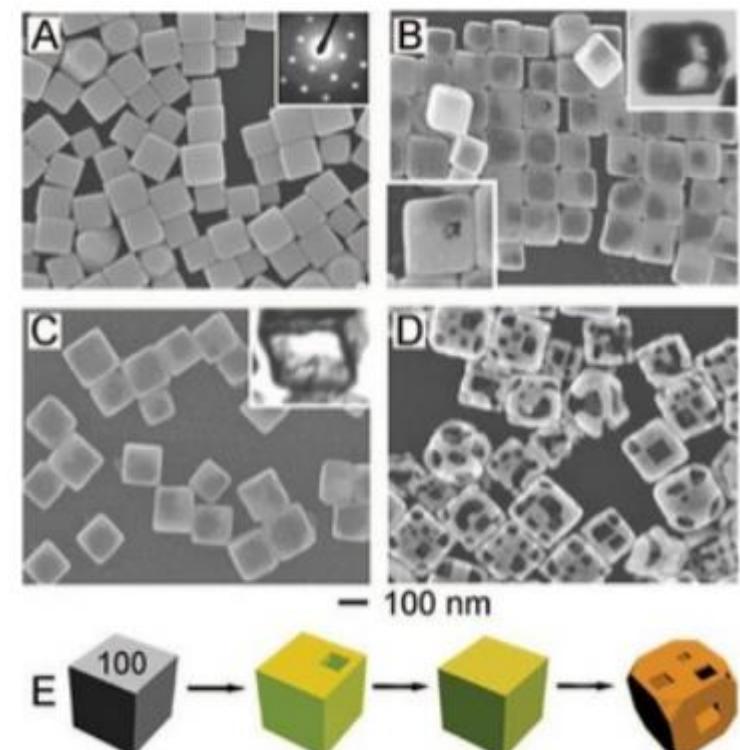


Nanoscale Metal Particles

- Metals also have unusual properties on the ~1–100-nm length scale.
- Fundamentally, this is because the *mean free path of an electron in metal at room temperature is typically about 1–100 nm*.
- So, when the particle size of metal is ~100 nm or less, one might expect unusual effects because the “sea of electrons” encounters a “shore” (the surface of the particle).
- Both *physical and chemical properties of metallic nanoparticles may be different from the properties of the bulk materials*.
- ✓ Gold particles less than 20 nm in diameter melt at a far lower temperature than bulk gold, for instance, and when the particles are between 2 and 3 nm in diameter, gold is no longer a “noble,” unreactive metal; in this size range, it becomes chemically reactive.
- ✓ At nanoscale dimensions, silver has properties analogous to those of gold in its beautiful colors, although it is more reactive than gold.

- Nanoscale metal particles have been the subject of intense research especially because of their unusual ***optical, magnetic, and catalytic properties.***
- The synthesis of metal nanocrystals in various shapes has become increasingly sophisticated and rational. By controlling the separate phases of nucleation and growth, and by using ligands that cap specific crystal faces during growth, it is possible to make metal nanocrystals of uniform size in a variety of interesting and useful shapes including cubes, truncated cubes, octahedra, triangular prisms, and high aspect ratio rods.
- By exploiting ***displacement reactions*** that replace one metal with another, complex hollow shapes such as nanocages (as shown in Fig. on the right) can be made starting with other shapes. In this case, solid silver nanocubes are transformed to gold nanocages.



Nanoscale Metal Particles: Optical Properties

Currently, research laboratories around the world are showing great interest in taking advantage of the **unusual optical properties** of metal nanoparticles.

- The optical properties of metallic nanoparticles of Ag, Au, etc. *arise from a complex electrodynamic effect that is strongly influenced by the surrounding dielectric medium.* We shall discuss this here.
- *Light impinging* on metallic particles causes *optical excitation of their electrons.* The *principal type of optical excitation that occurs is the collective oscillation of electrons* in the valence band of the metal.
- Such *coherent oscillations* occur at the interface of a metal with a dielectric medium and are called **surface plasmons.**
- *Quantized coherent oscillations of free electrons at the surface of the metal nanoparticles (and dielectric interface) are called the **Surface Plasmons (SPs).*** At a certain frequency of the incident light there is a **resonance** at which there is a maximum **absorption or scattering** of energy from the incident light wave and a peak is observed in the absorption/scattering spectra. This peak is called the **“surface plasmon resonance (SPR)” peak.**

Metals on the Nanoscale: Optical Properties

- In metal nanoparticles (that are much smaller than the wavelength of light,) the **surface plasmons are *localized*** and plasmon excitation occurs with high intensity. *The SPR in nanoscale particles is known as Localized Surface Plasmon Resonance (LSPR).*
- ✓ **Plasmonic Nanoparticles:** The nanoparticles that show *LSPR*.
- The peak intensity of the **surface plasmon absorption for gold and silver occurs in the visible region of the electromagnetic spectrum**, and so these **metallic nanoparticles are useful as pigments**.

Figure 1.12 Monodispersed gold nanoparticles of different sizes (2–200 nm) in water.

Note the **different colors due to different light interactions, which are dominated by particle size**. (Courtesy of Ted Pella, Inc., available on the



- **Surface plasmon resonance** is beginning to receive more recognition in the fields of chemistry, physics, and materials science due to the wide variety of ***possible applications*** including but not limited to ***optical sensing, data storage, light generation, biomedicine, and electronics.***
- Because of their growing popularity, they have become a topic of more research in order to try to understand their properties and how to harness and control their potential uses. Next, we will discuss what (surface) plasmon resonance is and some applications in which it is currently being used.

Optical Properties: Metal Nanoparticles

- The optical characteristics of nanosized metals are based on different principles than that of nanosized semiconductors.
- We have seen the quantum size confinement effects in semiconductor QDs for ~ 10 nm size QDs. Quantum confinement effects can be seen in metallic nanoparticles if their size is extremely small.
- Due to the **small Fermi wavelength of electrons in metals**, quantum confinement effects for **metallic spheres** become significant for radius values **far below 10 nm**: *perhaps on the scale of 1 – 2 nm or less.*
- However, *for larger than this size*, the optical properties of nanosized metals are mainly determined by the phenomenon of **surface plasmon resonance** which is caused by the **oscillations of the free electron gas in a metal**.
- Plasmon resonances are collective modes of oscillation of the electron gas in the metal. *This is a classical*, rather than quantum, *effect*. However, the **particle size does play roles** here.

OPTICAL EXTINCTION OF NANOPARTICLES: *Surface Plasmon*

- *In bulk metals* the *light is totally reflected* in the visible region and most metals therefore present a shiny (silvery) appearance.
- *Two exceptions* are *gold and copper* which have distinct colors due to *some absorption in the visible range due to inter-band transitions from the filled d bands to the sp conduction band*. Only the complimentary part of the light is visible and so these metals appear colored.
- On the other hand, *the metal powders are dark brown or black*. Their *large surface area causes the light to be nearly fully absorbed* due to repeated reflections.
- However, *if the particle size is reduced to nm range*, true colors appear again, notably for gold and silver.
- **What is the physical basis of the optical extinction of metal nanoparticles?**

- The physical basis of the **optical extinction of metal nanoparticles** is follows.
- If an obstacle, which could be a single electron, an atom or molecule, a solid or liquid particle, is *illuminated by an electromagnetic wave, electric charges* in the obstacle are set into *oscillatory motion* by the electric field of the incident wave.
- **Accelerated electric charges radiate electromagnetic energy** in all directions; **it is** this secondary radiation that is called the radiation *scattered* by the obstacle.
- In addition to reradiating electromagnetic energy, the excited elementary charges may *transform part of the incident electromagnetic energy into other forms* (thermal energy, for example), a process called **absorption**.
- **Scattering** and **absorption** are not mutually independent processes.

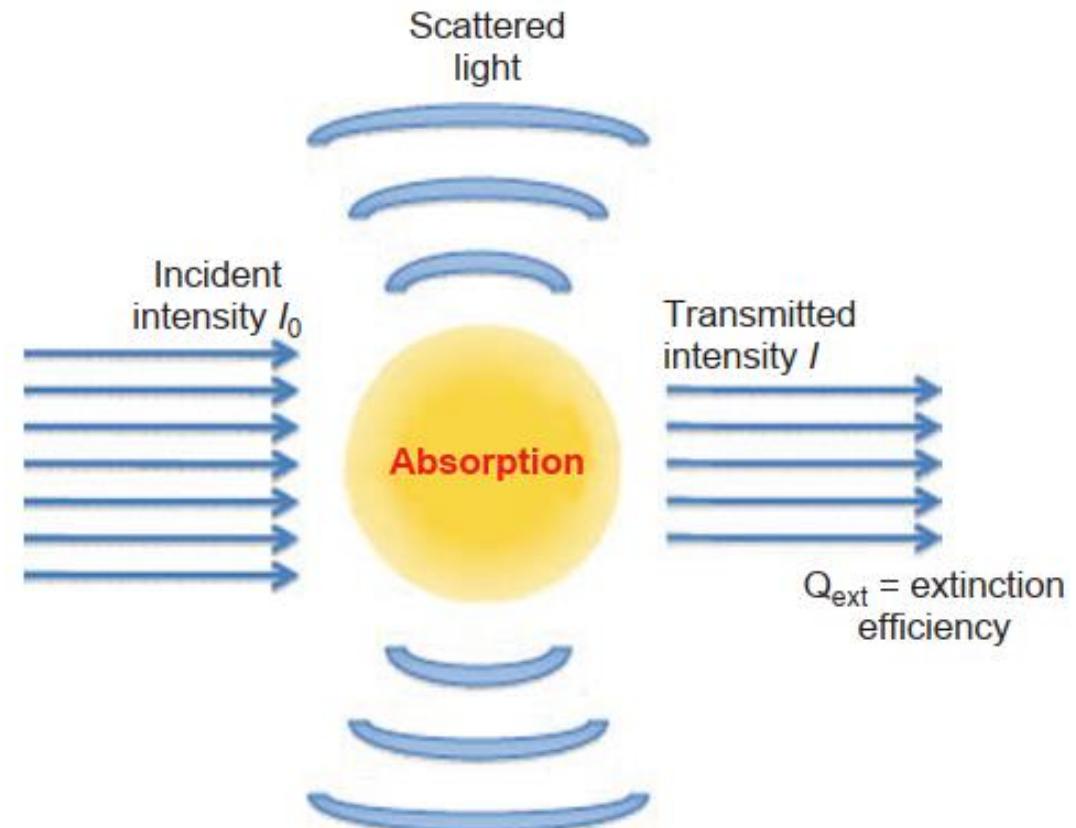
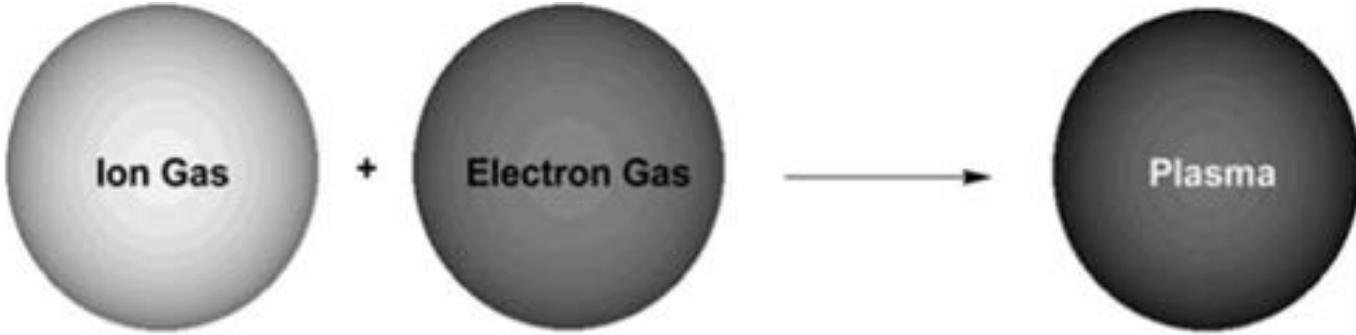


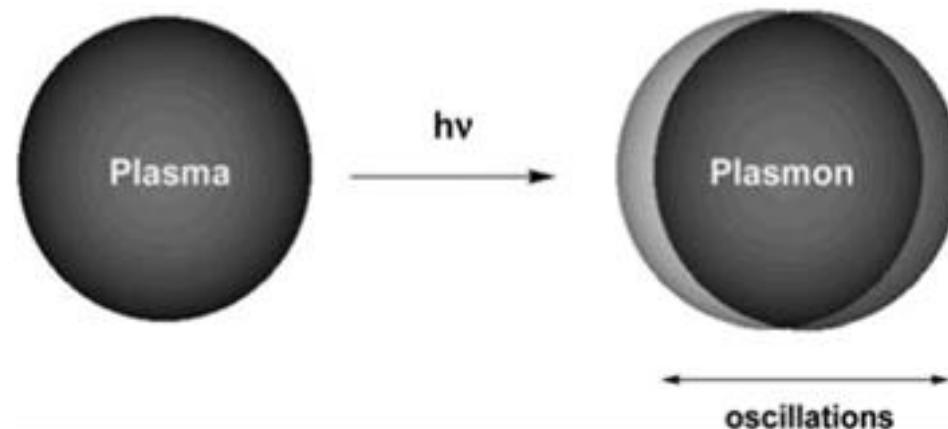
Fig. 6.18 Light extinction by a nanoparticle.

- Fig. 6.18 shows light extinction by a nanoparticle. After encountering a nanoparticle, incident light with an intensity I_0 is reduced to an intensity I and the amount of light extinguished is given by the extinction efficiency Q_{ext} .
- The lost light is either absorbed by the particle or converted to scattered light. The absorbed light is converted to heat and can be used for hyperthermia while the scattered light can be used to detect the location of the particle.

- Metals can be considered as confined plasma of positive ions (consisting of nuclei and core electrons which are fixed) and conduction electrons (free and mobile).
- In neutral case, the positive charge cloud of ions and negative charge cloud of electrons overlap with each other.

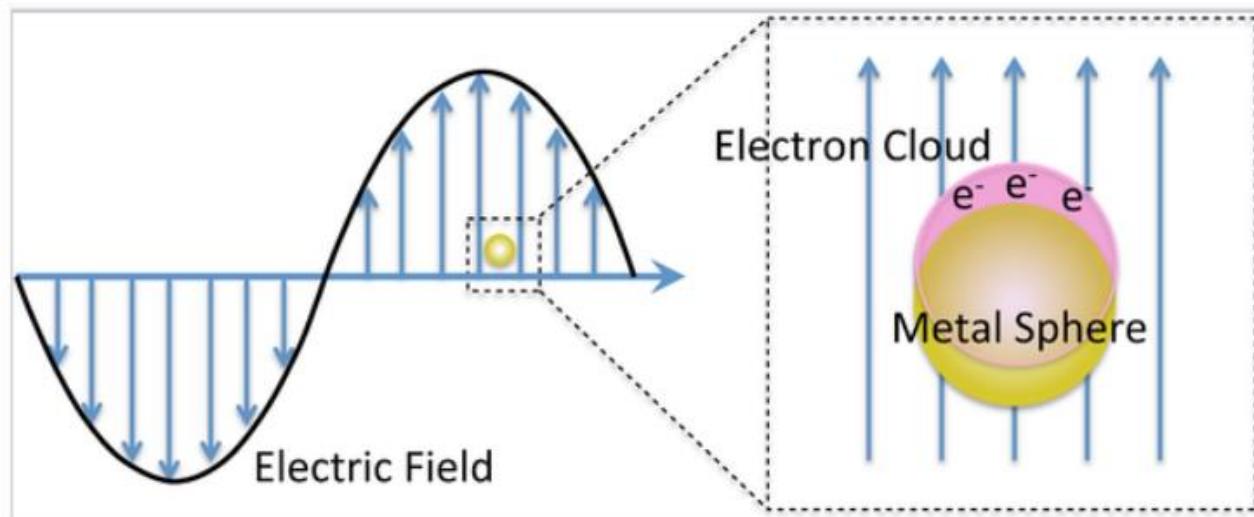


- By some external disturbance, i.e. irradiation by electrons or electromagnetic radiation, the charge cloud is disturbed, and electrons are moved away from the equilibrium position.



