambda \ln(10)} \left[\frac{\varepsilon_i}{(\varepsilon_r + \chi \varepsilon_m)^2 + \varepsilon_i^2} \right]$$



$E(\lambda)$ = Extinction spectrum = absorption + scattering

χ = shape factor (2 for sphere, > 2 for spheroid)

ε_m = external dielectric constant

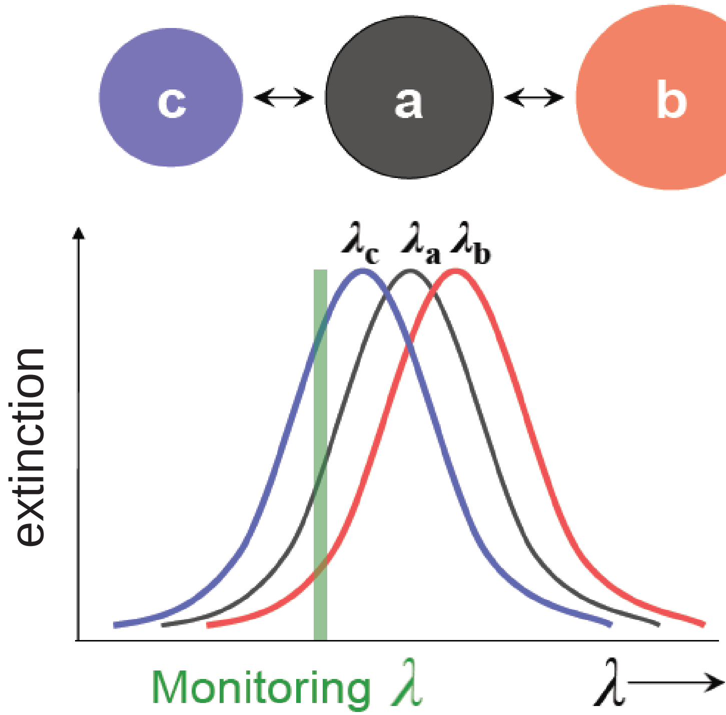
ε_r = real metal dielectric constant

ε_i = imaginary metal dielectric constant

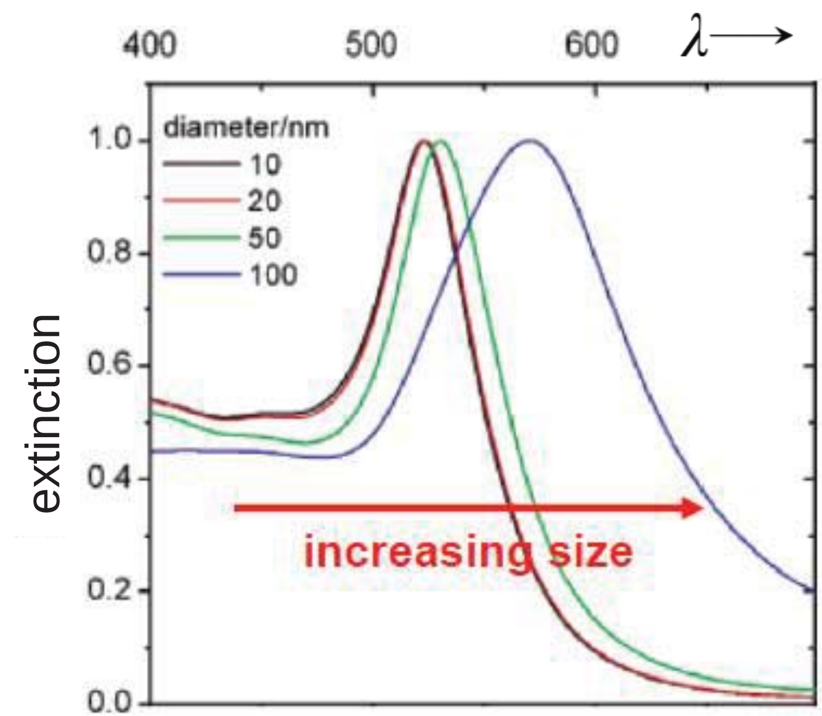
Mie, Ann. Phys. **25**, 377 (1908).

extinction: 消光比

Size dependence



Theoretical model



Measurement

Understand the size dependence qualitatively:

nanosphere size ↑ ⇒ charge distance ↑ ⇒ restoring force ↓ ⇒ resonance frequence ω ↓ ⇒ resonance wavelength ↑

qualitatively: 定性地

Shape dependence: LSPs of nanorods

- Response of nanospheroid/nanorod – Gans theory (extension of Mie theory)

$$\sigma_{ext}(\lambda)=\frac{2\pi V\varepsilon_{\mathrm{med}}^{3/2}}{3\lambda}\sum_j\frac{\left(1/P_j^2\right)\varepsilon''}{\left(\varepsilon'+\frac{1-P_j}{P_j}\varepsilon_{\mathrm{med}}\right)^2+\left(\varepsilon''\right)^2}$$

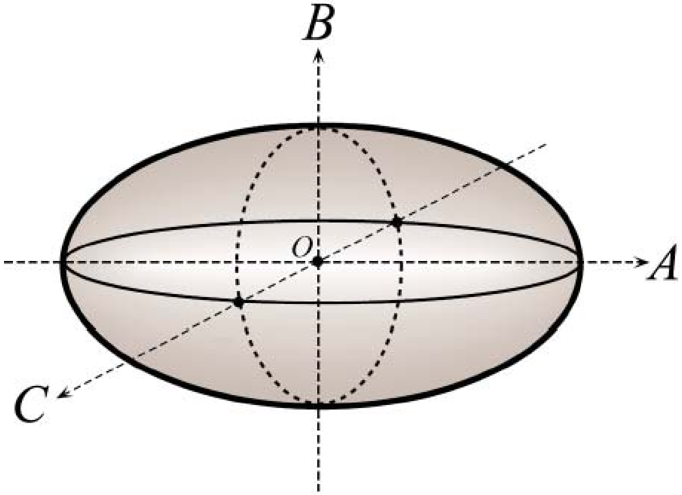
$$(A>B=C)$$

$$P_A=\frac{1-e^2}{e^2}\left[\frac{1}{2e}\ln\left(\frac{1+e}{1-e}\right)-1\right]$$

$$P_B=P_C=\frac{1-P_A}{2}$$

$$e=\sqrt{1-\left(\frac{B}{A}\right)^2}$$

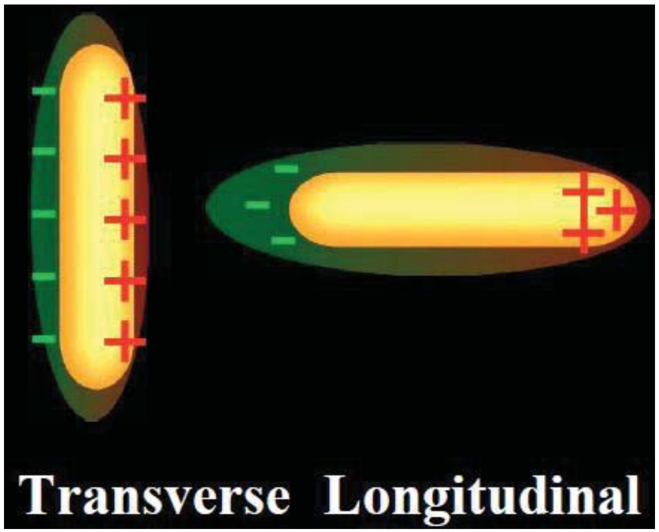
aspect ratio $R=\frac{A}{B}$

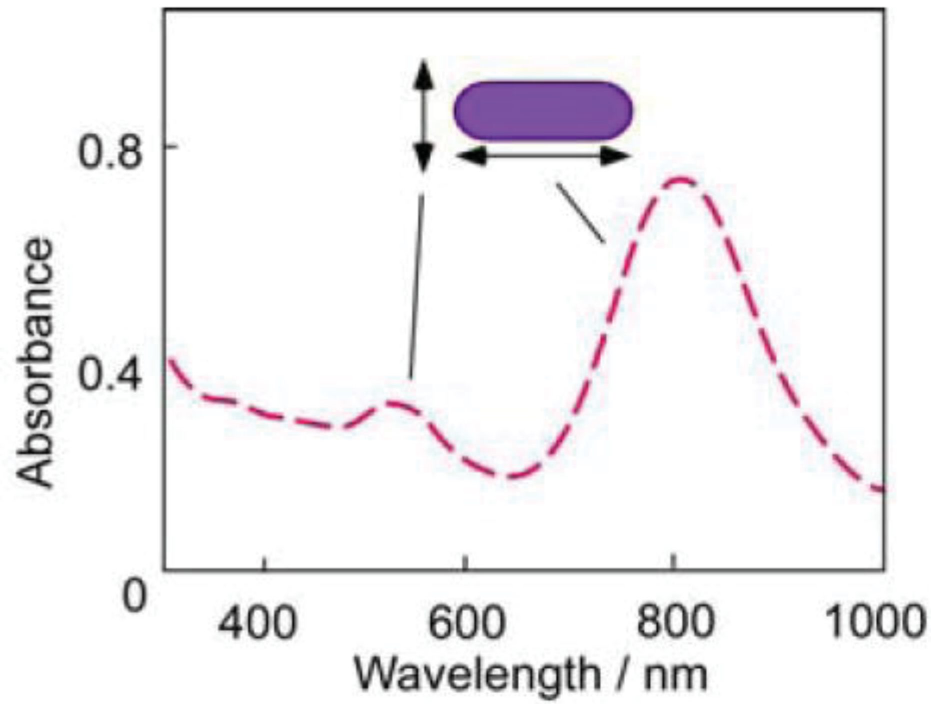


Link et al., J. Phys. Chem. B **103**, 3073 (1999).

spheroid: 椭球体，rod: 棒，aspect ratio: 长宽比

- There are two maxima in the extinction spectra, corresponding to two resonance modes:
  - a longitudinal mode (dipole oscillation along the long axis)
  - a transverse mode (dipole oscillation along the short axis)

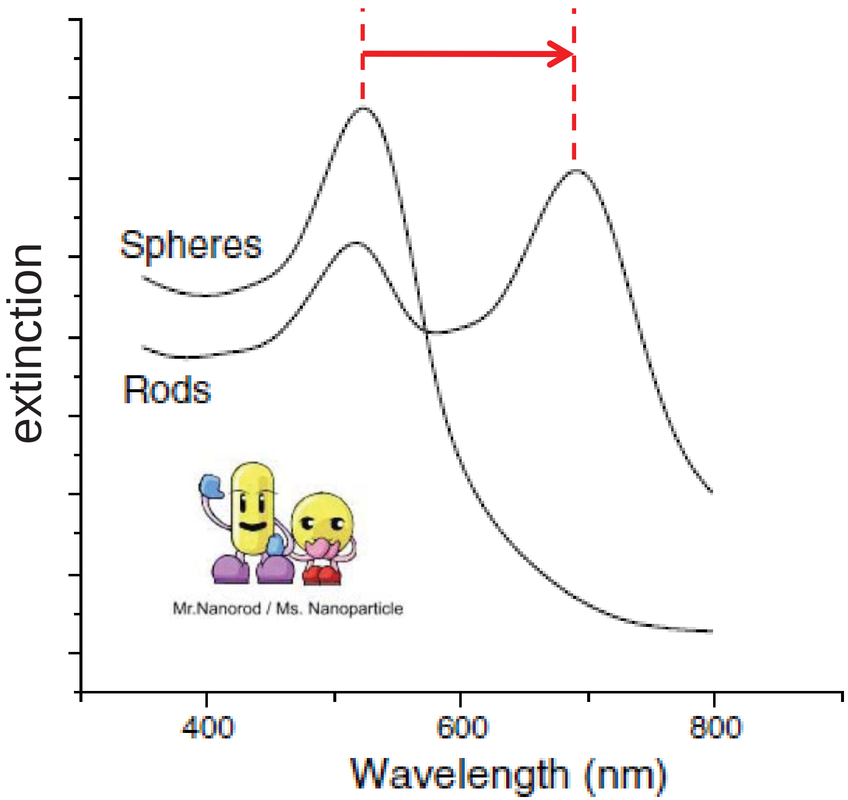


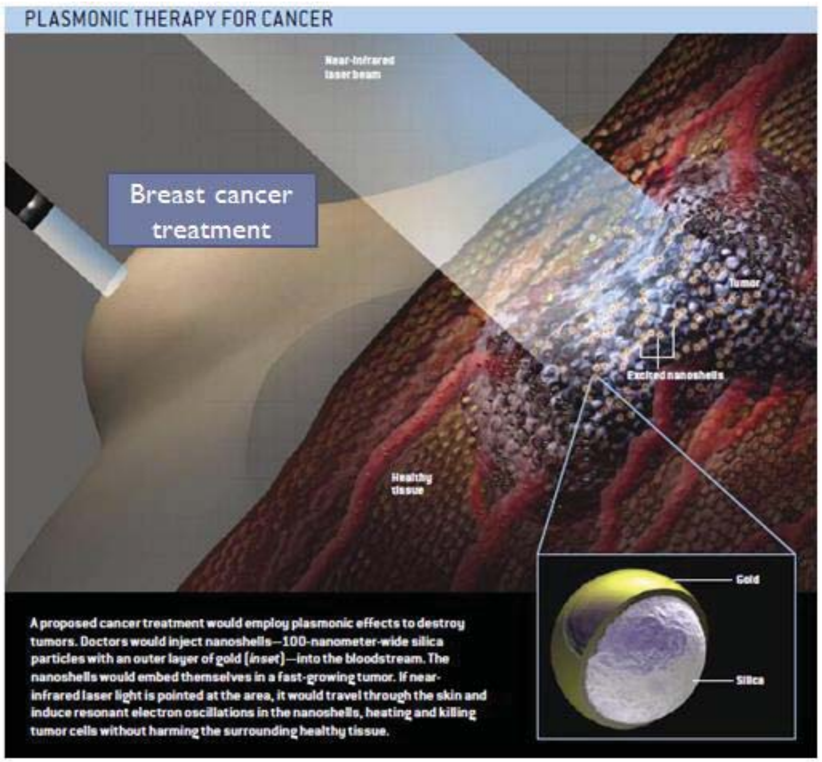


Gold nanorods show two absorption peaks;
Visible region: 520-530 nm, Transverse Mode
Near-infrared region: 700-1500 nm, Longitudinal Mode

extinction: 消光比

- The longitudinal mode has a significant red-shift compared to the resonance of a nanoshpere of the same volume
- Importance: aspect ratio ↑ ⇒ red-shift of longitudinal mode to near-IR ⇒ beneficial for biomedical applications (e.g., treatment of tumors)

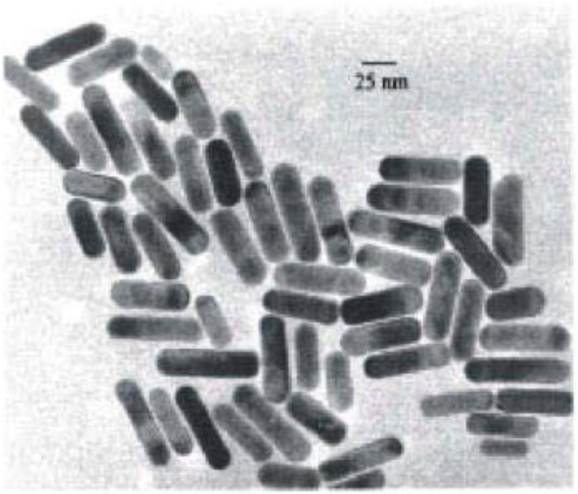


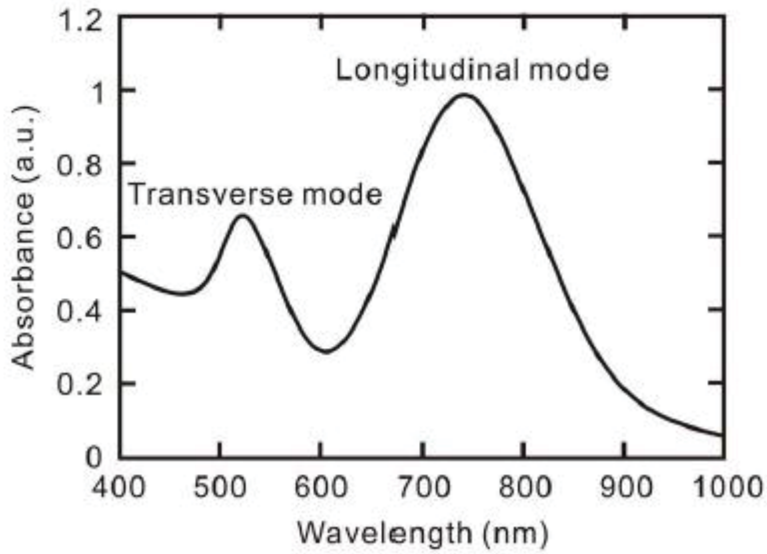


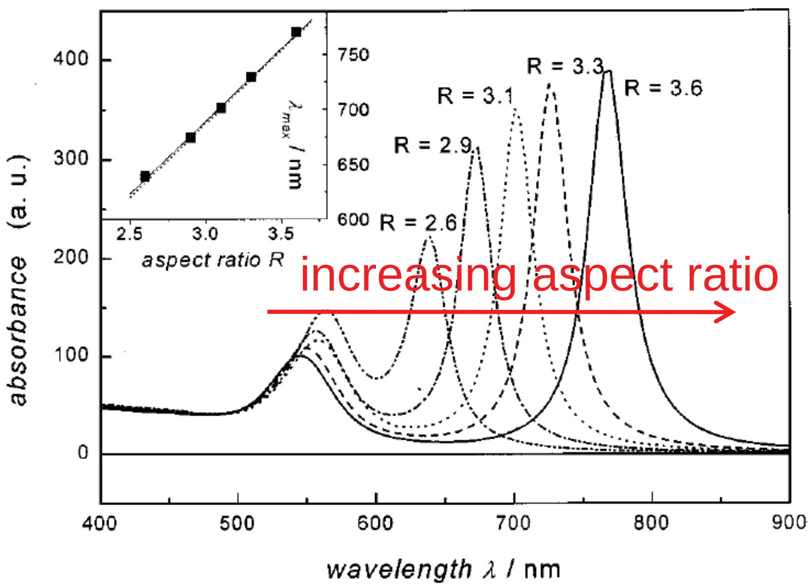
El-Brolossy et al., Eur. Phys. J. Special Topics **153**, 361–364 (2008).