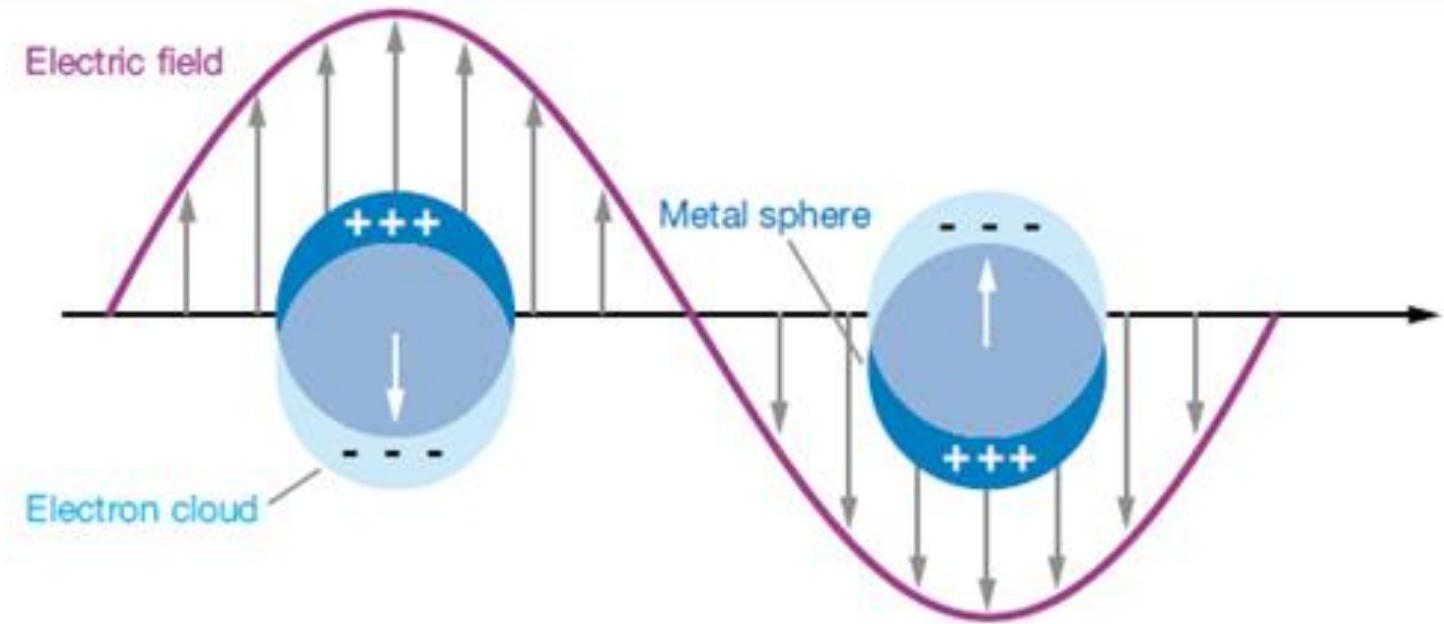
□ Theory of light scattering and absorption by metal nanoparticles

- The valence electrons in metal nanoparticles oscillate in the electric field of a light wave. While the nature of these oscillations is somewhat complex in metal particles that are non-spherical, the theory for spherical particles is relatively simple and in fact was worked out over 100 years ago by German physicist Gustav Mie.
- Mie considered the interaction of a spherical particle with a uniform electric field, E , oscillating at angular frequency ω ($= 2\pi f$).
- This is a good approximation when the particle diameter is much smaller than the wavelength of light, as shown on the right below.



- For example, when an electromagnetic radiation interacts with a metal, **the periodic electric field component of the electromagnetic radiation** causes a collective oscillation of the conductance electrons relative to the lattice of positive ions.
- The electric field displaces the electrons to create uncompensated charges at the nanoparticle surface (Fig. 16.1).

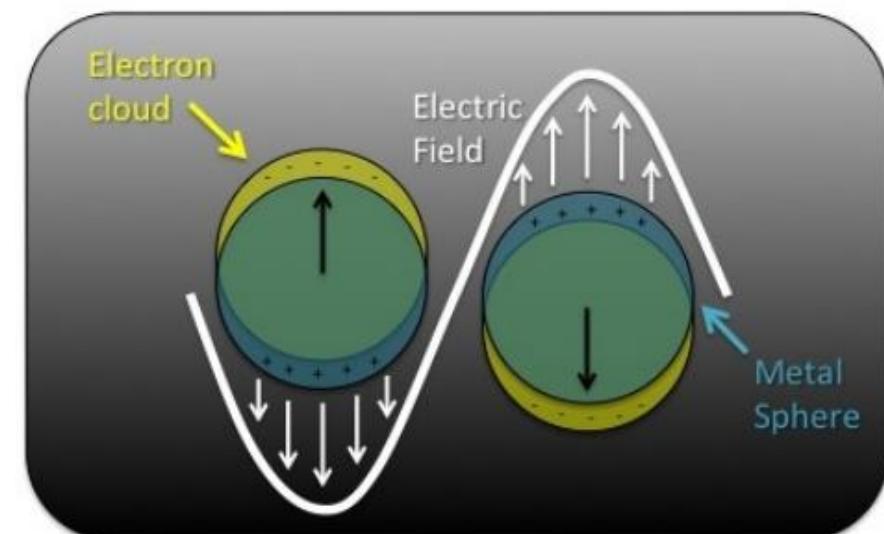
Scheme 16.1 In a metal, the **plasma** is created by the **combination of a (positive) ion gas and an electron gas**. The plasma is then disturbed by the absorption of a photon. The resulting **electrodynamic force** is causing an oscillation, which is known as **plasmon**.



- If the density of electrons in one region increases, they repel each other and tend to return to their original equilibrium position.
- As electrons move towards their original positions, they pick up kinetic energy and instead of coming to rest in equilibrium configuration, they overshoot. They oscillate back and forth.
- **The collective oscillations of conduction electrons in metals are called *plasmons*.**
- When the particle size is much smaller than the wavelength of light, a dipole is created due to the accumulation of the electrons at one end and the depletion of electrons at the other end. This dipole creates a restoring force for the electron cloud.
- Since the *penetration depth of an electromagnetic wave striking the metal surface is limited* (<50 nm for Ag and Au), only *plasmons caused by surface electrons are significant* and are commonly referred to as *surface plasmons*.
- At a certain frequency of the incident light there is a *resonance* at which there is *a maximum absorption or scattering of energy from the incident light wave and a peak is observed* in the absorption/scattering spectra. This peak is called the **“surface plasmon resonance (SPR)” peak**.

- The electrons in the nanoparticles made of metals couple with an external electromagnetic field to create a **localized** plasmon. This **plasmon cannot propagate** since *the nanoparticle is much smaller than the wavelength of the light*, however they will have a characteristic **resonance frequency** that causes absorption of the light at particular frequencies. This is plasmon absorbance is therefore termed as the “**localized surface plasmon resonance (LSPR)**”.
- This LSPR leads to **the buildup of polarization charges on the nanoparticle surface**. A *homogeneous field builds up* in the interior of the nanoparticle, *while a dipolar field is produced at the exterior, resulting in strong light absorption/scattering, the appearance of intense SPR bands, and the enhancement of the nearfield in the immediate vicinity of the nanoparticles*.

- The interesting optical properties of nanocrystalline Au, Ag, Cu, and a number of other metals, derive from the ***collective oscillation of their valence electrons***, a phenomenon known as ***surface plasmon resonance***.
- Remember that in these metals, the electron mean free path is long (about 100 times larger than the size of the atoms), so the valence electrons feel only the average positive charge of the atomic cores as they zoom around the crystal.
- *Light impinging on the metal acts as an oscillating electric field, pushing and pulling on the valence electrons at the characteristic frequency of the light wave.* The situation is very much like a pendulum or a weight on a spring. The electrons, pushed away from their equilibrium positions, ***feel a restoring force that is proportional to their displacement***. Their motion can be described by ***Hooke's Law: $F = kx$*** , where the spring constant k determines the "stiffness" of the spring.



- In the case of the plasmon resonance, k is proportional to the **number density of valence electrons** n , and the **square of the electronic charge** e : $k = ne^2/\epsilon_0$.
- The **resonant frequency of the plasma oscillation** is given by: $\omega_p = (k/m)^{1/2} = (ne^2/m_e\epsilon_0)^{1/2}$ where m is the electron mass. Here, ω_p ($\omega_p^2 = \frac{ne^2}{m\epsilon_0}$) is known as the **volume plasma frequency**. It is the **natural frequency of oscillation of a collection of electrons** for a given system.
- **At very high frequencies (ω) of measurement, the relationship between the refractive index and plasma frequency can be** approximated by

$$\sqrt{n^2} = 1 - \frac{ne^2}{m\epsilon_0\omega^2} = 1 - \left(\frac{\omega_p}{\omega}\right)^2 \quad (\text{Eq. 5.4})$$

where \tilde{n} is the complex refractive index function ($\tilde{n} = N + ik$; the real part is usually the refractive index, N , and the imaginary part is called the extinction coefficient, k).

- For **most metals, the plasmon resonance is in the ultraviolet** part of the spectrum, but for a **few metals like Au, Ag, and Cu it is in the visible range**.
- For metal particles that are much smaller than the wavelength of light, this effect is called the **localized surface plasmon resonance, or LSPR**.

- Simplest theory to describe ϵ is the Drude–Lorentz–Sommerfeld theory that has been developed. According to this theory, electrons, near conduction band edge, contribute to “ N ”, hence to ϵ . **The square of the refractive index function is the dielectric constant $\tilde{n}^2 = \epsilon$.**
- In general, dielectric constant of the material is complex in nature ($\epsilon = \epsilon' + i\epsilon''$) and for most of the materials, the dielectric property is independent of the strength of the electric field, but it *depends on the frequency of the external alternating electric field incident on the materials*. **(The real part of the dielectric is related to polarization and anomalous dispersion, while the imaginary part is associated with dissipation of energy into the medium.** In a simple forced damped oscillator, the real component describes the phase lag between the driving and response frequency (slowing down of light in a material, described by the refractive index) and the imaginary component is the damping factor (loss of energy or absorption of light, described by the absorption co-efficient in the Lambert Beer law, although in a real material the absorption is of course quantized)... its imaginary part reflecting loss of energy of the propagating light in matter).
- **The large imaginary part leads to rapid attenuation of the wave in the metal. The metal absorbs the radiation in this range.** This is the case for $\omega \leq 10^{12}$ Hz for copper, for example.

- Let us assume the particle is embedded in a uniform, **insulating material** (e.g. a solvent) that has a dielectric constant ϵ_{diel} . For insulators, ϵ_{diel} is a *positive real number*.
- The dielectric constant ϵ of a **metal** is actually a complex number: $\epsilon = \epsilon' + i\epsilon''$
- Here the real part, ϵ' , is **related to the refraction of light**, and the **imaginary part, ϵ'' , is related to light absorption**. Both ϵ' and ϵ'' are dependent on the frequency of the light.
- For metals **near the plasmon resonance frequency**, ϵ' is typically a **negative number**.
- The **cross-section for absorption** of the light wave by the particle is:

$$\sigma_{\text{absorption}} = \frac{9\omega}{c} \epsilon_{\text{diel}}^{\frac{3}{2}} V \underbrace{\frac{\epsilon''_{\text{metal}}}{(\epsilon'_{\text{metal}} + 2\epsilon_{\text{diel}})^2 + (\epsilon''_{\text{metal}})^2}}_{\text{Equation 11.6.5}}$$

and the **cross-section for scattering** is:

$$\sigma_{\text{scattering}} = \frac{3}{2\pi} \left(\frac{\omega^4}{c}\right) \epsilon_{\text{diel}}^2 V^2 \frac{(\epsilon'_{\text{metal}} - \epsilon_{\text{diel}})^2 + (\epsilon''_{\text{metal}})^2}{(\epsilon'_{\text{metal}} + 2\epsilon_{\text{diel}})^2 + (\epsilon''_{\text{metal}})^2} \quad (11.6.6)$$

- The sum of these two is the cross-section for extinction:

$$\sigma_{\text{extinction}} = \sigma_{\text{absorption}} + \sigma_{\text{scattering}} \quad (11.6.7)$$

- Note that the above equations are valid for the spherical nanoparticle which is distinctly smaller than the incident wavelength ($2R \ll \lambda$), so that ***only dipole oscillations have to be accounted for*** and higher terms (quadrupole oscillations, etc.) are neglected.
- We know that a beam of light incident on a surface can undergo reflection, absorption and transmission to different extents depending on *the material and the wavelength of the light*. Metal nanoparticles show light *absorption, scattering, and strong to weak light emission or fluorescence*.
- A curious feature of the above Equation (11.6.5) is that there is ***no absorption if $\epsilon''_{metal} = 0$*** , but there is also no absorption if $\epsilon''_{metal} = \infty$ (*in both the cases the right-most term fraction in above Eq. becomes zero*).

❖ **Resonance Condition for Spherical Nanoparticles**

- These **cross-sections become large** when the term in the denominator becomes **small**.
- Extinction would be maximum when $\epsilon'_{\text{metal}} + 2\epsilon_{\text{diel}} = 0$ when $\epsilon''_{\text{metal}}$ is **small**, which gives rise to a peak in **surface plasmon resonance (SPR) band** (maximum extinction cross-section for a given wavelength).
- This gives: $\epsilon'_{\text{metal}} \simeq -2\epsilon_{\text{diel}}$ (11.6.8)
- This is known as the **resonance condition** for a spherical particle.
- When does $-\epsilon'_{\text{metal}}$ become $2\epsilon_{\text{diel}}$?

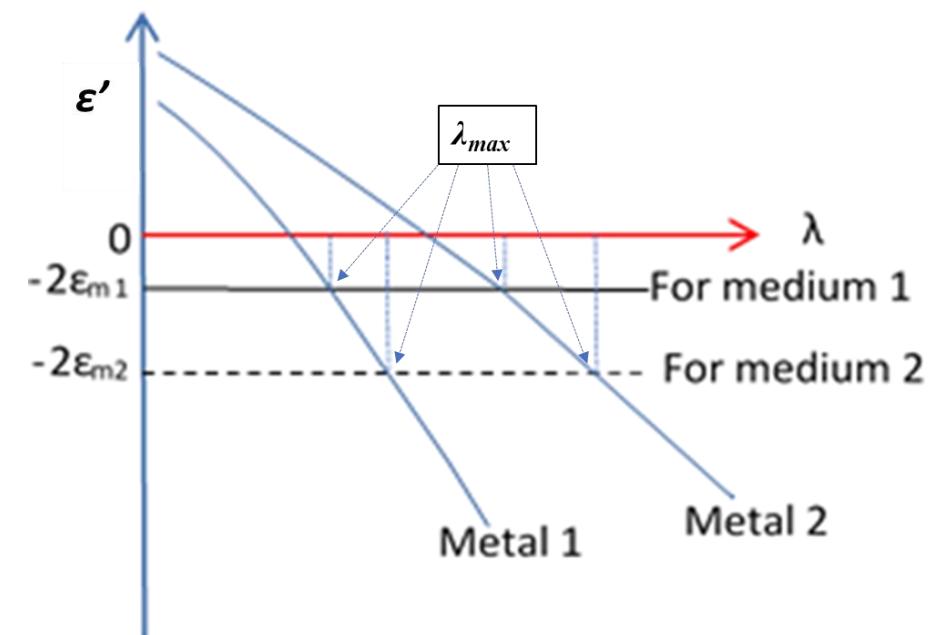


Figure 5.7 A schematic diagram showing the variations in the ϵ' (real part of the dielectric constants) of two different metals with wavelength (λ). Resonance conditions (λ_{\max}) are shown by vertical dotted lines for the corresponding metal nanospheres in **two arbitrary surrounding media** with dielectric constants ϵ_{m1} and ϵ_{m2} .