aspect ratio: 长宽比， tumor: 肿瘤

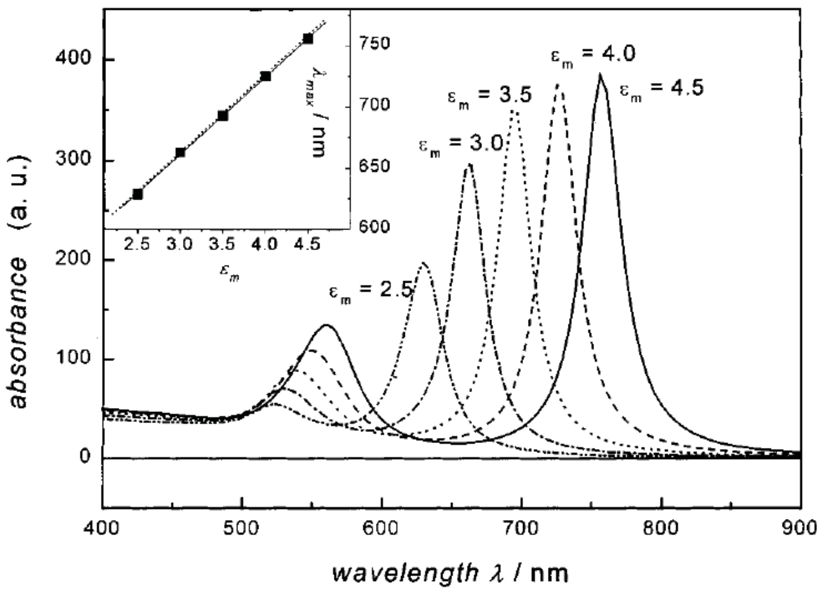
Gold nanorod experiment







Dependence on aspect ratio

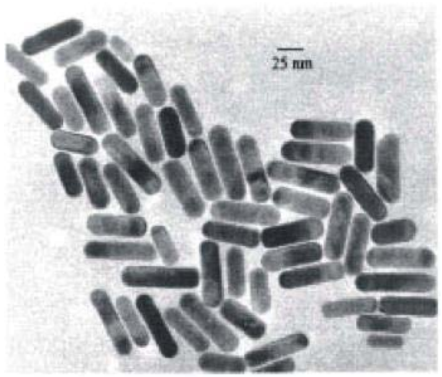


Dependence on surrounding medium

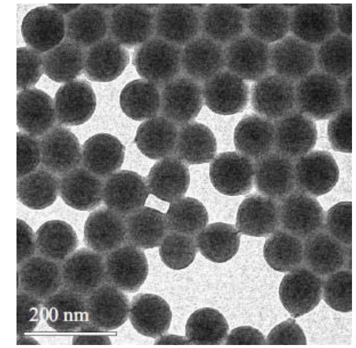
Link et al., J. Phys. Chem. B **103**, 3073 (1999).

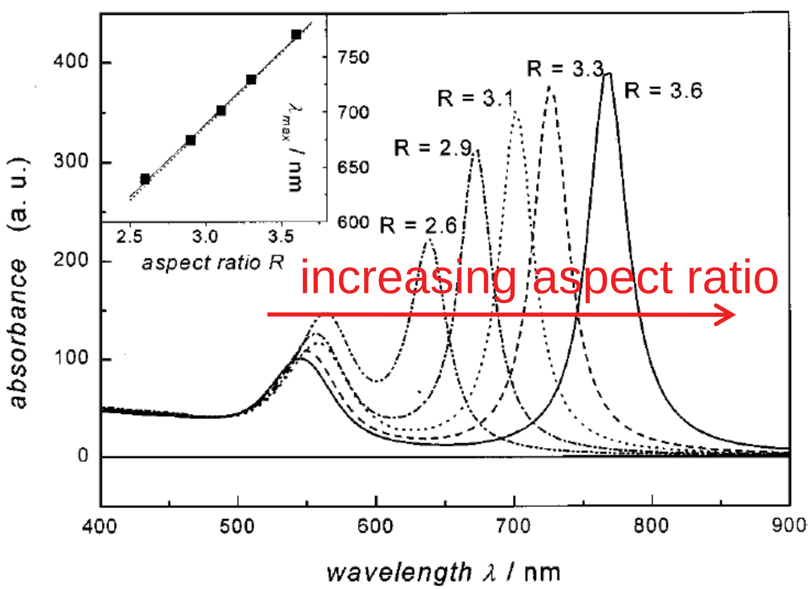
Nanorod vs. nanosphere: better tunability of resonance wavelength