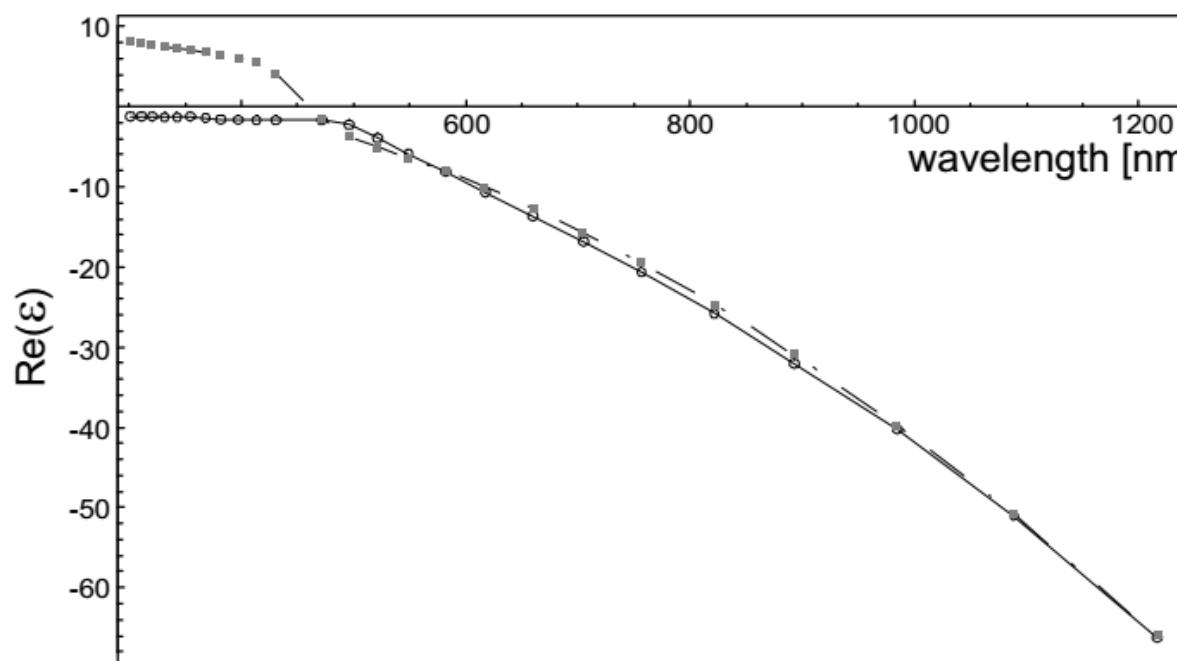
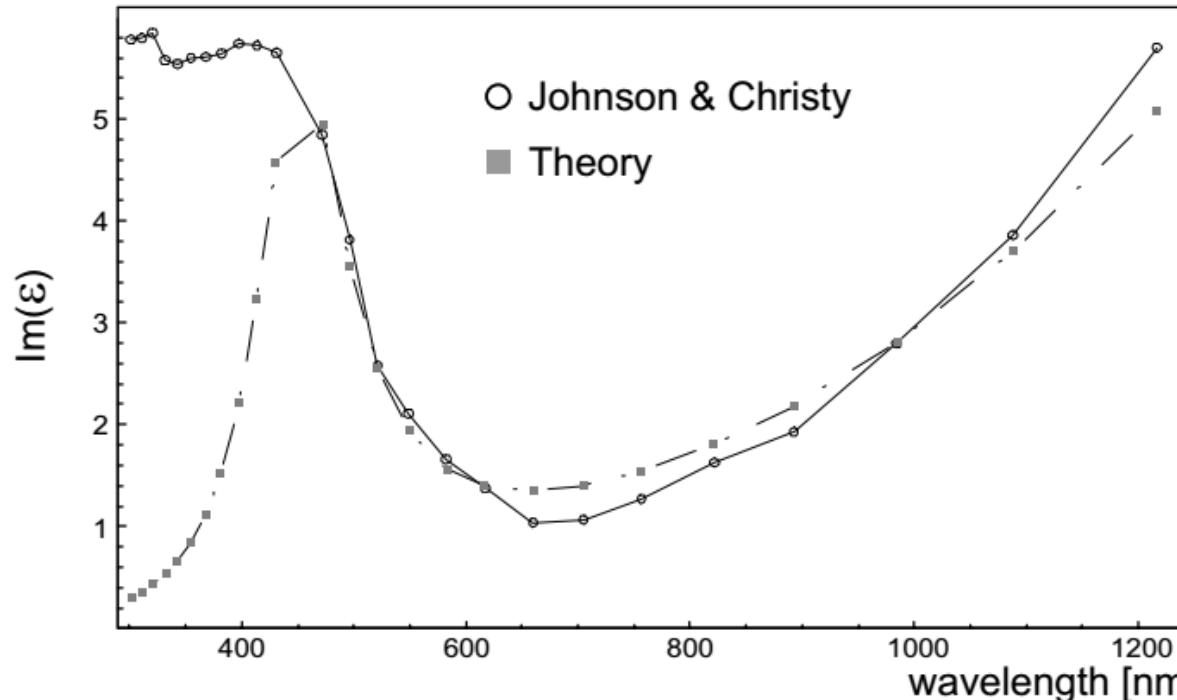


Figure 12.3: Dielectric function of gold: Experimental values and model.

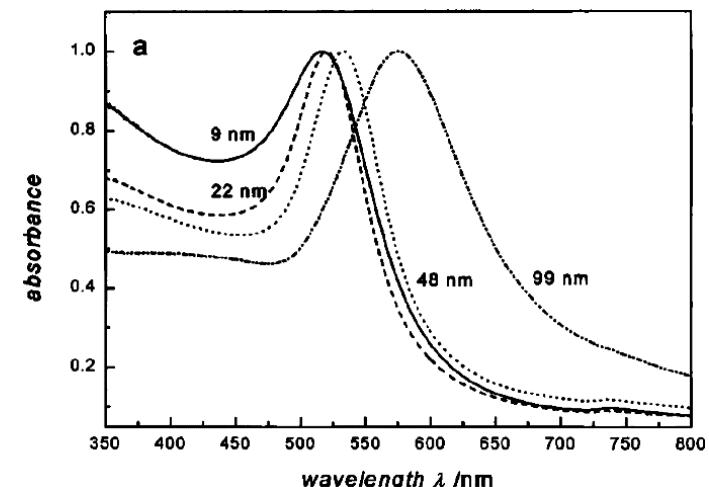
Upper panel: Imaginary part.

Lower panel: Real part.

Open circles: experimental values.

Squares: Model of the dielectric function taking into account the free electron contribution and the contribution of a single interband transition. Note the different scales for the abscissae.

- Figure 5.7 **illustrates the dependence of the wavelength of the LSPR peak on the dielectric constants** (hence on the **refractive index**) **of the surrounding media for two different metals**.
- **Note: the medium dielectric constant, $\epsilon_m = n_m^2$ where n_m is the medium refractive index.**
- σ_{ext} depends on ϵ_m , the **dielectric constant of the surrounding environment ($\epsilon_m = n_m^2$ where n_m is the medium refractive index)**.
- The *resonance condition* of a particle plasmon **depends sensitively on the dielectric constant of the environment**.
- Since the dielectric constant of a metal depends on the wavelength of light (ω), **the extinction coefficient is a function of the wavelength of light** and **has a peak**.
- For a few metal nanoparticles like gold, silver, etc., this resonance condition occurs in the visible wavelength in dielectric media like air, water, etc.



- A change of the refractive index of the surrounding medium therefore leads to a change in the position of the SPR peak. The *dependence of the wavelength of the LSPR peak on the refractive index of the surrounding environment* is given by the expression,

$$\lambda_{max}^2 = \lambda_p^2(\epsilon_{\infty} + 2\epsilon_{diel})$$

or $\lambda_{max}^2 = \lambda_p^2(\epsilon_{\infty} + 2n_{diel}^2)$ (11)

where $\lambda_p = 2\pi c/\omega_p$ (12)

where λ_{max} is plasmon wavelength, λ_p is the bulk plasmon wavelength, ω_p is the bulk plasmon angular frequency, c is the speed of light in free space.

- Equation 11 suggests **a redshift in the LSPR band peak with the increase in the n_{diel} , refractive index, of the environment (where $n^2_{diel} = \epsilon_{diel}$)**.
- Since, the refractive index of the surrounding media depends on the *nature of the solvents and the presence of various ligands or adsorbed (bio)macromolecules on their surfaces*, the LSPR peak positions are functions of these factors.
- The *peak wavelength shift* thus **can be used as a transducer of sensors**, such as *refractive index, chemical and biological molecules*.

❖ *Resonance Condition for Spherical Nanoparticles*

- *This dependence of the wavelength of the LSPR peak on the dielectric constants of the surrounding media can be used to sense the changes occurring in vicinity of the particles.*
- For 15 nm diameter gold nanoparticles **in water**, this happens at about 520 nm, resulting in the characteristic wine-red color of colloidal gold solutions. **Changing the solution environment** (e.g., by **adsorbing a molecule** onto the gold surface) **changes $\epsilon_{\text{dielectric}}$** and thus **alters the color slightly**.
- Upon attachment of specific antibodies, the resonance of the particle shifts notably which can be exploited for **sensitive detection of minute amounts of analyte**.

- Like the *aggregation of (noble) metal nanoparticles* (disregarding whether they are ligand-stabilized or not), which leads to more pronounced changes of their absorption spectra due to plasmonic interaction, **this shift** is also ideal for the **design of optical biosensors**.
-

Plasmonic Nanoparticles: The nanoparticles that show optical properties, known as **LSPR**.

Plasmon: Quantized coherent oscillations of free electrons

Surface Plasmon Resonance (SPR): Quantized coherent oscillations of free electrons at the surface (at the metal and dielectric interface). SPR is also known as **Localized Surface Plasmon Resonance (LSPR)**.

.....

- There are **three important consequences** of the LSPR effect:
- Near the plasmon resonance frequency, ***metal nanocrystals absorb and scatter light very strongly***. This makes them *brightly visible, and the strong light absorption can be exploited for light-induced local heating*. These properties are being applied in medical diagnostics and therapy, e.g., for detection and photothermal destruction of cancer cells. By adjusting the size and shape of the gold nanoparticles, which are more stable than Ag and Cu in biological media, the plasmon frequency can be tuned to the tissue-transparent near-IR region of the spectrum between 700 and 900 nm. Small quantities of plasmonic Ag and Au particles also make brightly colored and strongly scattering pigments.
- The **plasmon frequency is sensitive to the refractive index of the particle's surroundings**, i.e., its chemical environment. This makes metal nanoparticles of special interest for ***sensing and biosensing applications***.
- The ***local electric field of the incoming light wave is greatly enhanced at the particle surface***. This ***gives rise to huge enhancement factors in optical processes such as Raman scattering and fluorescence***. Thus, certain analytical spectroscopic techniques are greatly enhanced by LSPR.

- This LSPR leads to **the buildup of polarization charges on the nanoparticle surface**. A *homogeneous field builds up in the interior of the nanoparticle, while a dipolar field is produced at the exterior,resulting in strong **light absorption/scattering**, the appearance of intense **SPR bands**, and **the enhancement of the near field in the immediate vicinity of the nanoparticles**.*
- The **peak wavelength**, **peak height**, and **bandwidth** depend on the nanoparticle's
 - ✓ **chemical composition**,
 - ✓ **size**,
 - ✓ **geometrical shape**,
 - ✓ **surface charge**,
 - ✓ **surface-adsorbed species**,
 - ✓ **the dielectric property of the surrounding environment**,
 - ✓ **and interparticle interactions**.

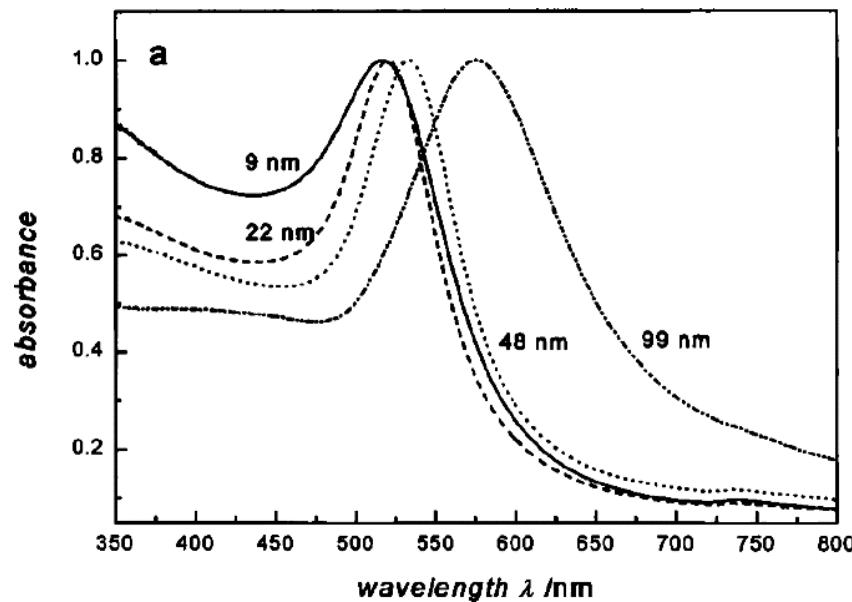


Fig. 5.4. Experimental extinction spectra of gold nanoparticles of diameters 9, 22, 48 and 99 nm.

- The *position of the plasmon absorption band and its intensity* are sensitive to the *size and shape of nanoparticles* (spheres, rods, ellipsoids, disks, triangular plates, cubes) as well as to the *dielectric characteristics of the surrounding material*, that is, **metallic nanoparticles can be considered as “tunable” inorganic chromophores.**
- Cu, Ag, and Au NPs, with their *s*-valence electron nearly free, are highly polarizable showing a strong absorption of the incident light and sharp plasmon resonances in the *visible region*, (LSPR(Au) ~520 nm, LSPR(Ag) ~400 nm, and LSPR(Cu) ~560-570 nm).
- This LSPR absorption is responsible for the appearance of colors in the sols of these metals as only the part of the visible light complementary to the absorption wavelength reaches the eye.



Figure 2. Tunability of plasmon resonance in colloidal solutions. A series of ***colloidal silver nanoparticle solutions*** show a variety of colors due to the different sizes and shapes of the nanoparticles within each solution. Photograph courtesy of Keiko Munechika, Ginger Lab.



Figure 1.12 Monodispersed ***gold nanoparticles of different sizes*** (2–200 nm) in water.

Note the different colors due to different light interactions, which are dominated by particle size. (Courtesy of Ted Pella, Inc., available on the

World Wide Web at http://www.tedpella.com/gold_html/goldsols.htm.)

- Nanoparticles of **other metals** such as platinum, palladium, and iron do not show such resonance. This is because in these metals the resonance is suppressed due to mechanisms such as ***strong conduction electron relaxation*** or ***radiation damping due to scattering***.
- In fact, **many metal sols appear yellow or brown in color**. The reason for this is that the ***plasma frequencies of most metals lie in the UV, and the color of the nanoparticle colloid is due to the tail of the surface plasmon band***: being broad, it tends to produce a yellow color. Upon aggregation or growth, the band tends to broaden and deepen, so that the color changes slowly to a deeper brown.
- *(Do you know why the yellowish tinge observed in white dresses made of cellulose? We use products like Ujala or Robin Blue to make it look white!)*

❖ Particle Size Effects on LSPR:

- It is important to note that the *cross-section for scattering is proportional to the square of the volume of the particle, V^2 (where, r is radius)*, whereas the **absorption is proportional to V** (r^3). It turns out that σ_{abs} scales with r^3 whereas σ_{scat} scales with r^6 . Consequently, for **large particles extinction is dominated by scattering** whereas for **small particles it is associated with absorption**. This means that very **small gold particles (< 5 nm) are strongly absorbing** but **not** strongly scattering. It was found **that for NPs with $d \sim 20$ nm the absorption process dominates**, that is, $C_{scat} \sim 0$, such that $\sigma_{ext} \approx \sigma_{abs}$. Larger particles (> 30 nm) **scatter light very strongly**. **Depending on the application, therefore, we choose larger or smaller particles**.
- This effect can be used to detect extremely small metal particles down to 2.5 nm diameter which are used as labels in biological samples. The *transition between the two size regimes is characterized by a distinct color change*. For example, small gold particles absorb green and blue light and thus render a red color. On the other hand, larger gold particles scatter predominantly in the green and hence render a greenish color.

□ **Size Effect on LSPR** (contd.)

- As mentioned earlier, nanoparticles (NPs) can **absorb** and **scatter** energy, and depending on their size and shape, *one mechanism can dominate over the other*.
- To understand the range of the **different processes as a function of size**, the **absorption and scattering phenomena were studied** for spherical NPs using the Mie exact solution (Figs. 5.2 & 6.20).
- The spectra (Fig. 5.2b for Ag nanoparticles) show that at about 320 nm all the efficiencies have a local minimum that corresponds to the wavelength at which the **Ag dielectric function**, both real and **imaginary parts, almost vanishes**. Therefore, this feature of the spectra is inherent to the material properties and *independent of the particle geometry*.
- ✓ **Below 320 nm, the absorption of light is mainly due to the inter-band electronic transitions**; therefore, *this feature of the spectra is also independent of the shape*.

□ **Size Effect on LSPR** (contd.)