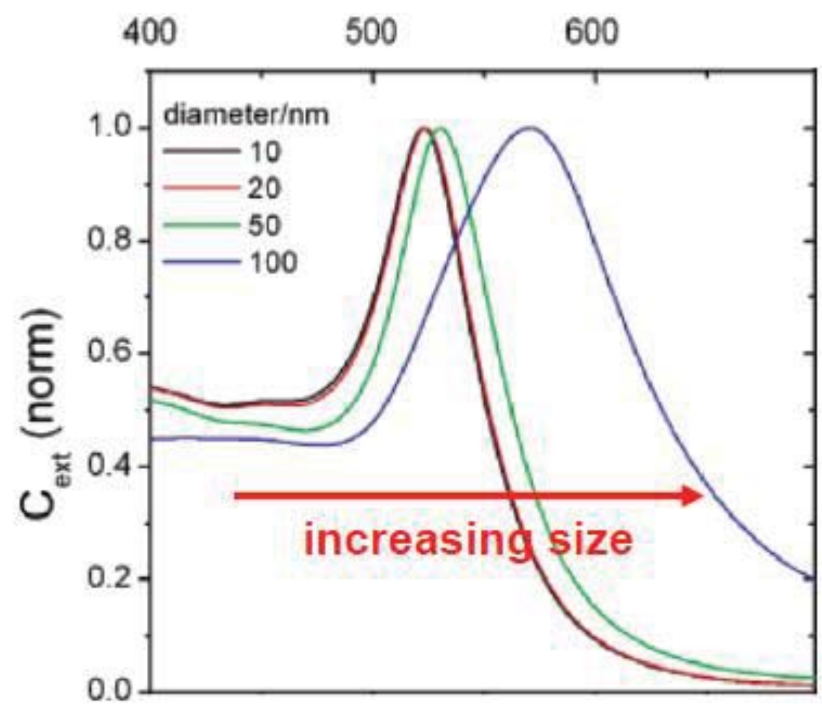
nanorod



nanoshpere



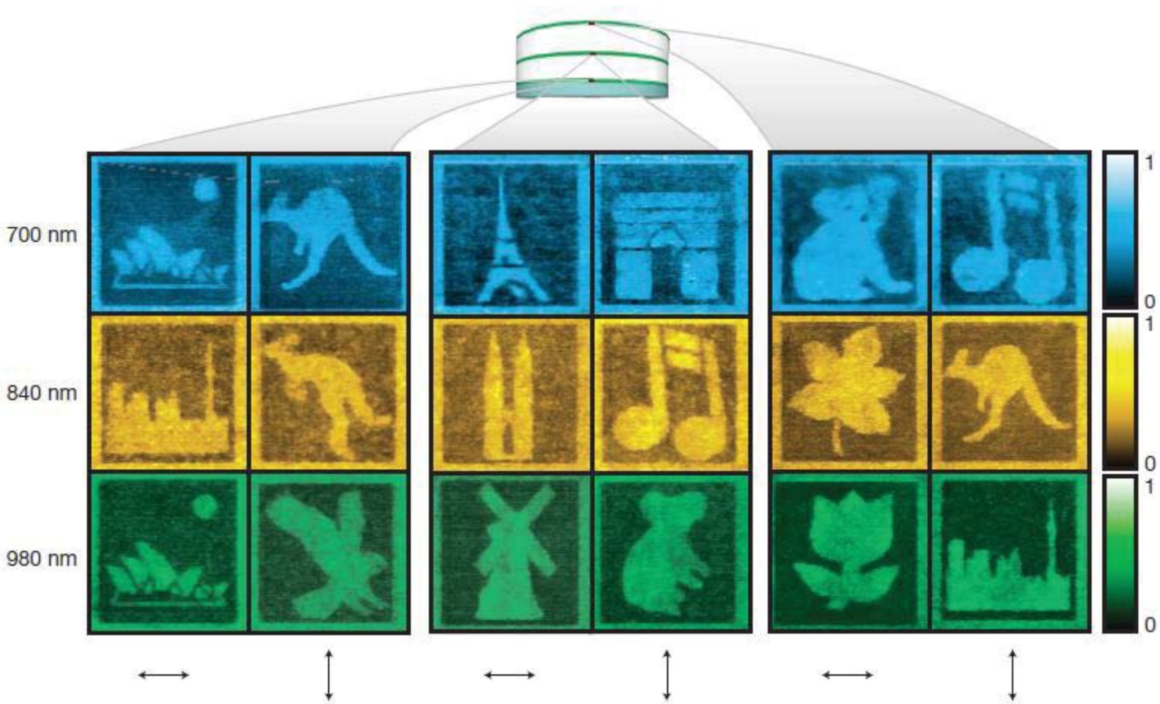




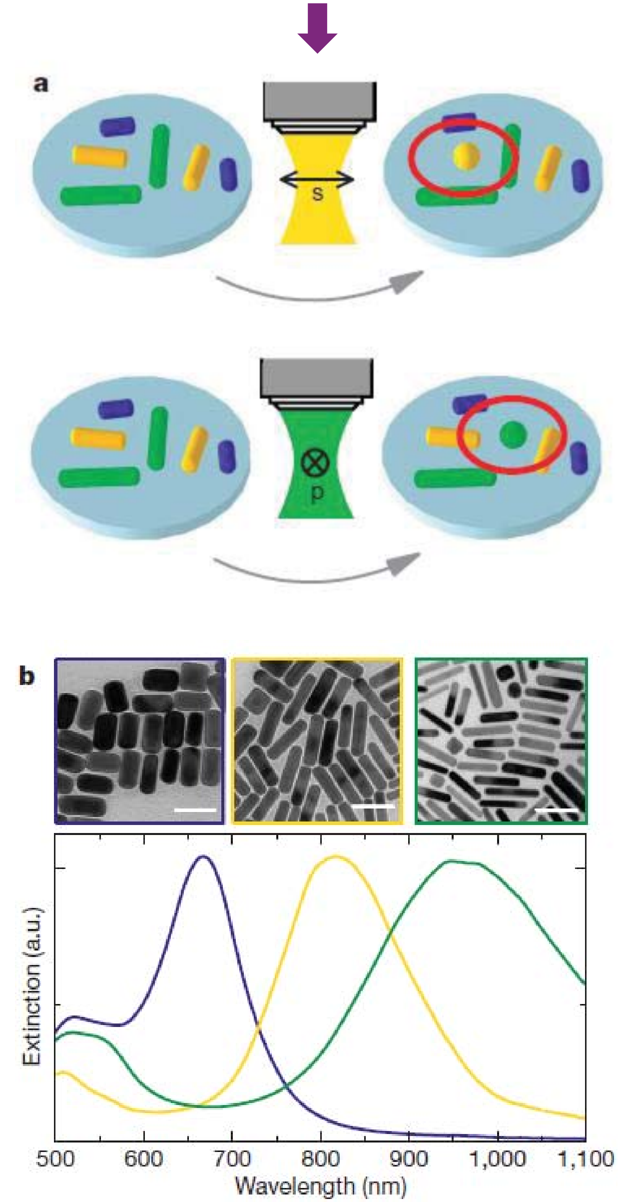
tunability: 可调谐性

Application example:

Five-dimensional optical data storage with gold nanorods

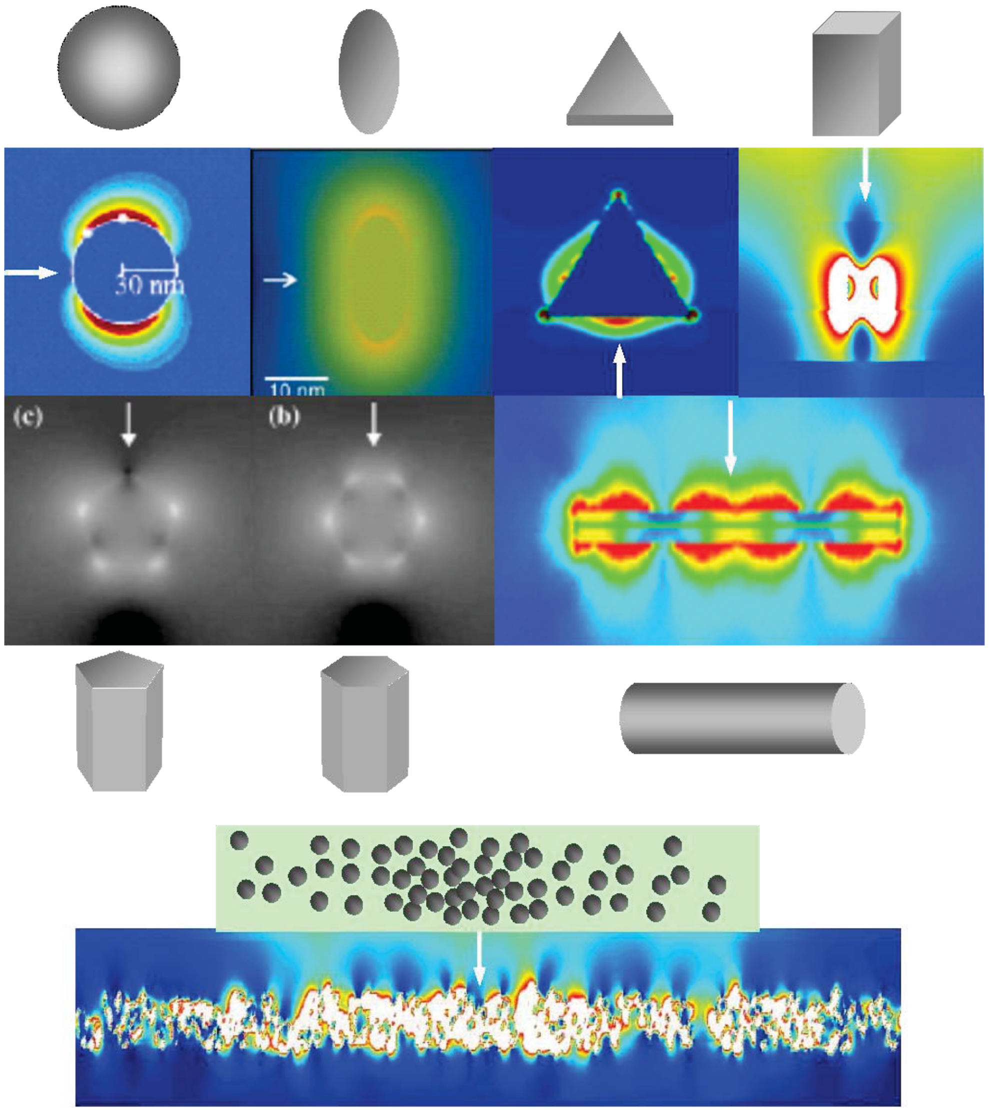


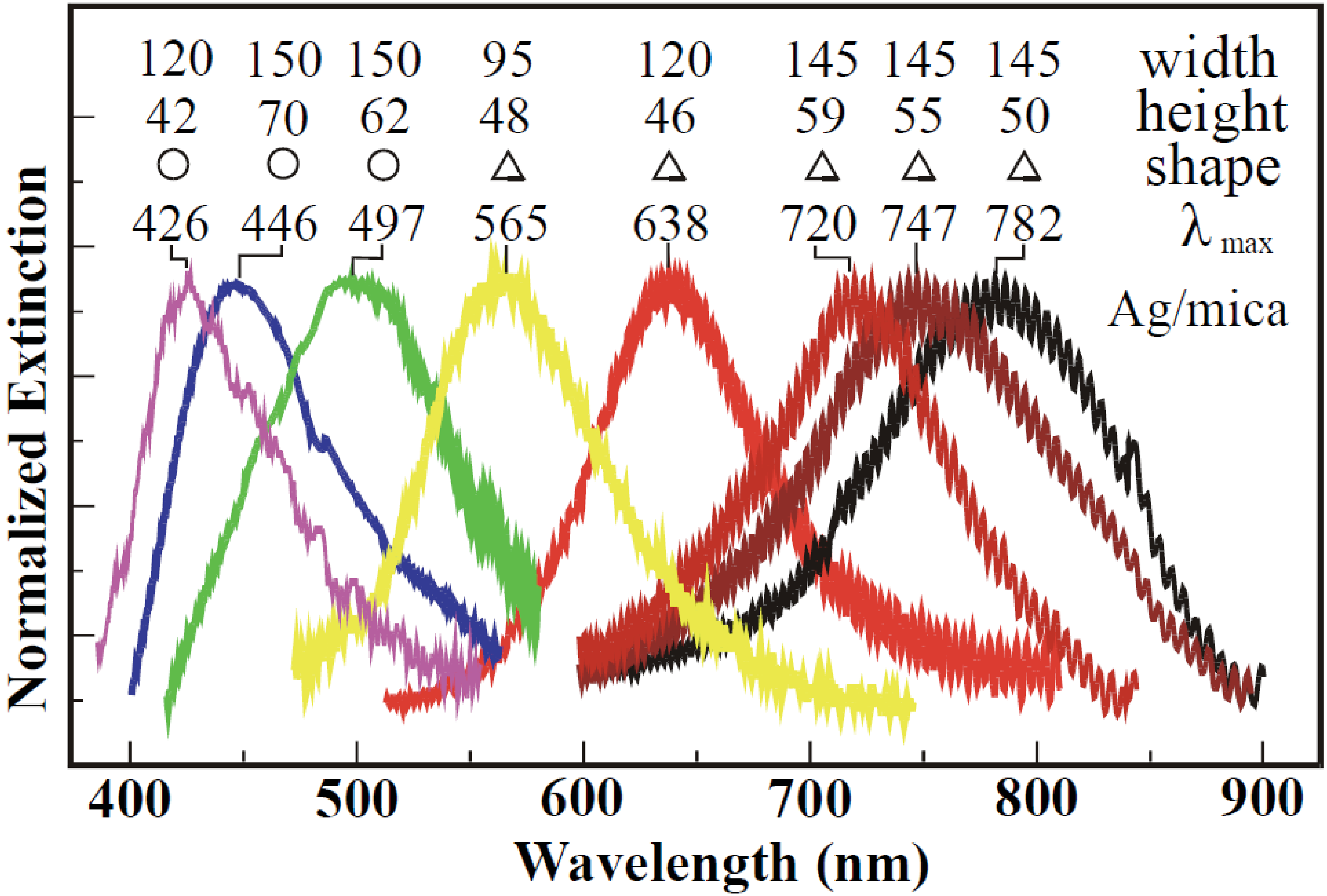
Photothermal patterning



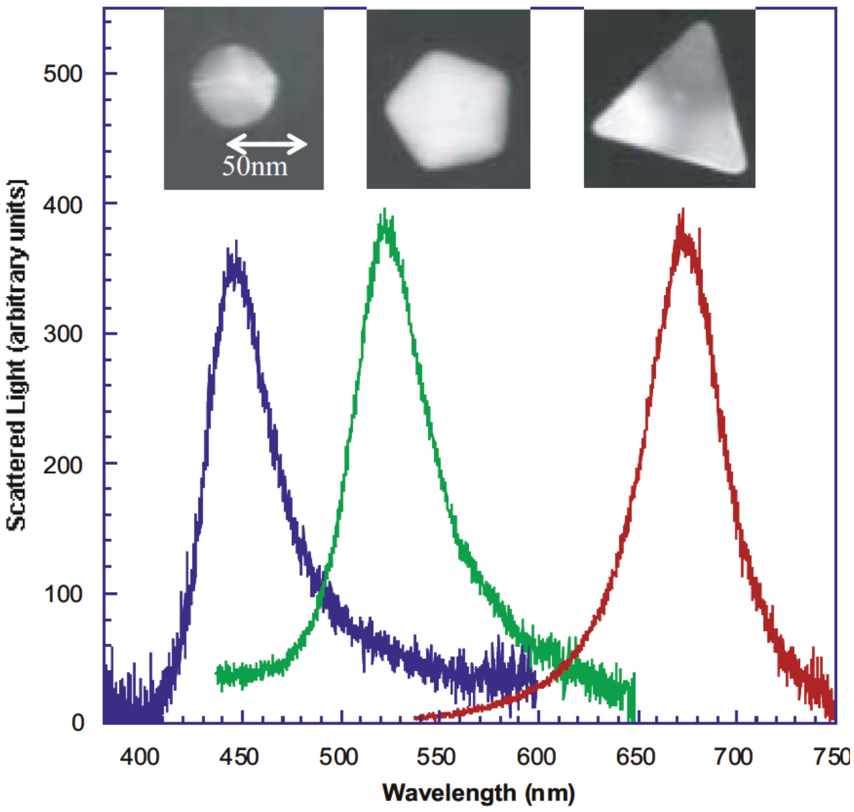
Zijlstra et al., Nature **459**, 410 (2009).

More about size and shape dependence

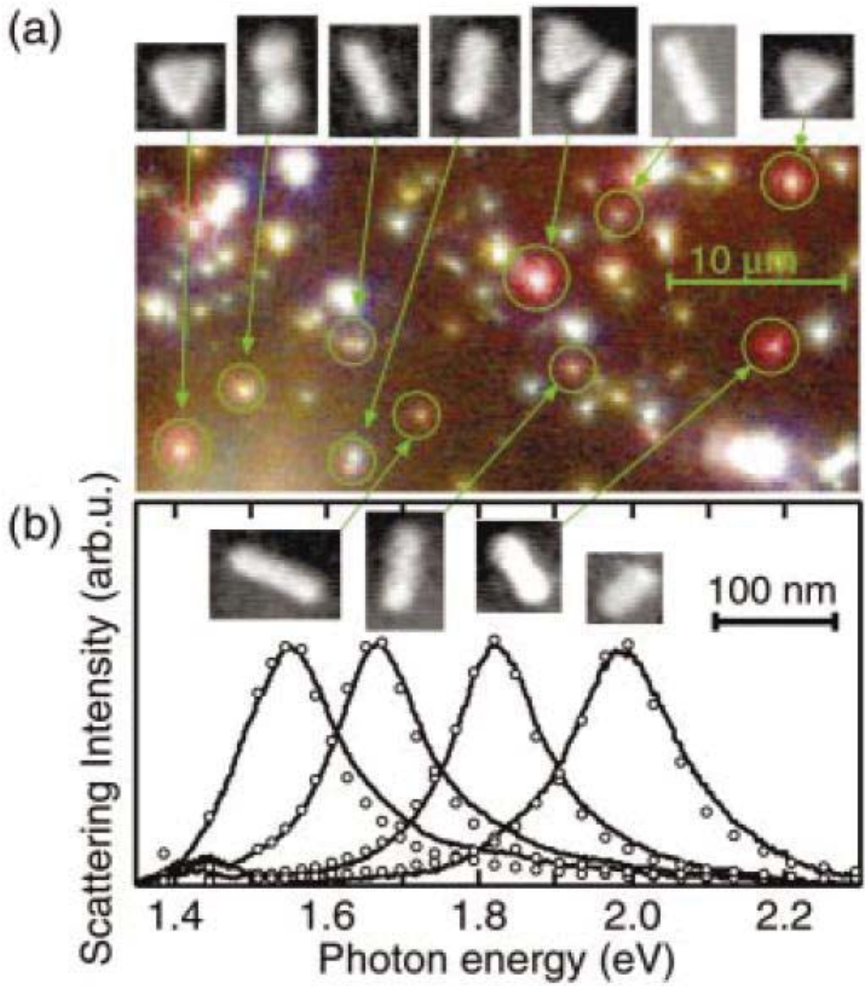




Jensen et al., J. Phys. Chem. B **104**, 10549 (2000).

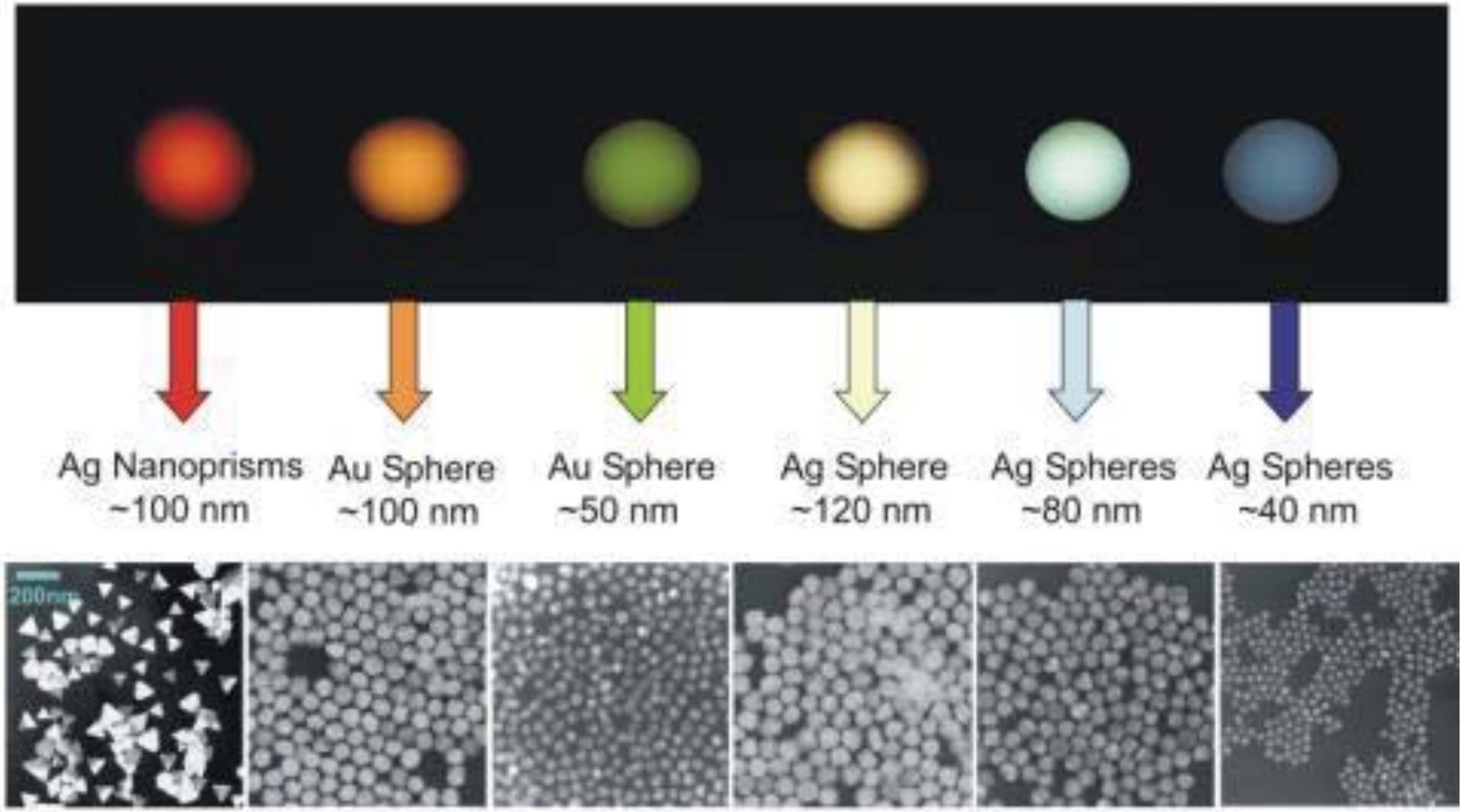


Mock et al., J. Chem. Phys. **116**, 6755 (2002).