- ✓ It was found that for NPs with $d \sim 20$ nm the absorption process dominates, that is, $\sigma_{sca} \sim 0$, such that $\sigma_{ext} \approx \sigma_{abs}$.
- ✓ For such small NPs, the absorption efficiencies show *a single peak always located at the same wavelength ($\lambda \approx 355$ nm)*, *but the intensity increases linearly with the sphere size*.
- ✓ However, *as d increases, light scattering becomes important rapidly and dominates* the response of NPs with $d \sim 100$ nm.
- Note that the importance of light absorption over scattering depends not only on the NP's size, but also on its shape, composition, and environment.
- *The LSPR absorption peaks for small particles (5 nm < diameter < 20 nm) of gold and silver are localized near 530 nm and 415 nm respectively.*

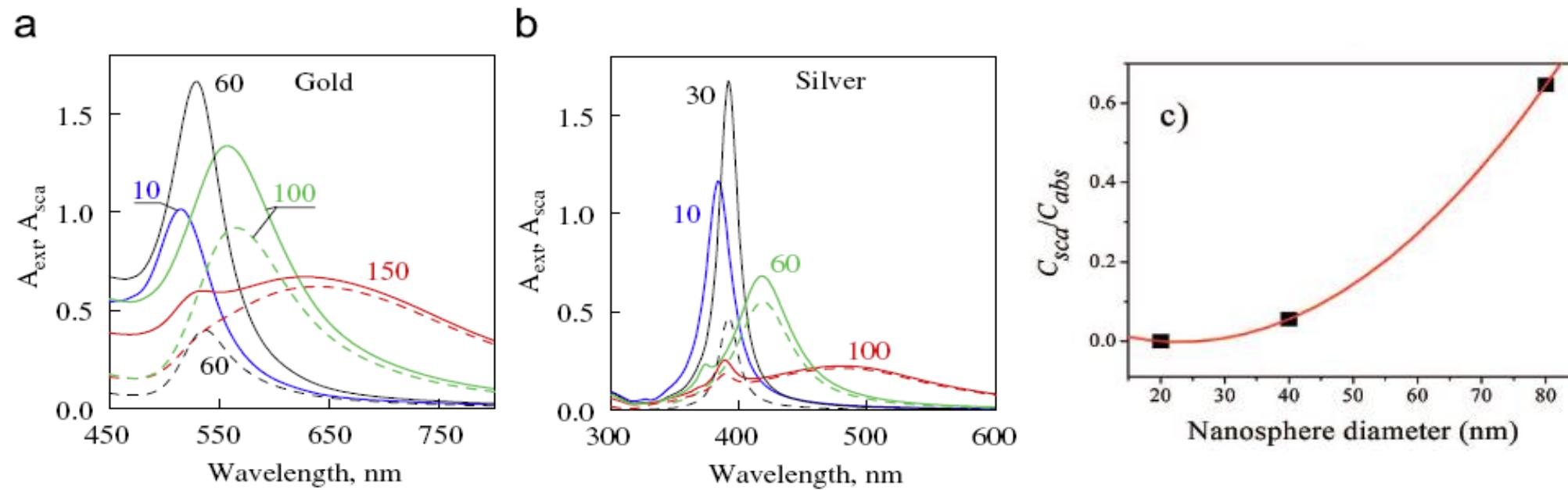


Fig. 5.2. Extinction (solid lines) and scattering (dashed lines) spectra of gold (a) and silver (b) spheres in water. Numbers near curves correspond to the particle diameter. (c) ***Increase in the plasmon scattering to absorption ratio by increase in particle volume in gold nanospheres. Note that for small particles the extinction is mainly due to the absorption***; scattering (dashed lines) appear for larger particles.

(N.G. Khlebtsov, L.A. Dykman, Journal of Quantitative Spectroscopy & Radiative Transfer (2010) 111, 1–35.)

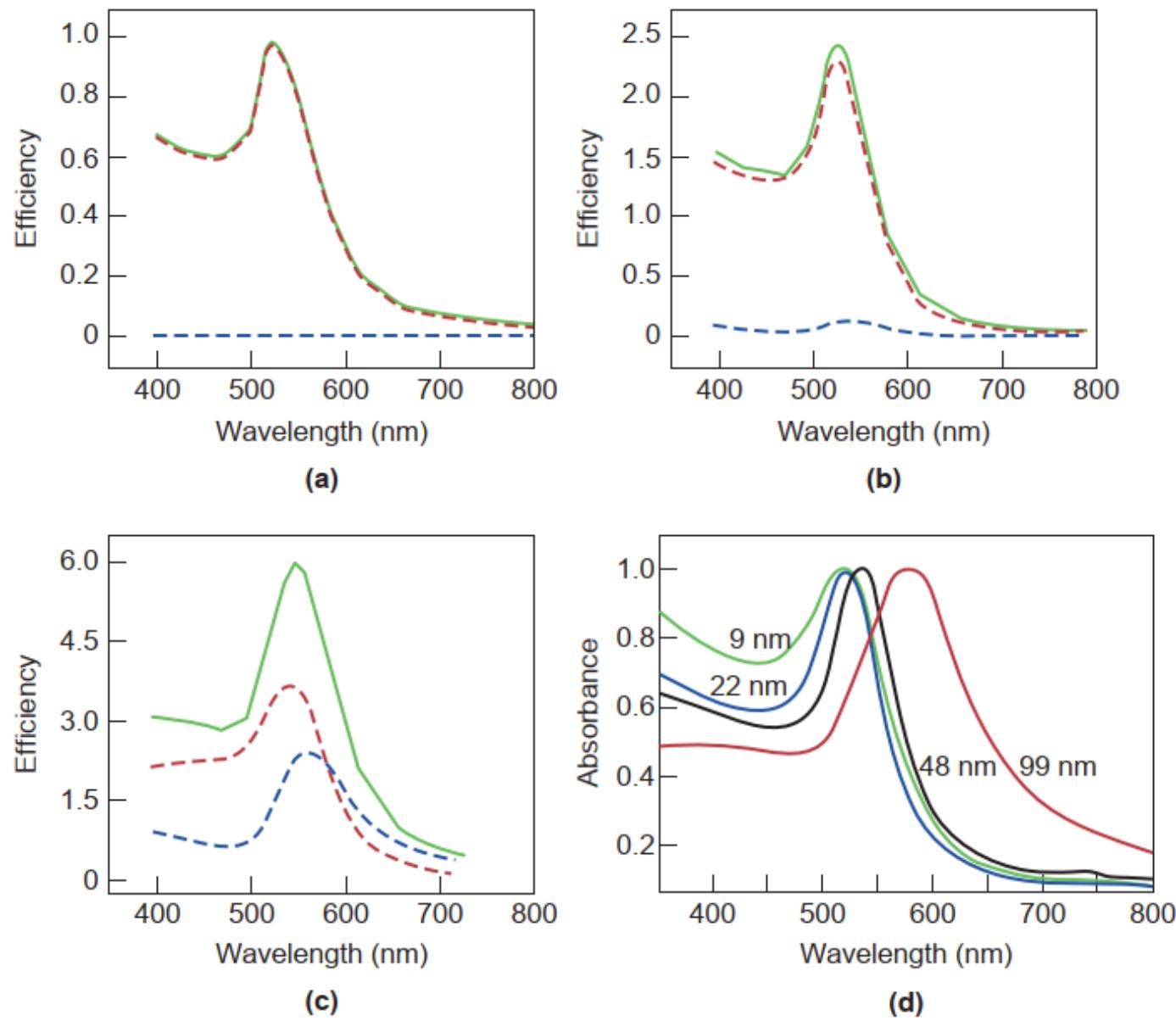


Fig. 6.20 Extinction vs. size for Au nanoparticles. Calculations of the absorption (red dashed curves), scattering (blue dashed curves) and extinction efficiency, Q_{ext} , (green solid curves) as a function of the wavelength of the incident light for Au nanospheres of diameter (a) 20 nm, (b) 40 nm, and (c) 80 nm. (d) Measured extinction spectra of Au nanoparticle suspensions of different diameters varying from 9-99 nm.

*Note that up to a **diameter** of ~ 50 nm the position of the peak is independent of particle size.*

□ **Size Effect on LSPR (contd.)**

- *Above 30 nm, the quadrupole and the multipole terms* in the Mie summation become significant while....
- ✓ *below 5 nm, the collision of the electrons with the surface of the particle becomes more important as the particle size becomes smaller than the electron mean free path.* The electrons are scattered at the metal surface in an elastic and completely random way, inducing a fast loss of the plasmonic oscillation coherence. *The smaller the metal sphere, the faster the coherence loss and the bigger the band broadening* (Fig. 5.6.).

□ **Size Effect on LSPR (contd.)**

- *The spectroscopic responses of larger metallic nanoparticles are different due to the excitation of higher-order modes such as quadrupoles and retardation and skin-depth effects.* For larger particles, the oscillations of electrons become *less coherent*, and higher modes of plasma oscillation (e.g., quadrupolar and multipolar) appear.
- ✓ When the particle size is much larger than the mean free path of the electrons ($L \sim 10-20$ nm for gold), electrons can be significantly *accelerated* within the metal between collisions leading to scattering losses. Due to these factors, *the surface plasmon peak broadens and additional peaks appear as the particle size is increased.*

Gold nanoparticle's **size effect**

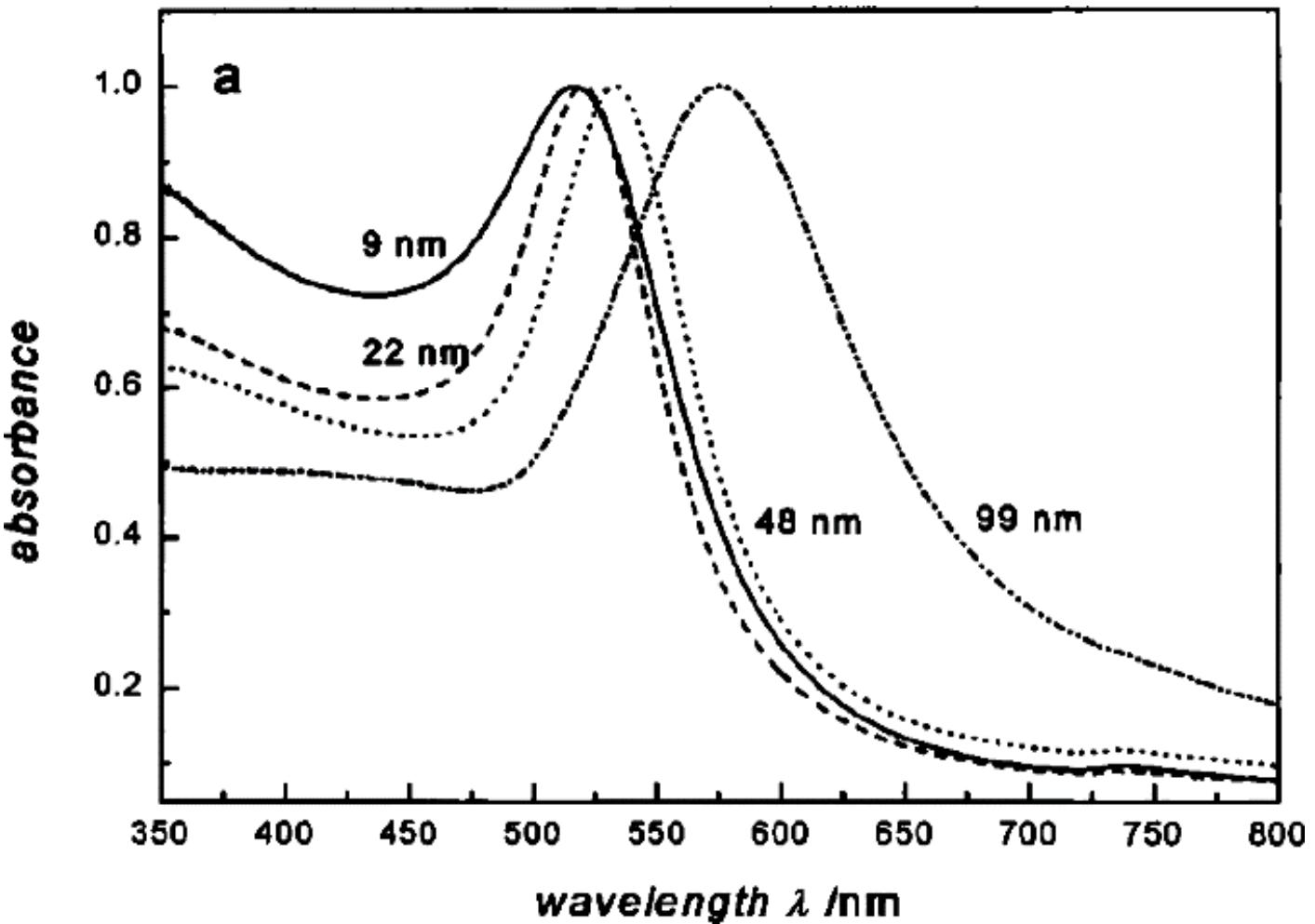


Fig. 5.4. Experimental extinction spectra of gold nanoparticles of diameters 9, 22, 48 and 99 nm. *The shift in the peak occurs due to the contributions from quadrupolar higher resonances as well as due to the contribution of the scattering* (reprinted with permission from American Chemical Society).

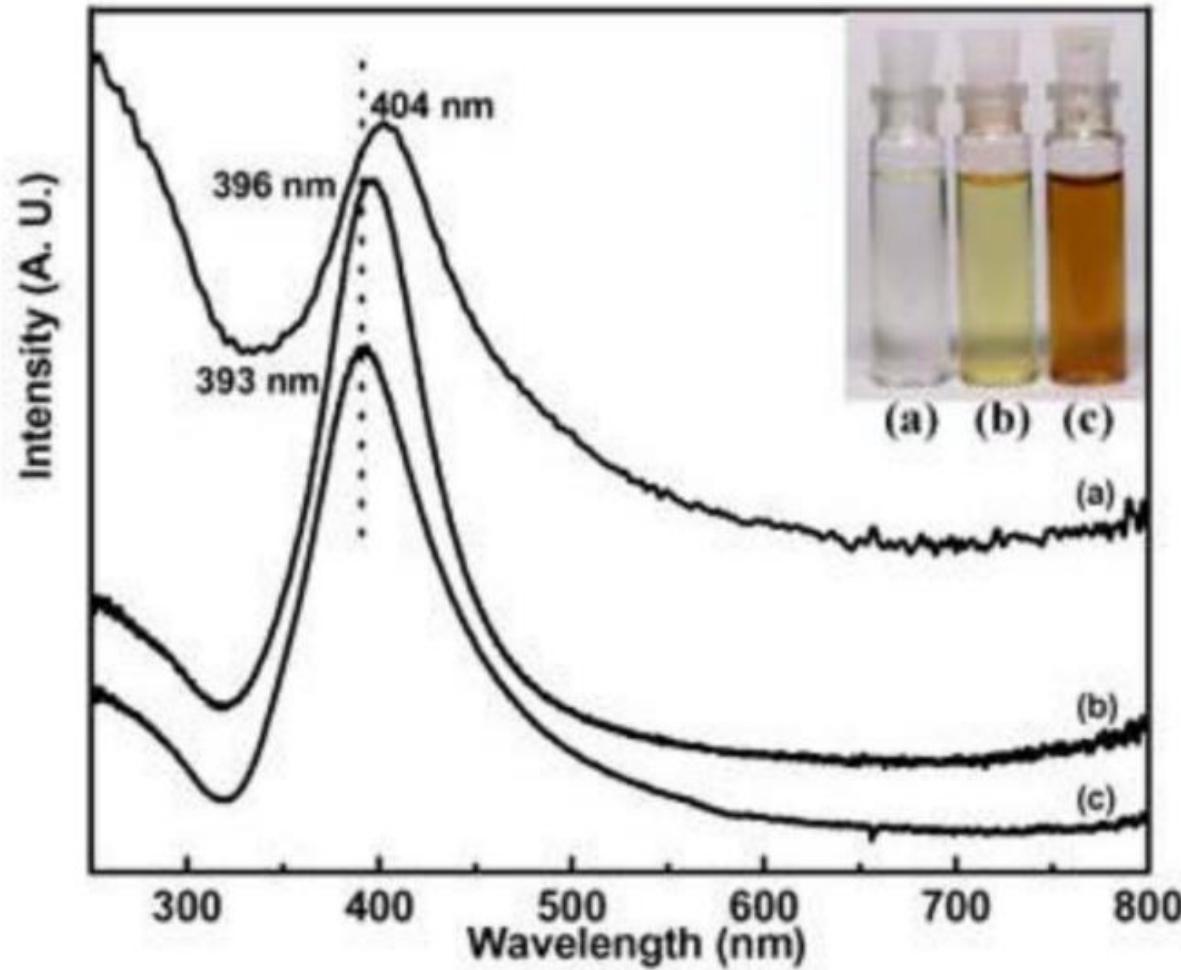


Figure 7. UV-Vis absorption spectra of nanosized silver particles. (Inset) Different colors arising from different sizes. *The shift in the peak occurs due to the contributions from quadrupolar higher resonances as well as due to the contribution of the scattering.*