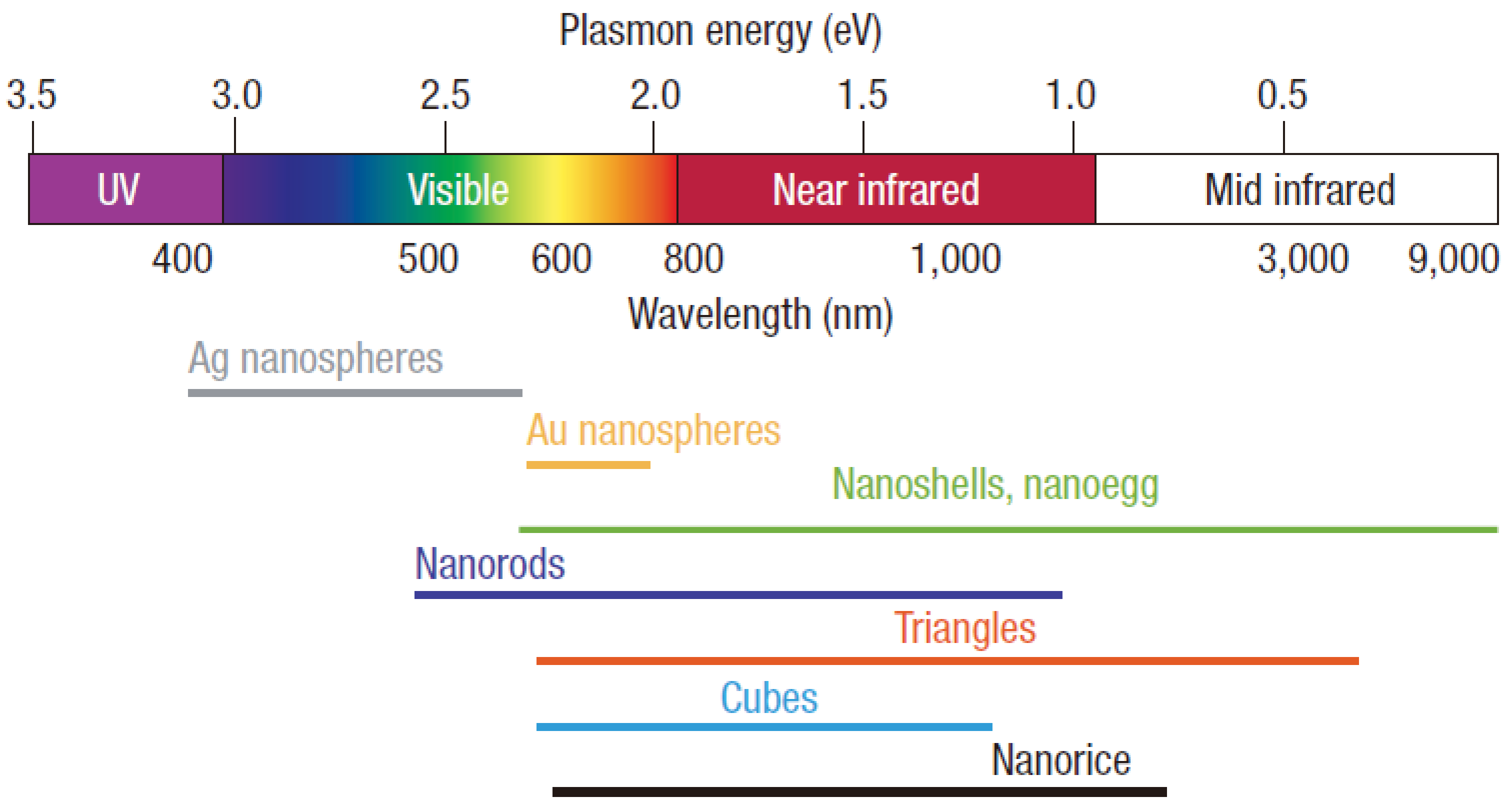
Kuwata et al., APL **83**, 4625 (2003).

Rayleigh Light-Scattering of Nanocrystals: Shape, Size, and Composition Matter



* The scale bar is the same for all the images.

A range of LSPR for a variety of particle shapes:



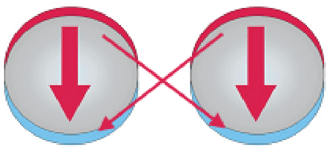
Lal et al., Nature Photon. **1**, 641 (2007).

3. Coupling of LSPs between nanoparticles

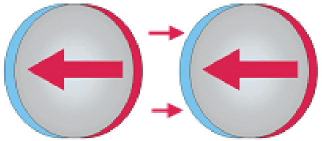
For single nanoparticle:

An isolated sphere is symmetric,
so the polarization direction does not matter.

For closely spaced nanoparticles – near-field intercoupling:



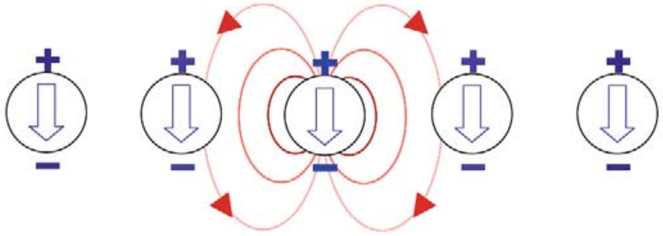
TRANSVERSE:
restoring force *increased* by coupling to neighbor
→ Resonance shifts to higher frequency



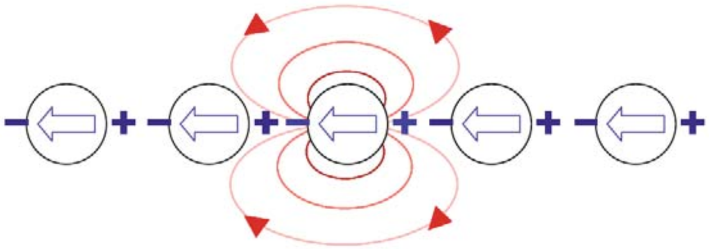
LONGITUDINAL:
restoring force *reduced* by coupling to neighbor
→ Resonance shifts to lower frequency

isolated: 孤立的，intercoupling: 相互耦合

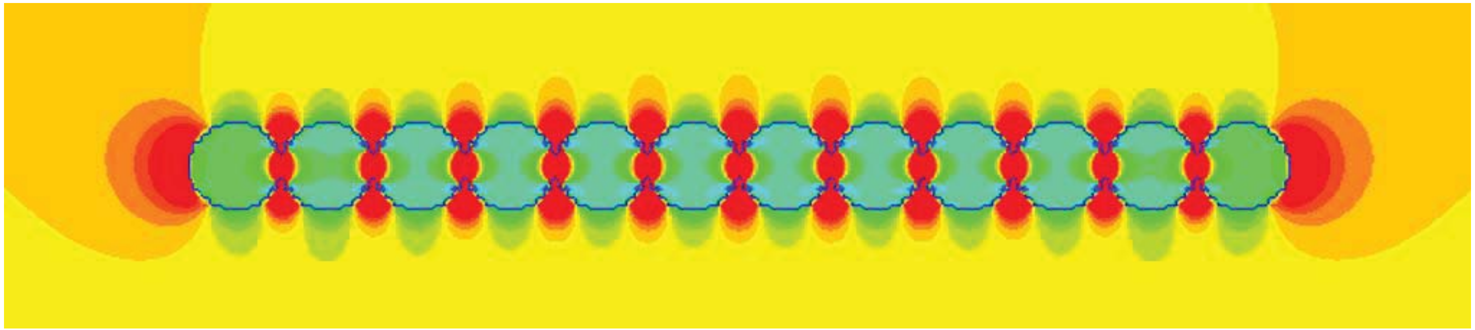
Increased restoring force
Higher (blue-shifted) frequency



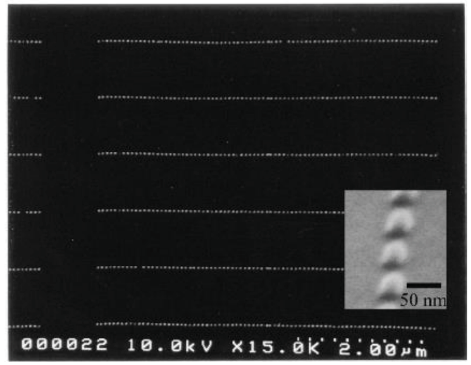
Reduced restoring force
Lower (red-shifted) frequency