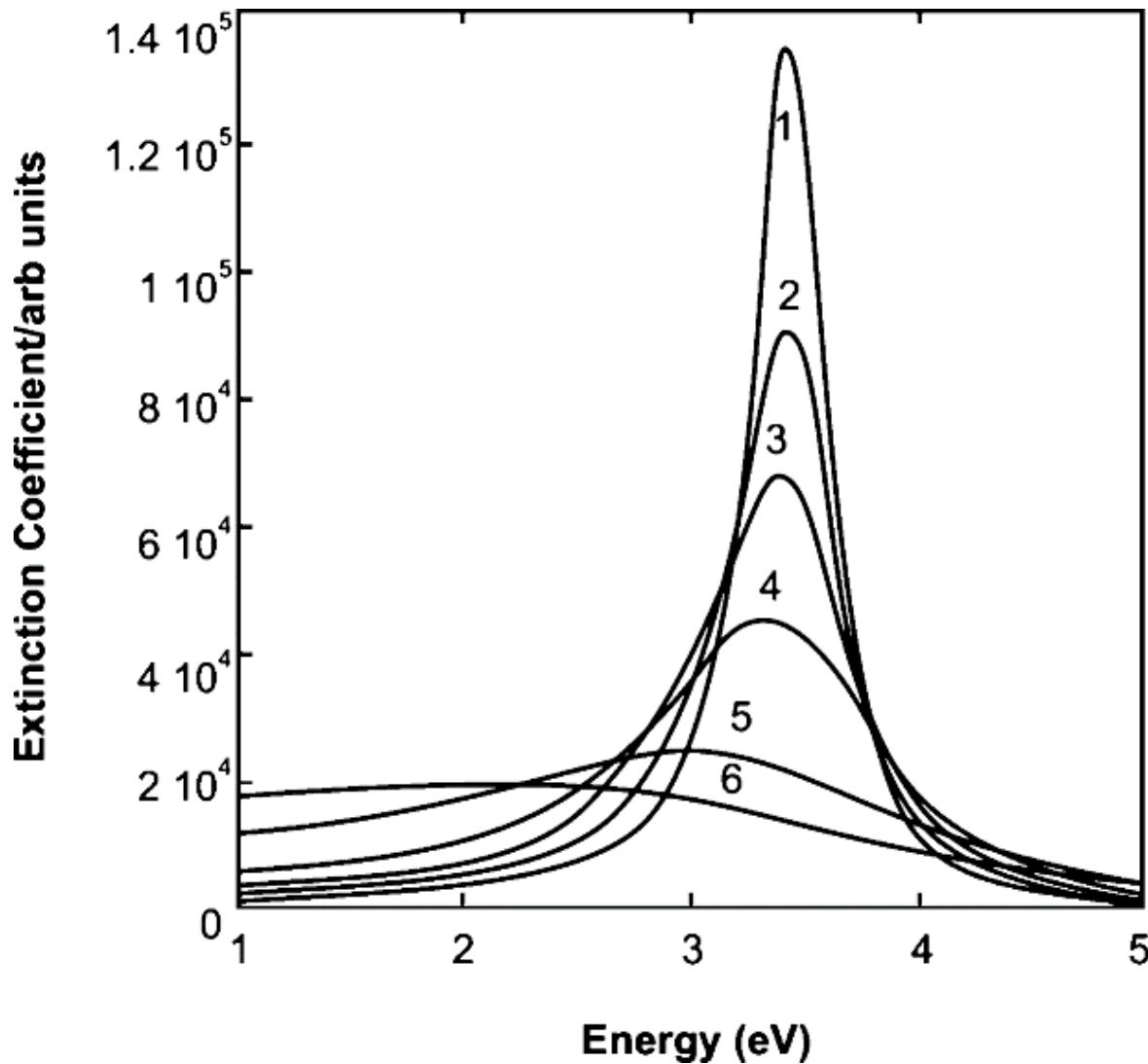
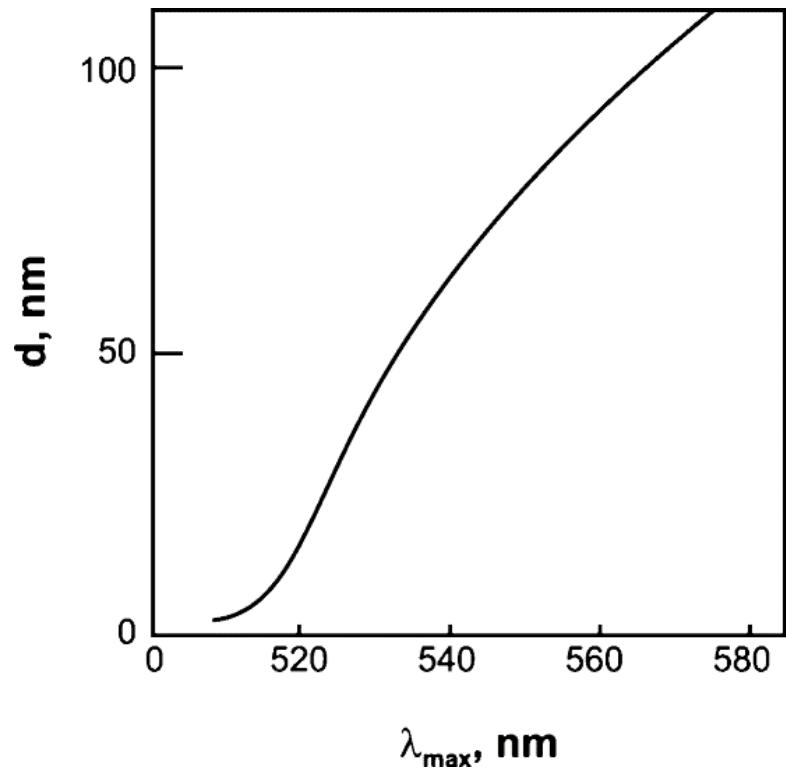


Fig. 5.6. Effect of decreasing the particle size below the mean free path of the electrons in the bulk metal (i.e. usually below 5 nm); the particle size is decreasing from 1 to 6.

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- When the particle *size decreases*, the *increased rate of electron surface collision changes the dielectric constant of the metal such that the SPR band is largely damped and broadened*. This phenomenon is called *intrinsic size effect*. *This usually happens for particle sizes below about 5 nm.*
- The effect is shown schematically in Fig. 5.6 which shows plots of the extinction coefficient vs. energy (inversely related to wavelength) of the incident light for particle sizes smaller than the mean free path.
- Note that *very small nanoparticles (<~2 nm) do not display this LSPR phenomenon, as their electrons exist in discrete energy levels*, and bulk metal has a continuous absorbance in the ultraviolet (UV)/visible/infrared (IR) regions without any resonance.
- *By reducing the size of the particles further below the mean free path*, critical scale is attained *when dimensions become comparable to the Fermi wavelength of metals*, $\lambda_F \sim 1-2$ nm. *Electrons in these subnanometric-sized particles do not have a continuous DOS, which is necessary to support the plasmon and therefore SPR disappears.*

- The shift in the position of the peak in the extinction coefficient with particle size for the case of gold as determined experimentally by the various researchers has been combined into a single plot by Khlebtsov and Dykman (Fig. 5.5). The plot can be used as a calibration curve to determine the particle size from the absorption spectra.



For insulators and semiconductors, the Mie peak is close to the position of the bulk absorption bands, and the immediate effect of decreasing particle size is much smaller.

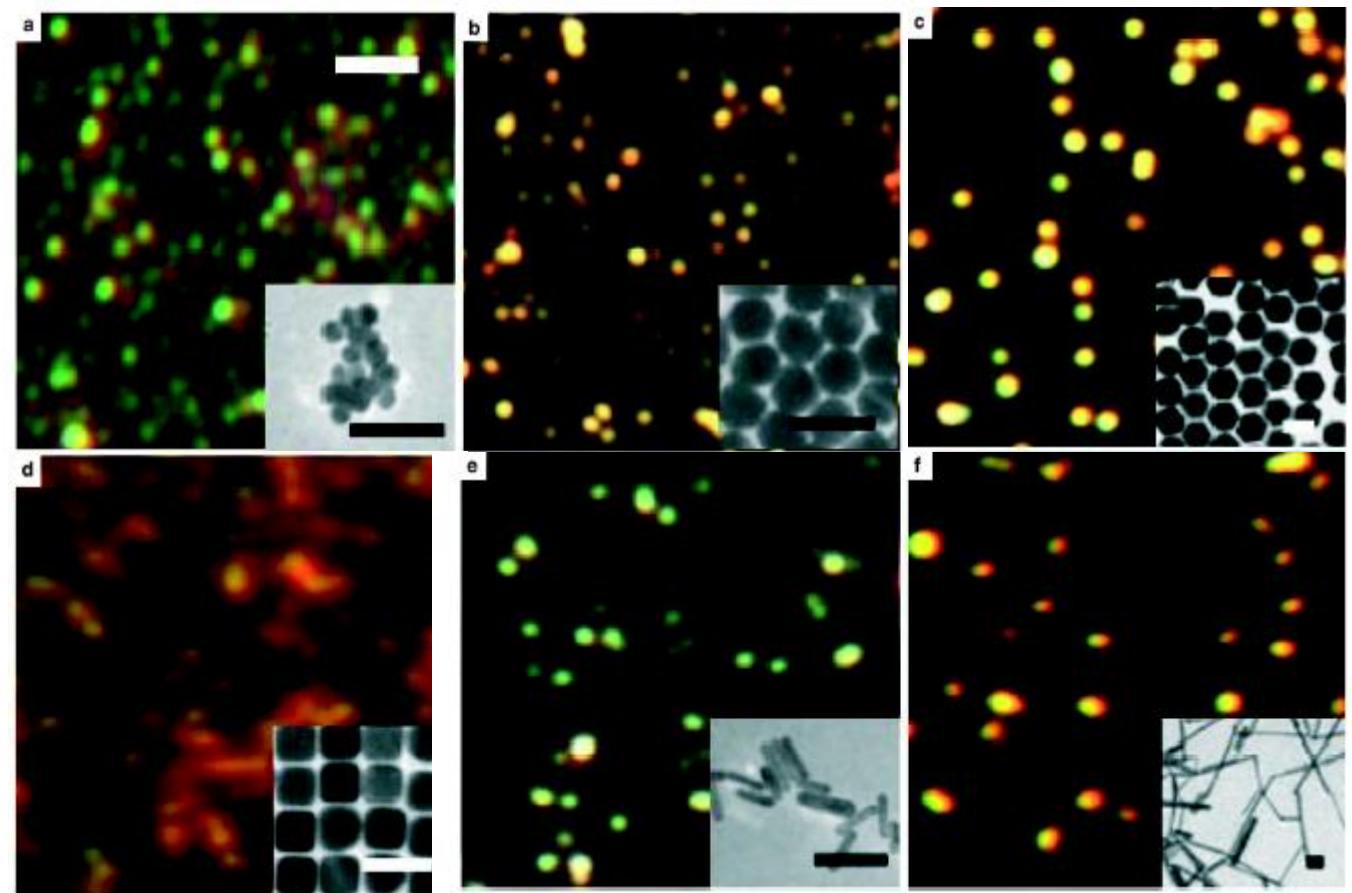
Fig.5.5. Shift in the experimentally determined extinction peak position with particle diameter for gold spheres in water.

Metals on the Nanoscale: Shape-Dependent Optical Properties

Insets: TEM of the nanoparticles

- (a) 23-nm-diameter spheres : Green.
- (b) 70-nm-diameter spheres: Yellow.
- (c) Hexagonal : Yellow.
- (d) Cubic : Orange-red.
- (e) Rods (aspect ratio= 4.4) : Pale green.
- (f) Rods (aspect ratio= 16): Dark yellow.

Dark-Field Light-scattering Images from Gold Nanoparticles of Different Shapes



Scale bars : 2 μ m in light scattering images and 100 nm in TEM images.

☐ **Particle Shape Dependence of LSPR**

- As noted above, *the surface plasmon peak shows a shift with a change in the particle size. A much more drastic effect on the surface plasmon absorption can be observed when NP shape changes.*
- Indeed, *electrons can oscillate to a different amplitude along the three axes of the anisotropic metal NPs*. Such *different oscillations result in a splitting of the plasmon band into two or more bands*.
- ✓ For instance, the plasmon absorption of Au nanorods (NRs) splits into two bands corresponding to the oscillation of free electrons along and perpendicular to the long axis of the rods: longitudinal and transverse modes, respectively. The ***transverse mode*** shows a resonance at about 520 nm, which is coincident with the plasmon band of spherical particles, while the resonance of the ***longitudinal mode*** is red-shifted and **strongly depends on the NR aspect ratio R** (*defined as the length of the rod divided by its width, i.e., a/b in Fig. 7.3*).

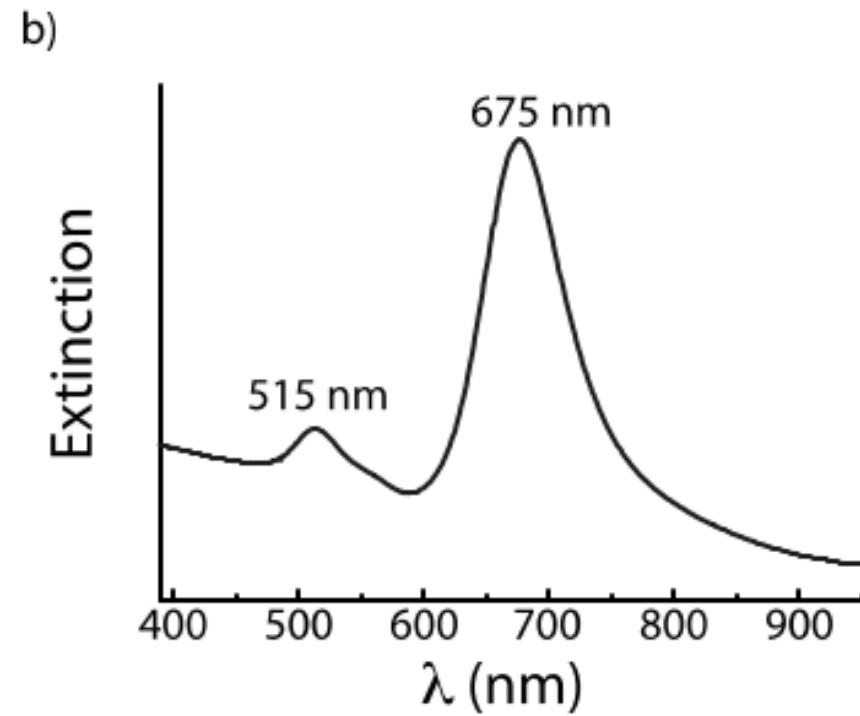
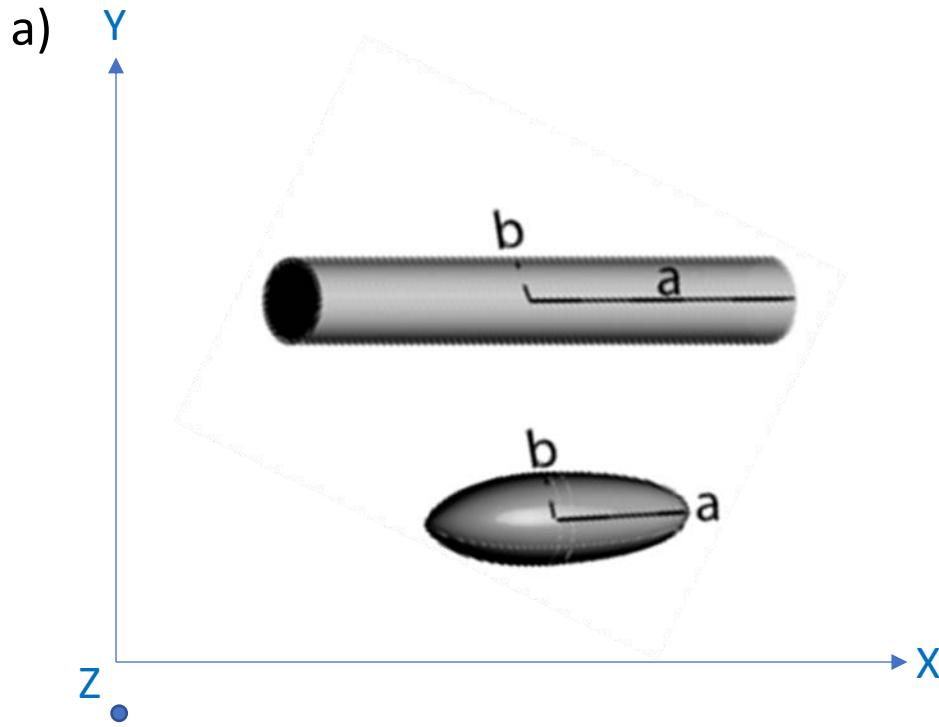


Figure 7.3 (a) Spheroidal metal NP and nanorod with respective axis: *a is the principal axis and b is the axis perpendicular to the principal one*. (b) Extinction spectrum of Au nanorods with **aspect ratio (a/b)** of about 2.5. The lower energy longitudinal mode is due to the electron cloud oscillation along the spheroid principal axis (along *a*-axis, x-direction), while the high energy transverse one is referred to the electron oscillations perpendicular to the principal axis (along *b*-axis, y-direction).