Another consequence: near-field enhancement in gaps

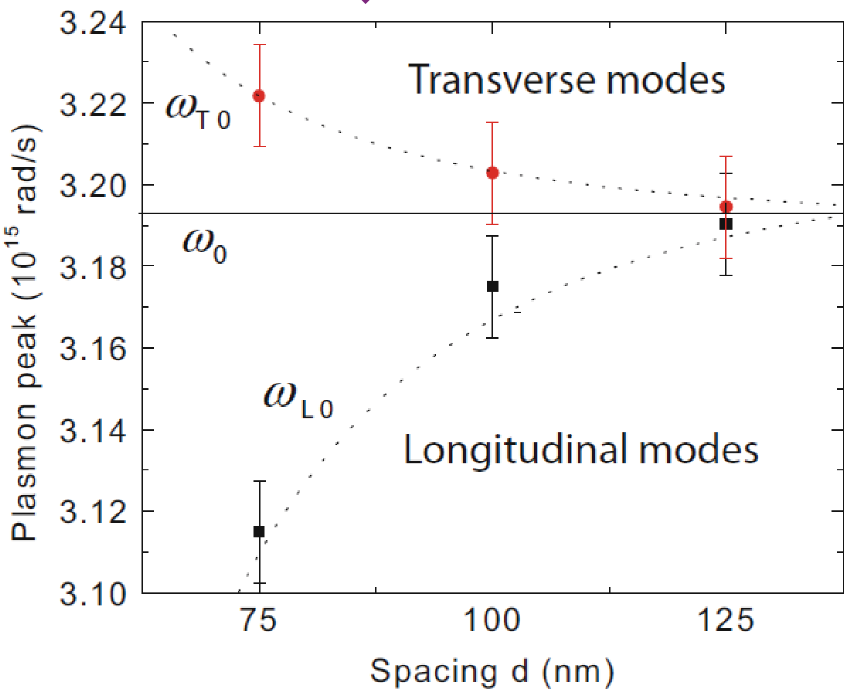


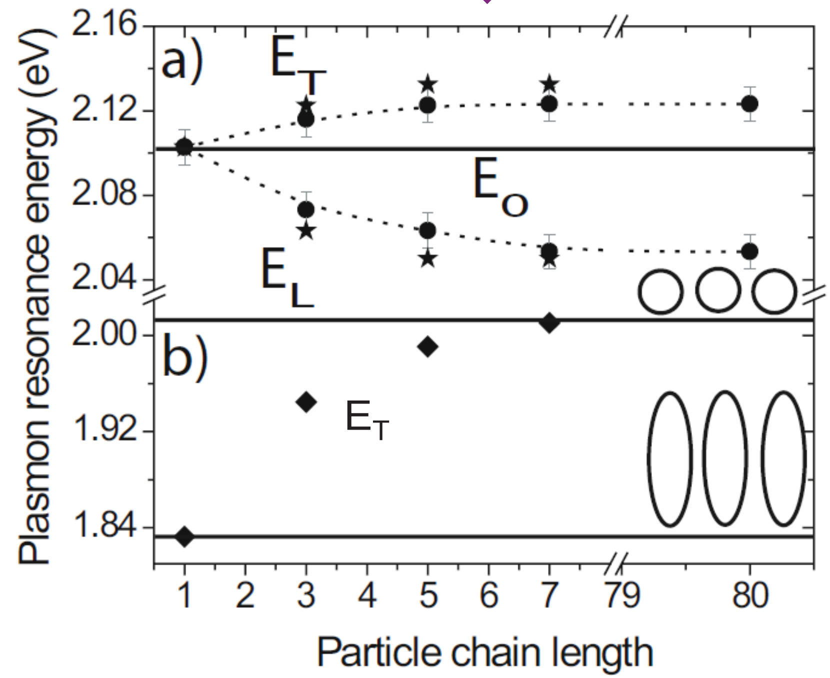
Experimental verification:



Dependence on spacing

Dependence on particle chain length



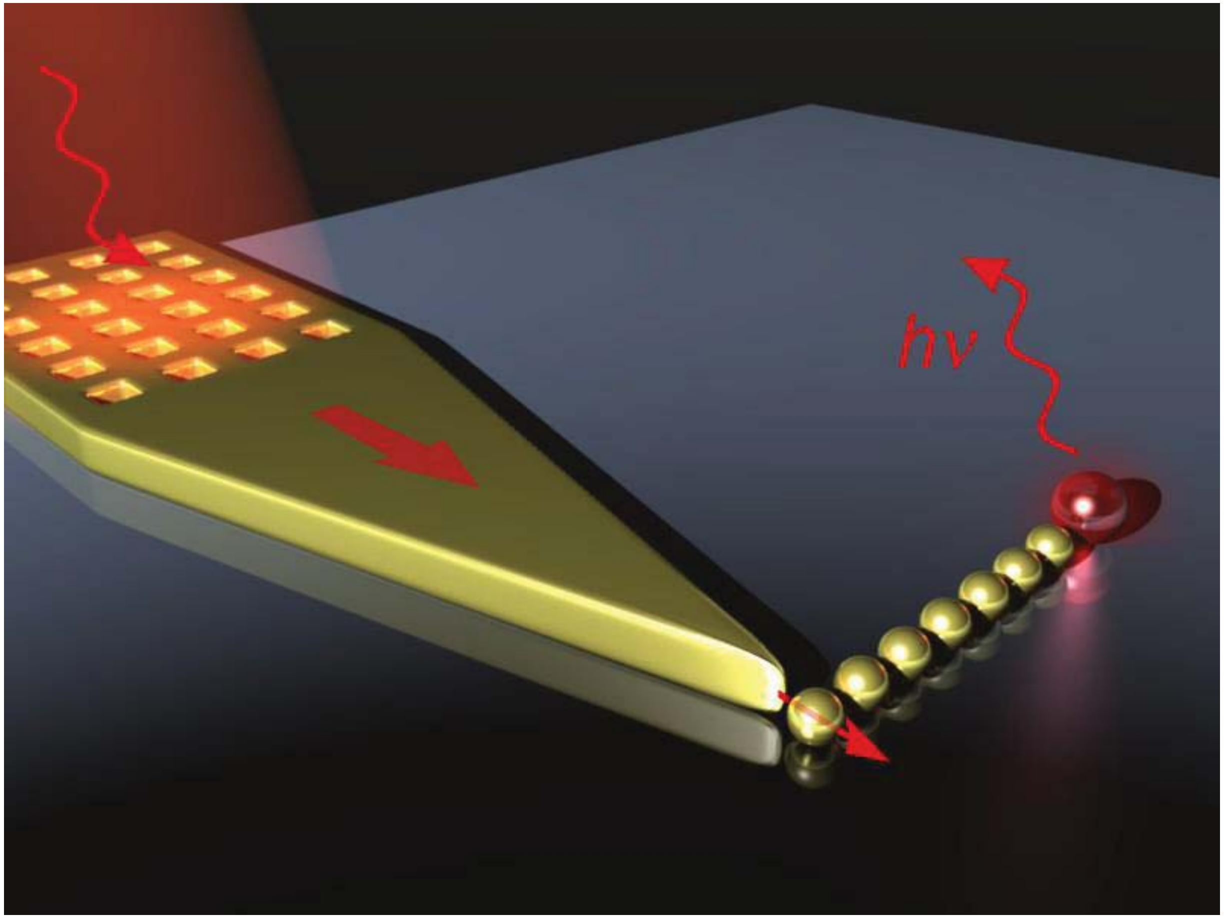


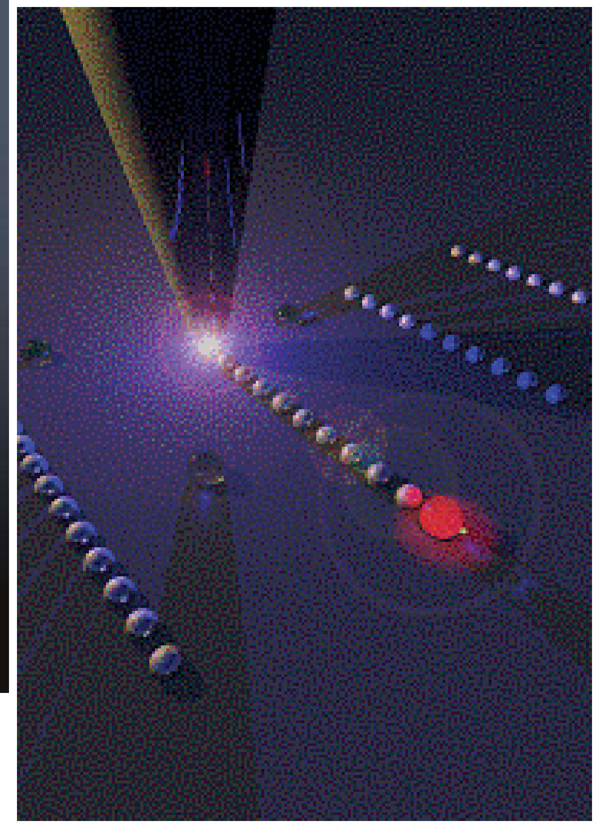
Maier et al., PRB **65**, 193408 (2002).

Maier et al., APL **81**, 1714 (2002).

verification: 验证

Application example: nanoparticle chain used as SPP waveguide

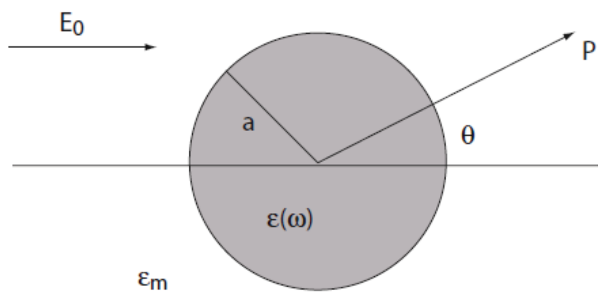




4. LSPs of complex nanostructures – nanoshell

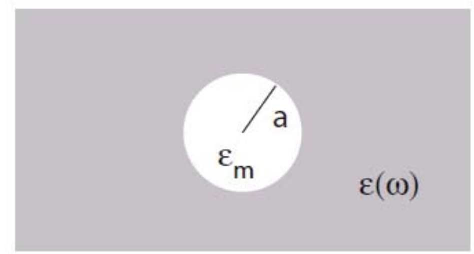
Let’s first consider nanosphere vs. nanocavity:

nanosphere



Interchange of ε and ε_m

nanocavity



polarizability

$$\alpha = 4\pi a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \qquad \alpha = 4\pi a^3 \frac{\varepsilon_m - \varepsilon}{\varepsilon_m + 2\varepsilon}$$

Fröhlich condition

$$\mathrm{Re}\left[\varepsilon\left(\omega\right)\right] = -2\varepsilon_m \qquad \mathbf{Re}\left[\varepsilon\left(\omega\right)\right] = -\frac{1}{2}\varepsilon_m$$

ω_{lsp} for Drude metal

$$\omega_{lsp} = \frac{\omega_p}{\sqrt{1+2\varepsilon_m}} \overset{\text{in air}}{=} \frac{\omega_p}{\sqrt{3}} \qquad \omega_{lsp} = \frac{\omega_p}{\sqrt{1+\frac{1}{2}\varepsilon_m}} \overset{\text{in air}}{=} \sqrt{\frac{2}{3}}\omega_p$$

shell: 壳体

Nanoshell – plasmon hybridization

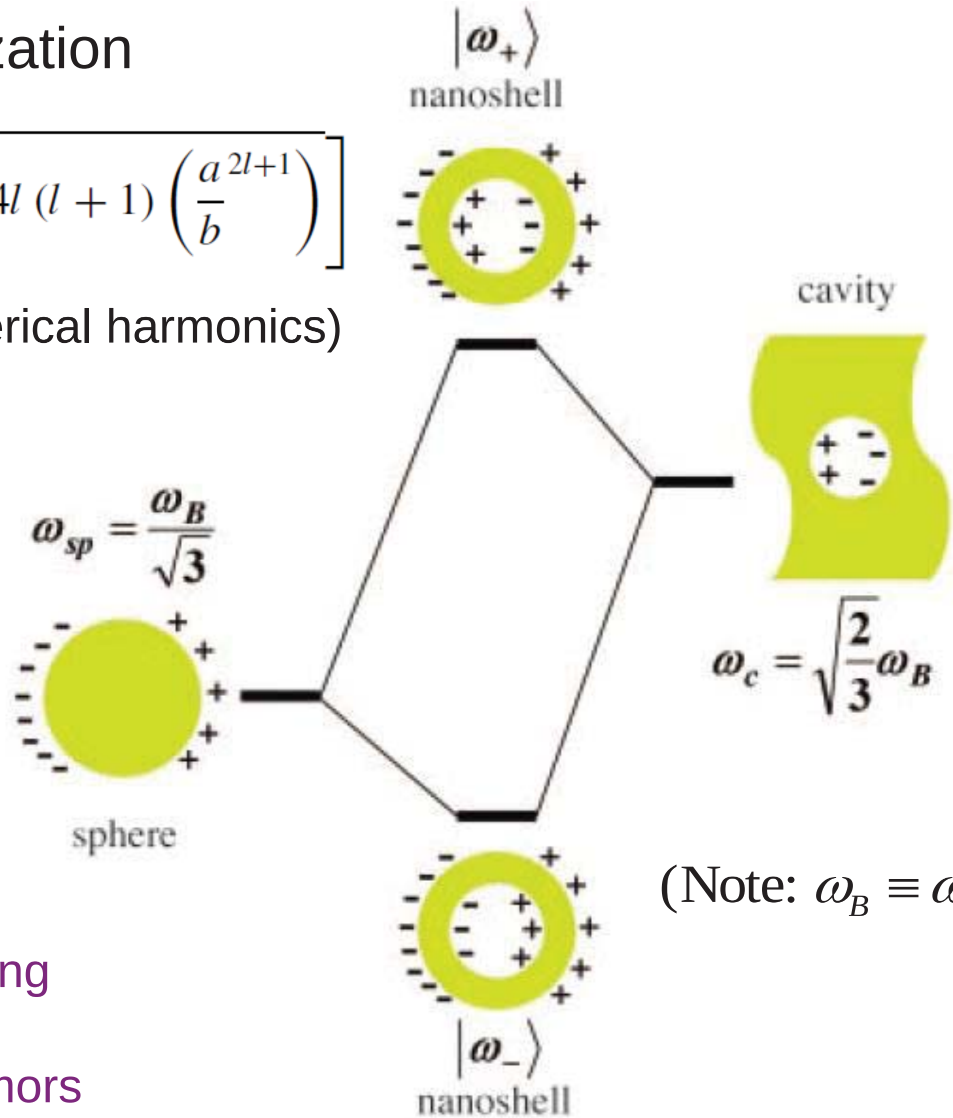
$$\omega_{l,\pm}^2 = \frac{\omega_p^2}{2}\left[1 \pm \frac{1}{2l+1}\sqrt{1+4l\,(l+1)\left(\frac{a}{b}\right)^{2l+1}}\right]$$

(l: orders of spherical harmonics)

- Nanoshell modes =
  shpere mode + cavity mode
  → an antibonding ω_+ mode
  → a bonding ω_- mode

- Consequences:
  → resonance shifts to near-IR
  → reduced resonance linewidth

- Superior to nanospheres for sensing and biomedical applications (e.g., treatment of nanoparticle-filled tumors via absorption-induced heating)

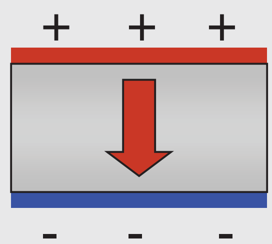
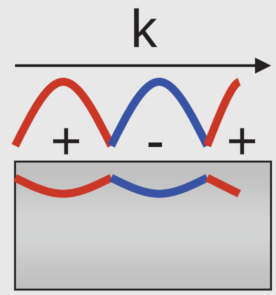
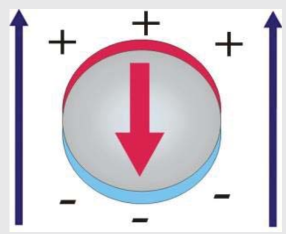


(Note: $\omega_B \equiv \omega_p$)

Prodan et al., Science **302**, 419 (2003).

hybridization: 复合， bonding: 键合， tumor: 肿瘤

5. Comparison of volume plasmons, SPPs, and LSPs

	Volume plasmons	**SPPs**	**LSPs (nanosphere)**
Schematic			
Mode property	Propagating mode in bulk metal	Propagating mode on metal surface	Non-propagating confined mode
Wave property	Longitudinal	Transverse & Longitudinal	–
Characteristic frequency	$\omega_p = \sqrt{\dfrac{Ne^2}{\varepsilon_0 m}}$	$\omega_{sp} = \dfrac{\omega_p}{\sqrt{1+\varepsilon_d}}$	$\omega_{lsp} = \dfrac{\omega_p}{\sqrt{1+2\varepsilon_d}}$
Interaction with light	No interaction (non-EM wave)	Coupled with photon to form polariton	Resonant extinction (scattering +absorption)

Summary

- Localized surface plasmons (LSPs):
  LSPs: non-propagating SPs confined on nanoparticle/nanocavity, color effect, various metal nanoparticles
- Resonance condition of LSPs:
  metal nanoparticle treated as effective electric dipole, LSPs of nanospheres (quasi-static approximation), Fröhlich condition, size- and shape-dependence (Mie theory), LSPs of nanorods (Gans theory), sensing and biomedical application of LSPs
- Coupling of LSPs between nanoparticles:
  transverse and longitudinal modes, near-field enhancement in gaps
- LSPs of complex nanostructures – nanoshell
  LSPs of nanosphere & nanocavity, plasmon hybridization in nanoshell
- Comparison of volume plasmons, SPPs, and LSPs