- The energy separation between the two bands increases with the increase in R . The Gans model describes well the LSPR behavior of these systems.
- The simplest form of a nonspherical shape **is a spheroid**. For spheroids, a classical quasistatic approach serves well to describe the spectral position, width, and strength of the dipolar plasmon resonance.
- Based on classical approaches, *for a metal nanoparticle sufficiently small compared to the wavelength of light λ* , there **is a resonance condition associated with each axis j of a spheroid**:

$$\➤ \varepsilon = \varepsilon_m \left(1 - \frac{1}{L_j} \right)$$

where **ε is the complex wavelength-dependent dielectric function of the metal**, **L_j is the geometrical depolarization factor along the axis j** , and ε_m is the dielectric function of the surrounding medium.

- $L_1 = L_2 = L_3 = \dots \dots \dots$ for **spherical** particles...?

- $L_1 = L_2 = L_3 = 1/3$ for *spherical* particles.
- For *prolate spheroidal* particles ($L_1 = L_2 < L_3$), the dipole resonance *splits into two* absorption bands —*longitudinal* and *transverse modes* —where the induced dipole oscillates *along and perpendicular* to the *long axis* of the spheroid, respectively.
- The *longitudinal resonance band shifts towards longer wavelengths (red-shift)* and *increases in absorption cross-section* as *the aspect ratio of the spheroid increases*, whereas *the transverse resonance band remains near the wavelengths of the spherical particle absorption band*.
- This example of the simplest nonspherical shape demonstrates that *nonspherical nanoparticles will exhibit multiple optical extinction bands due to their anisotropy*.

Normalized Absorbance

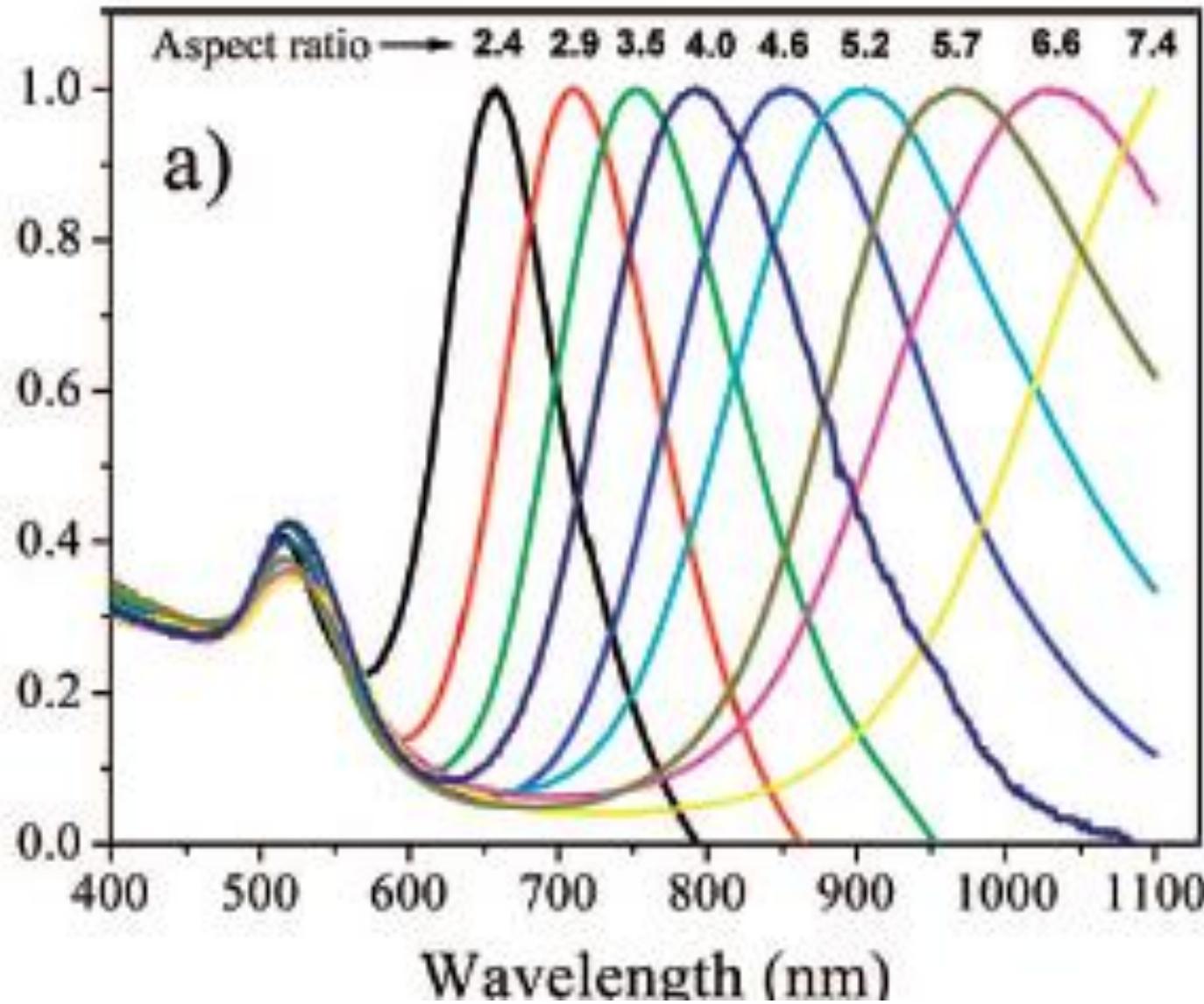
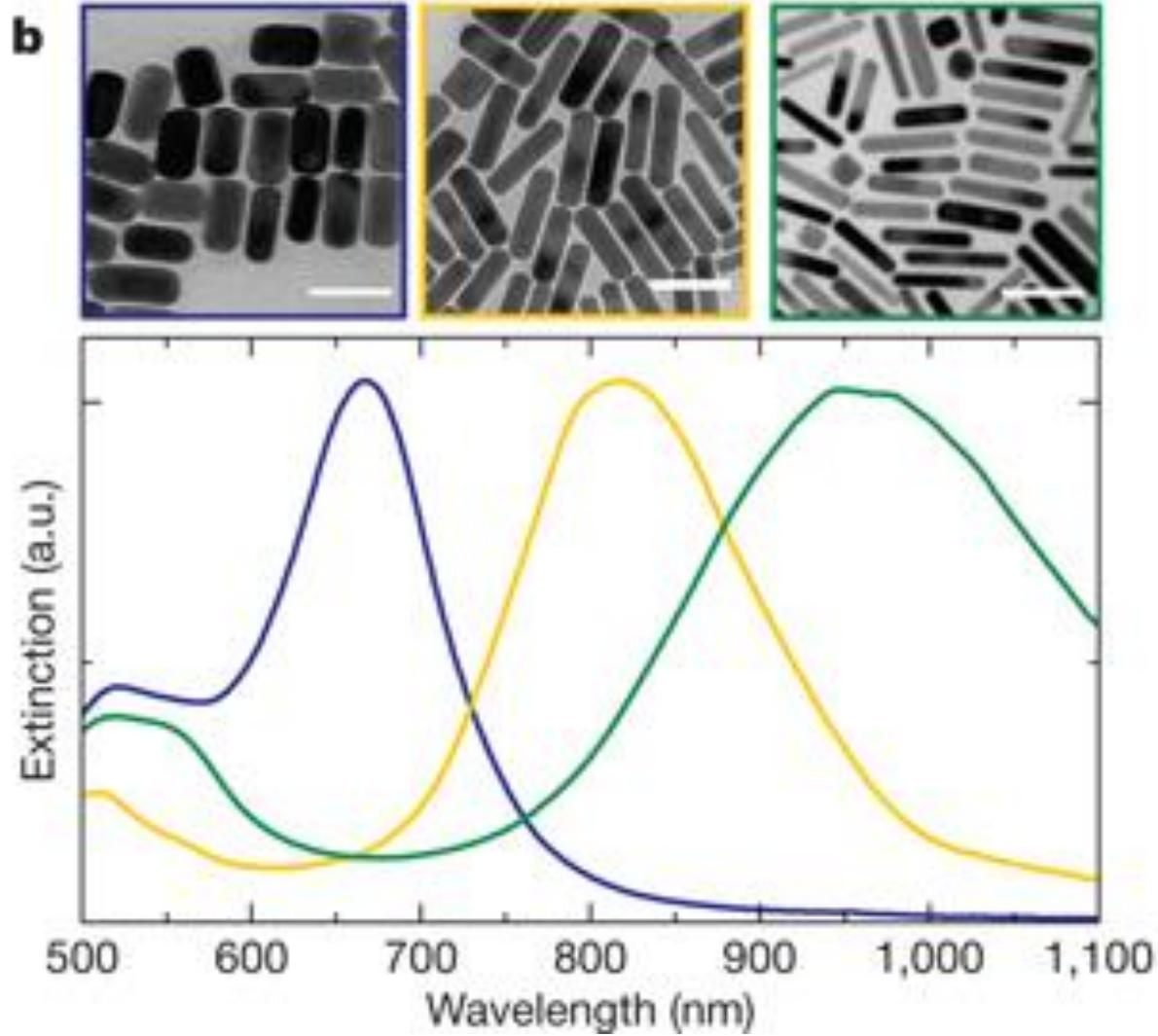


Fig. 5.7. Extinction coefficient of gold nanorods with different aspect ratios (Length/Width); the transverse band at about 520 nm remains nearly unchanged while there is a large shift towards longer wavelengths in the longitudinal mode as the aspect ratio increases. (Reprinted with permission from Elsevier. Copyright (2010)).



Exptl.: Gold nanorods of different aspect ratios and corresponding extinction spectra.

(P Zijlstra *et al. Nature* **459**, 410-413 (2009))

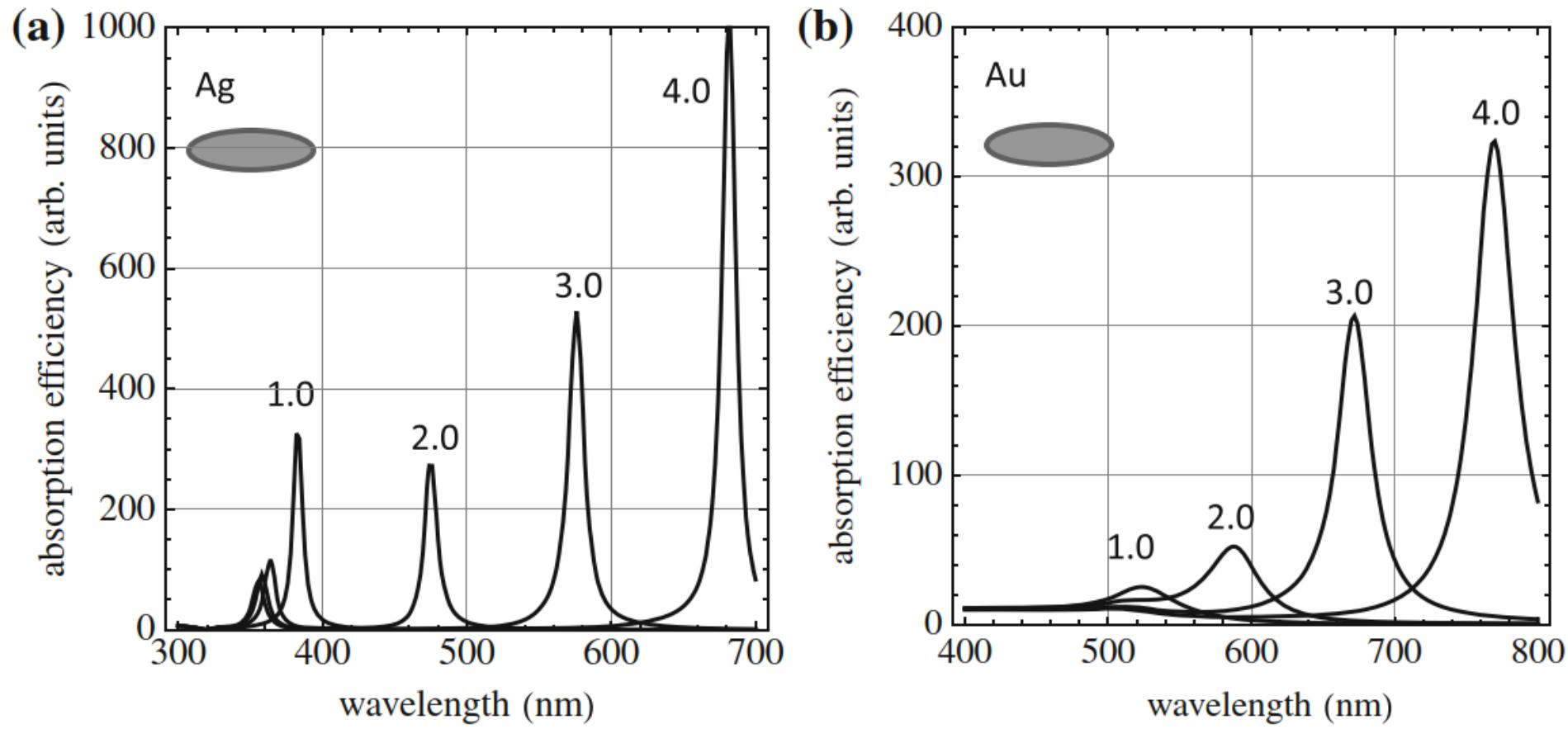


Fig. 3.8 Absorption efficiency of (a) silver and (b) gold nanorods in air at various *aspect ratios*.

LSPR of more complex structures

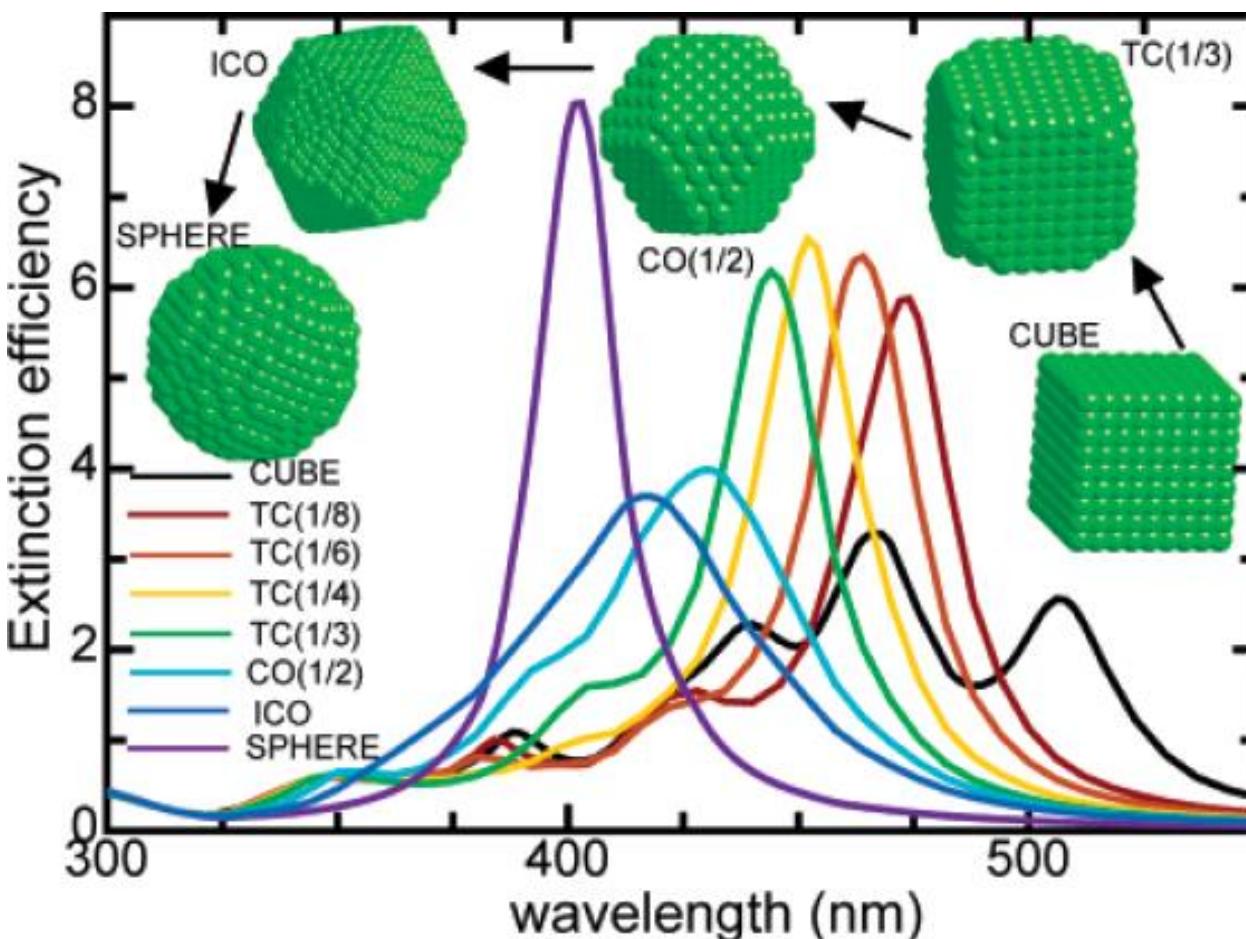


Figure 5. Extinction efficiencies as a function of the wavelength of the incident light of a silver cube, different truncated cubes, and a spherical nanoparticle.

TC=truncated cube; CO=cuboctahedron; ICO=icosahedron.

Because of their high symmetry, simple structures such as isolated small spheres exhibit a single plasmon resonance. More complex structures often yield multi-featured resonance spectra. For example, nanocube, due to several distinct symmetries for dipole resonance, shows more peaks. In addition, the position of the most intense peak for the nanocube is **red-shifted** compared with that of the sphere. Such a shift is caused by the accumulation of surface charges at the corners of the nanocube and is observed, in general, for any NP with sharp corners. In these systems, the increased charge separation reduces the restoring force for electron oscillation, which in turn results in a shift of the resonance peak to lower energy.

Core-Shell Nanoparticles and LSPR

Metal nanoshells are nanostructures that consist of a dielectric or hollow core surrounded by a thin (10–20 nm) shell of metal, in most cases gold. The Halas group developed this tunable nanostructure and showed that the LSPR of the metal shell nanostructure depends strongly on the relative dimensions of the metal shell and the dielectric core.

Figure 1 shows a schematic diagram of a variety of core-shell particles. Surface of the core particle can be modified using bifunctional molecules and then small particles can be anchored on it (Figure 1 *a*). Nanoparticles grow around the core particle and form a complete shell (Figure 1 *b*). In some cases, a smooth layer of shell material can be deposited directly on the core by co-precipitation method (Figure 1 *c*). Small core particles such as gold or silver (10–50 nm) can be uniformly encapsulated with silica (Figure 1 *d*). Also a number of colloidal particles can be encapsulated inside a single particle (Figure 1 *e*). Core particles can be removed either by calcination or by dissolving them in a proper solvent. This gives rise to ***hollow particles also known as quantum bubbles*** (Figure 1*f*). Concentric shells also can be grown on core particles to form a novel structure known as ***multishell or nanomatrushka*** (named after the Russian doll; Figure 1 *g*).

Figure 1. Variety of core-shell particles.

a, Surface-modified core particles anchored with shell particles.

b, More shell particles reduced onto core to form a complete shell.

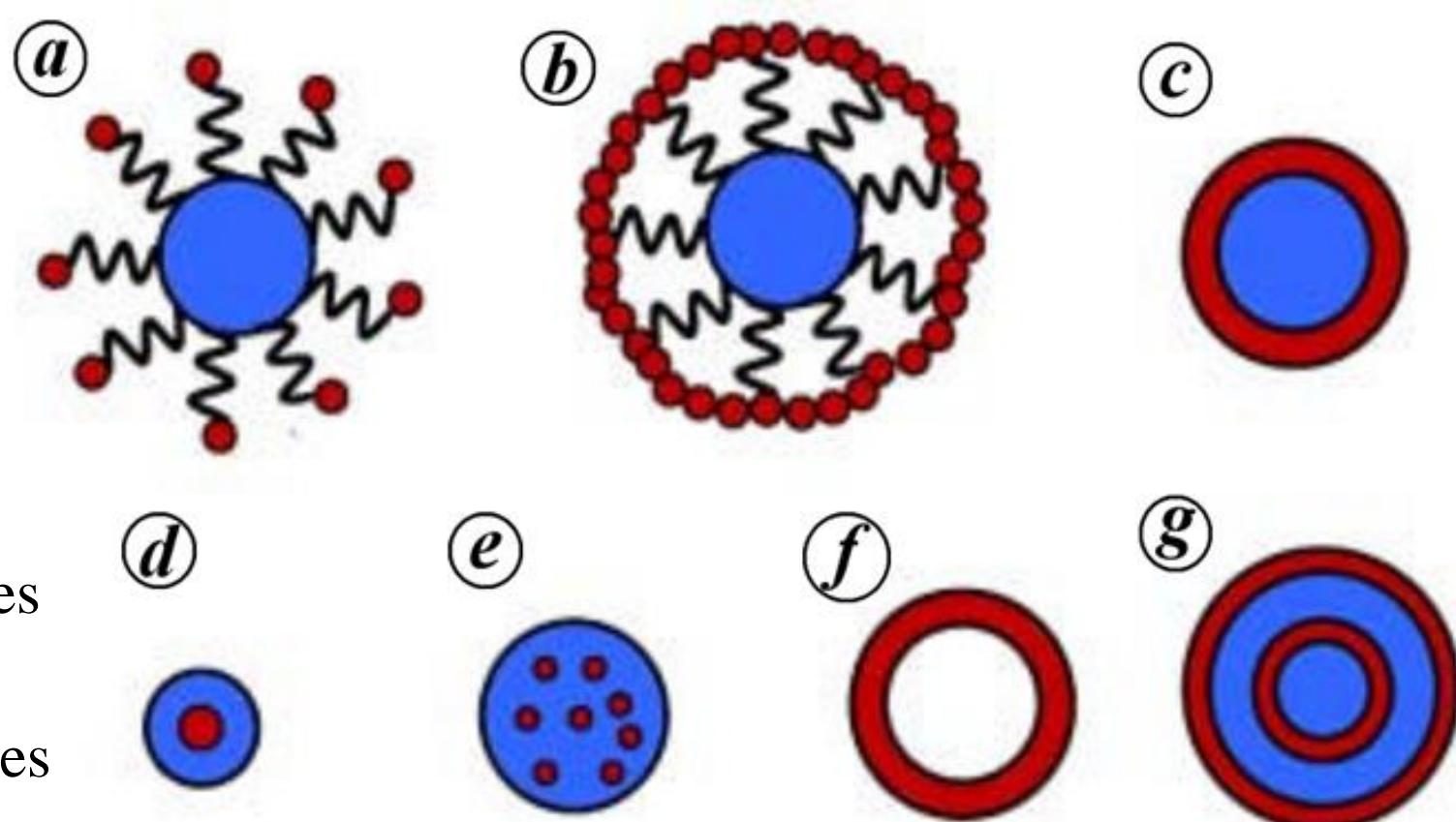
c, Smooth coating of dielectric core with shell.

d, Encapsulation of very small particles with dielectric material.

e, Embedding number of small particles inside a single dielectric particle.

f, Quantum bubble.

g, Multishell particle, *nanomtryushka*



Gold Nanoshells & LSPR

....Simple core-shell plasmonic nanoparticles consist of a dielectric core (e.g., silica, polystyrene, or sodium sulfide) which is covered by a thin layer of metallic shell, typically either gold or silver.

Nanoshells possess highly favorable optical and chemical properties for biomedical imaging and therapeutic applications.

Gold nanoshells (GNSs) based on a silica core were originally developed by Halas and coworkers (Rice University). Typically, the scaffolds (silica cores) are prepared by the Stöber method, and later on, small GNPs are grown onto the silica to form a relative uniform thin shell (see the Fig.).

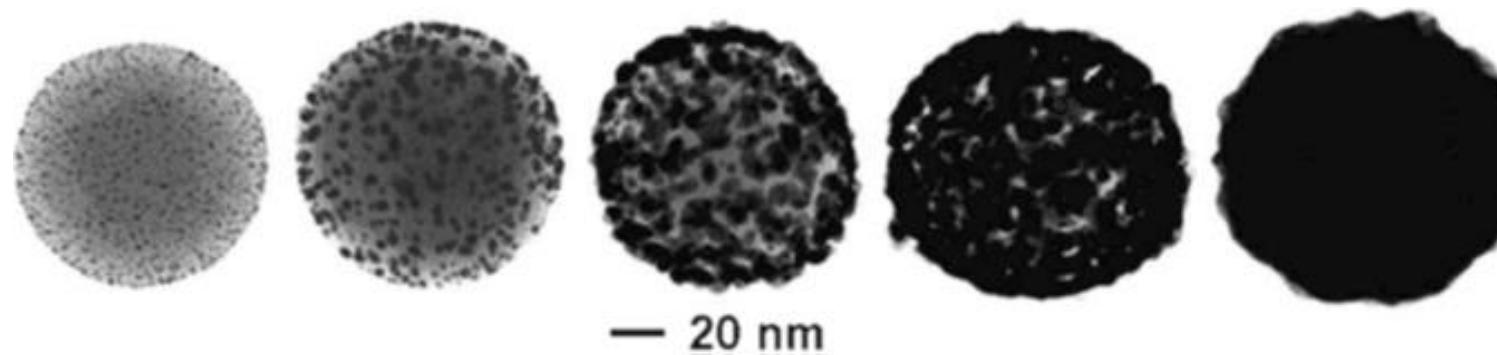
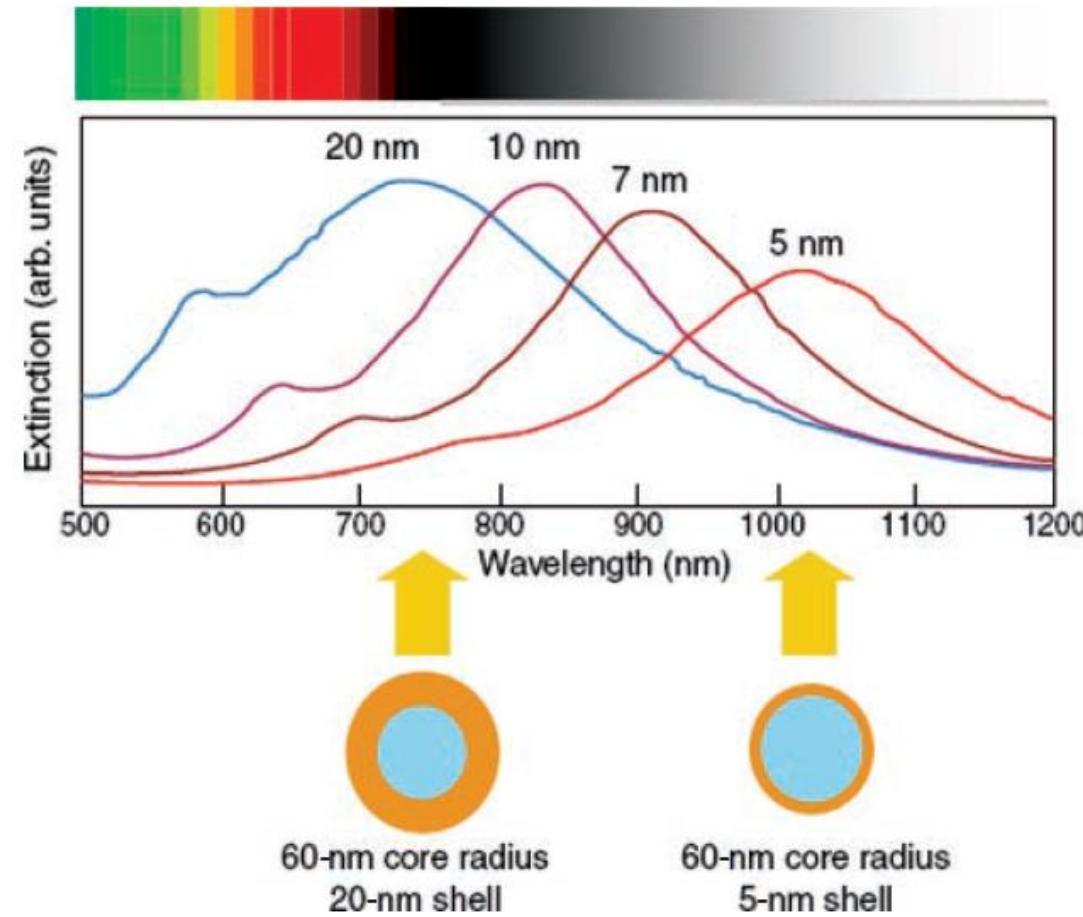


Figure 1.13 Transmission electron microscopy images of nanoshell growth phases from silica core (left) to gold - covered nanoshell (right).



Figure 1.2. Optical spectra of Au shell – silica core nanostructures as a function of their core/shell ratio. (Left, top): Photograph showing color tunability of gold nanoshell particles with different shell thicknesses dispersed in water
Core:shell ratio decreases from left to right.



(Right, top): Variation in LSPR band with shell thickness. Core:shell ratio increases from left to right. (Photo by C. Rodloff. Courtesy of Professor Halas's group of Rice University, USA.)

Typically, the optical features of these structures characterized by a tunable plasmon band that gives rise to intense optical absorption and scattering. The modulation of the plasmon band can be reached controlling the thickness of the Au shell relative to the diameter of the core; thus, the plasmon band of **nanoshells** can be tuned across the visible and near-IR (NIR) regions of the electromagnetic spectrum (in the range of 700–1300 nm) (Figure 1.2).

Decreasing the gold shell thickness for a given core size cause the plasmon resonance to shift toward the NIR region.

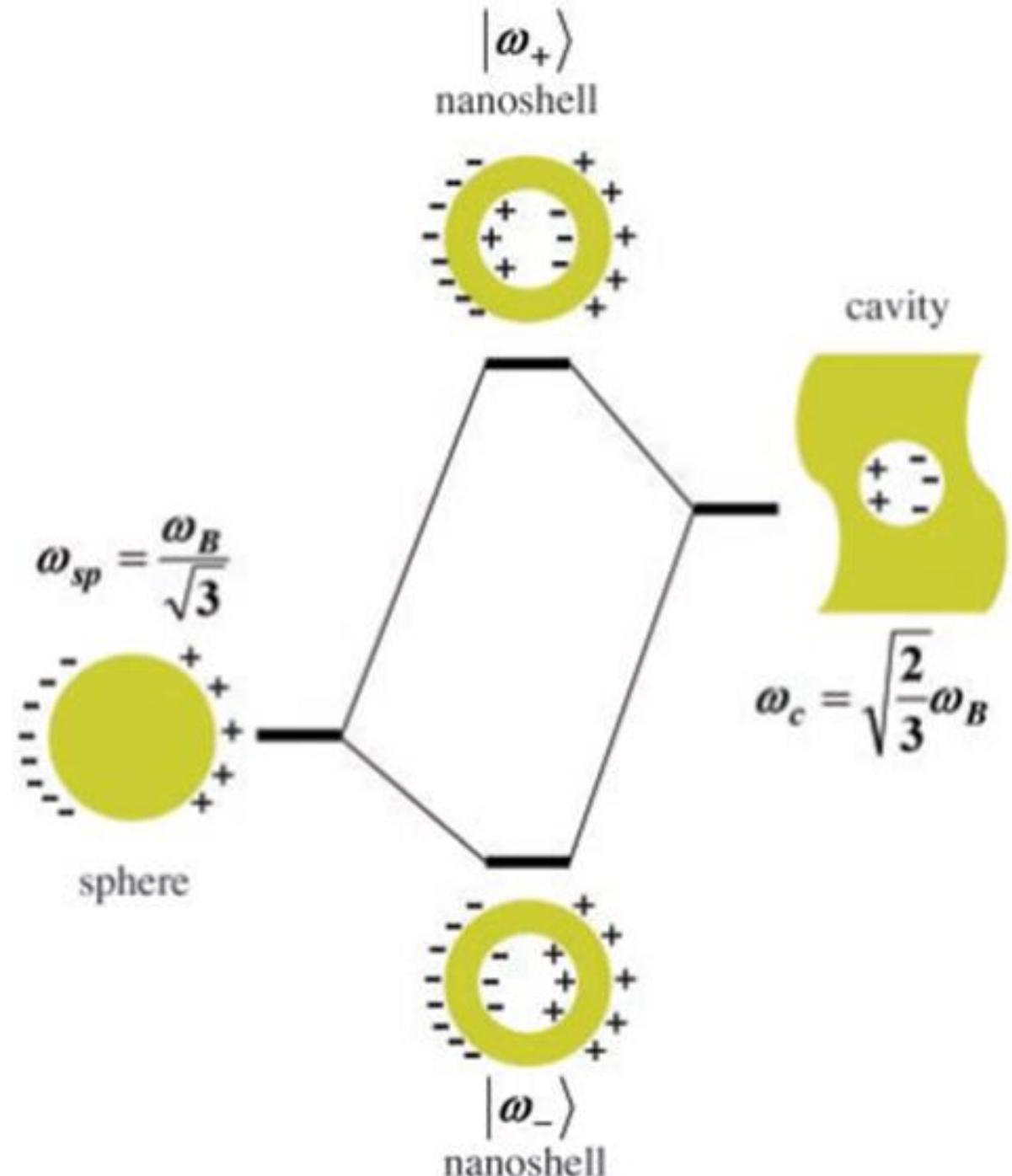
Due to their biocompatibility and on demand plasmon band, these structures have been widely applied in PTT by NIR light. Moreover, the commercial product AuroLase™ Therapy uses AuroShell™ particles (nanoshells) with a near-infrared laser source to thermally destroy cancer tissue without significant damage to surrounding healthy tissue; these particles are already in advanced stages of FDA clinical trials for breast cancer treatment.

The LSPR of the metal shell nanostructure depends strongly on the relative dimensions of the metal shell and the dielectric core. As the gold shell thickness is decreased, there is red-shift in the nanoshell LSPR from the visible region (~520 nm for a solid gold nanosphere) towards the near-infrared region.

Mie model is unable to describe the LSPR of metal structures made of several concentric layers, which can be interesting for sensing applications.

More recently, a novel mathematical model, the *plasmon hybridization model* has been developed to describe LSPR in core–shell system. In this model, the plasmon response of the nanostructures can be understood as the interaction or “hybridization” of plasmons supported by nanostructures of elementary shapes: a core and a metal cavity. A hollow metallic nanosphere, or nanoshell, supports plasmon resonances with frequencies that are a sensitive function of the inner and outer radius of the metallic shell. The sphere and cavity plasmons are electromagnetic excitations that induce surface charges at the inner and outer interfaces of the metal shell. Because of the finite thickness of the shell layer, the sphere and cavity plasmons interact with each other. The strength of the interaction between the sphere and cavity plasmons is controlled by the thickness of the metal shell layer. This interaction results in the splitting of the plasmon resonances into two new resonances: the lower energy symmetric or “bonding” plasmon (ω_-) and the higher energy antisymmetric or “antibonding” plasmon (ω_+) (Fig. 1).

Fig. 1. An energy-level diagram describing the plasmon hybridization in metal nanoshells resulting from the interaction between the sphere and cavity plasmons. The two nanoshell plasmons are an antisymmetrically coupled (antibonding) ω_+ plasmon mode and a symmetrically coupled (bonding) ω_- plasmon mode.



- Simple arguments can be applied to provide a qualitative understanding of more complex plasmon resonances and their geometrical dependence.
- In fact, *plasmon resonances of complex structures can be viewed as the result of a "hybridization" of elementary plasmons of simpler substructures.*
- To give an example, consider the resonances of a **hollow metallic shell** (viz. gold nanoshell) as shown in Fig. 12.21 (a).
- The *elementary resonances of this particle are found by decomposition into a solid metal sphere and a spherical cavity* in bulk metal.
- Fig. 12.21(b) shows how the elementary modes can be combined to form hybrids.
- *A low energy (red-shifted) hybrid mode is obtained for an in-phase oscillation of the elementary plasmons* whereas *the anti-phase combination represents a higher-energy mode that is blue-shifted.*
- The degree of interaction between the elementary modes is determined by the spatial separation of the modes (shell thickness).

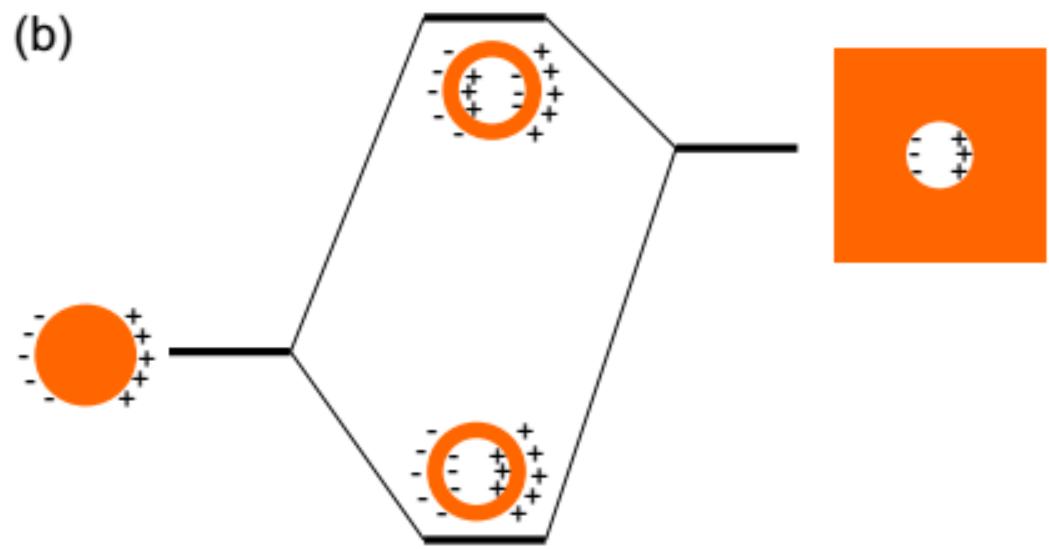
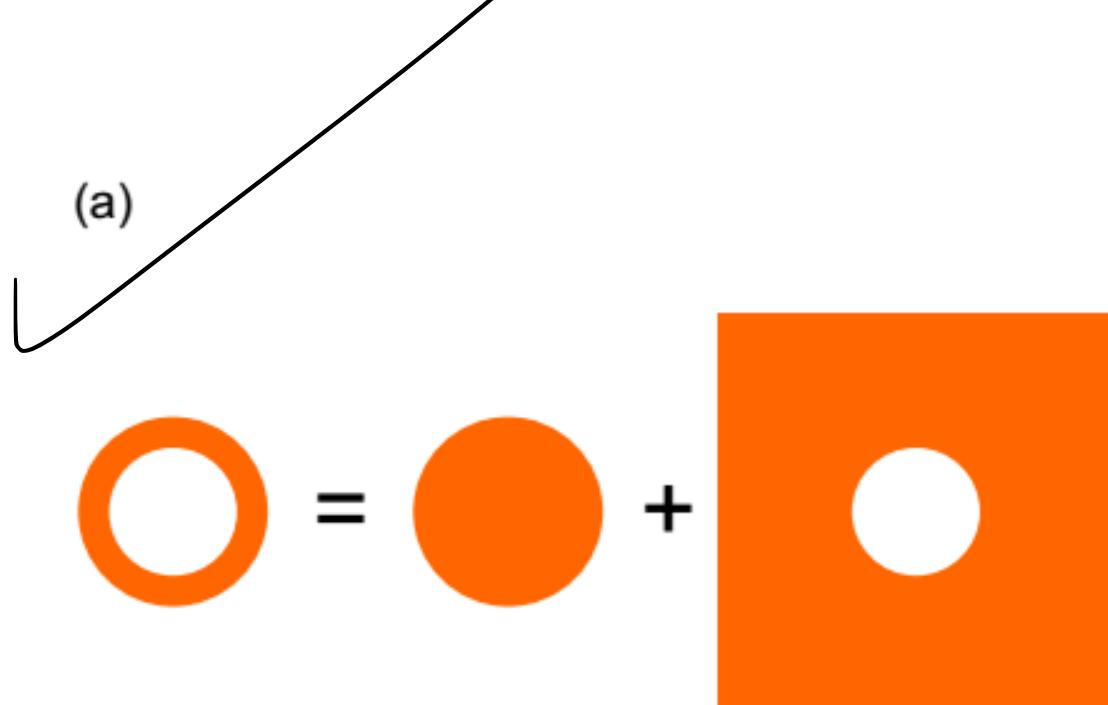


Figure 12.21: Generation of multi-featured surface plasmon resonances by hybridization of elementary modes for the example of a *gold nanoshell*.
(a) Elementary structures, (b) Energies of elementary and hybridized modes.

❖ LSPR of more Complex Structures: *Particle aggregation or Proximity effects*

- The *Mie model* works well only for spherical nanoparticles (NPs) in solution, or solid-state matrix, with **low concentration** where **NPs mutual interactions can be neglected**.
- **Increasing the NP concentration or by some other mechanisms**, when **two metal nanoparticles are brought in proximity to each other**, the inter-particle distance becomes smaller (till aggregation), **the near-field on one nanoparticle is influenced by its neighbors**. Thus, the **electric field E** felt by each particle is the sum of the **incident light field E_0** and the **near-field E_{nf} of the neighboring particle**.
 - $$E = E_0 + E_{nf}$$
- As a *result of this near-field interaction, plasmon oscillations of the two nanoparticles become coupled*. **This plasmon coupling modulates the LSPR frequency of the coupled-nanoparticle system**. This phenomenon is well described by the Maxwell–Garnett theory.
- Such complex structures often yield multi-featured resonance spectra and **strongly enhanced local fields in gaps (“hot-spots”)** between or at intersection points of different particles. An important problem in ‘plasmonics’ is the question of how metal particles should be designed and arranged with respect to each other to produce the strongest possible field enhancement.

➤ Similar **hybridization considerations** can be adopted to understand the multiple plasmon resonances that occur for asymmetric particles such as e.g. **pairs of metal particles**. Here, besides the **hybridization effect**, different resonances can occur for **different directions of polarization of the excitation light**. For example, consider a pair of spherical particles as sketched in Fig. 12.22 (a)-(c).

➤ The elementary plasmon resonance (a) is **hybridized when two particles are sufficiently close such that the dipole of one particle induces a dipole in the other particle**. Possible hybrid modes of the combined structure are sketched in Fig. 12.22 (b) and (c). For different polarizations, different modes of the system are excited which may shift to lower or higher energies for increased coupling. For example, the low energy modes of Fig. 12.22 (b) and (c) shift to the red, respectively to the blue, for decreasing inter particle distances. This is because for decreasing distance in the first case the opposite charges close to the gap reduce the energy of the configuration whereas in the second case the overall energy (Coulomb repulsion) is increased.

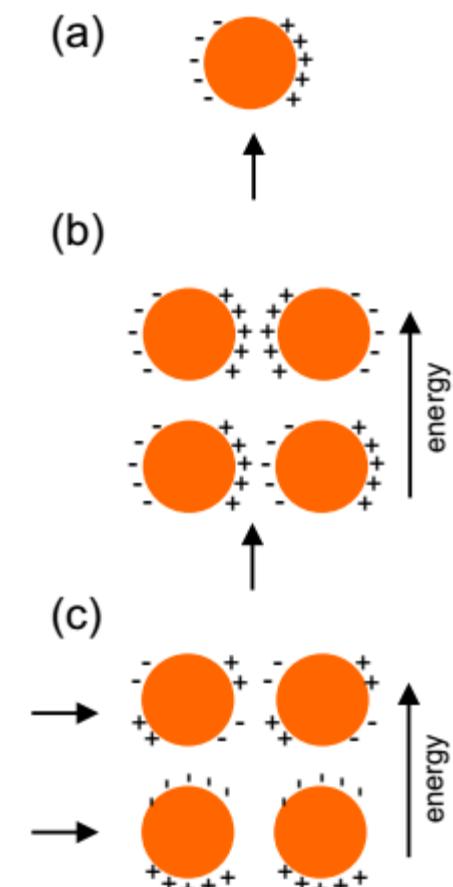


Figure 12.22: Shape effects in particle plasmon resonances. (a) Elementary mode of a spherical particle. The arrow indicates the **polarization direction** of the exciting field. (b),(c) Surface charge distributions of hybrid plasmon modes associated with particle pairs. The polarization direction is perpendicular (b) and parallel (c) to the long axis of the particle axis.

➤ For instance, in spherical gold nanoparticles, assembly or aggregation into a close-packed structure results in a strong red-shift of the LSPR wavelength from the LSPR maximum of ~520 nm of an isolated colloidal nanoparticle. ***The redshift is a manifestation of the favorable coupling of the plasmon oscillations of the proximal nanoparticles***, i.e., a lower energy (or frequency) is required to drive the coupled plasmon oscillation modes of the assembly.

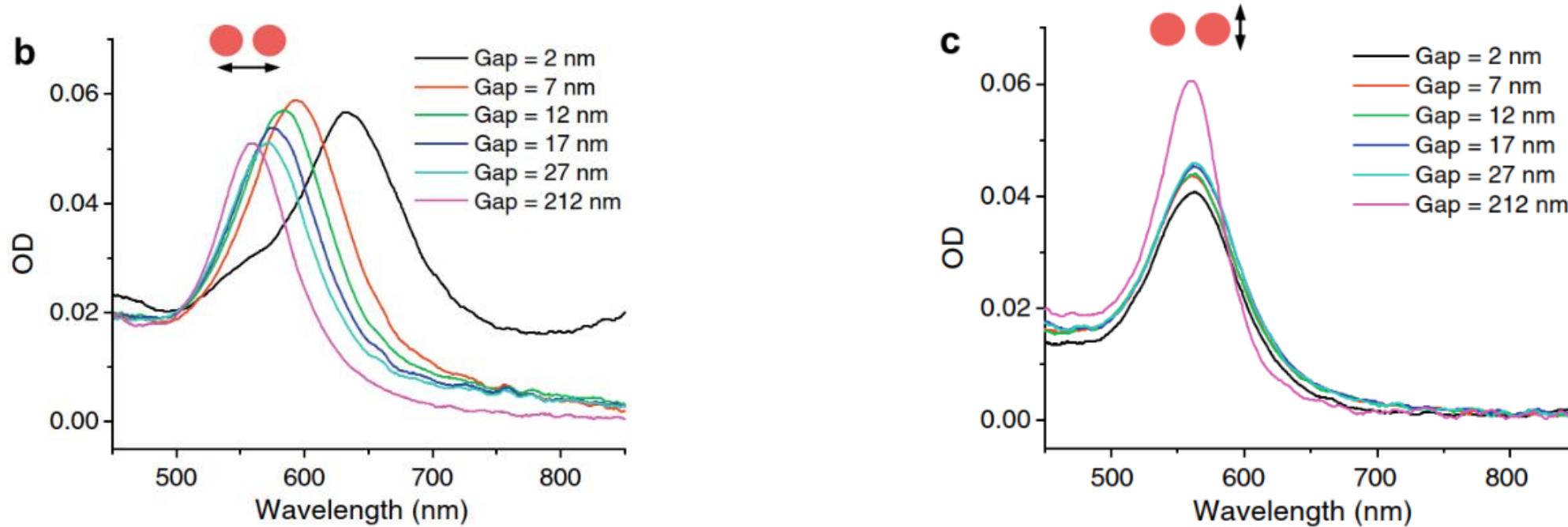
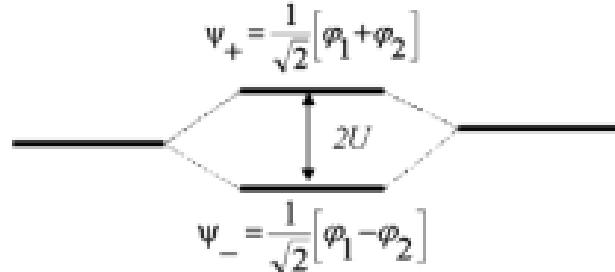


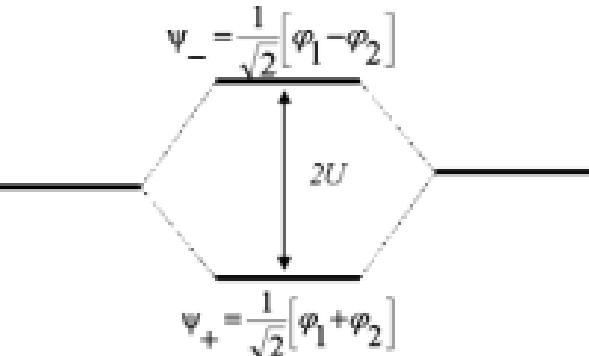
Fig. 2. Extinction spectra show that the LSPR of the nanoparticle pair (b) red-shifts with decreasing gap for polarization along the inter-particle axis and (c) blue-shifts very slightly with decreasing gap for polarization orthogonal to the inter-particle axis. Reprinted with permission. (***OD = Optical Density = Absorbance***)

a

EXCITED STATE

**b**

EXCITED STATE



GROUND STATE

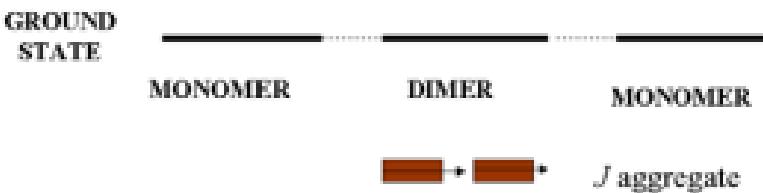
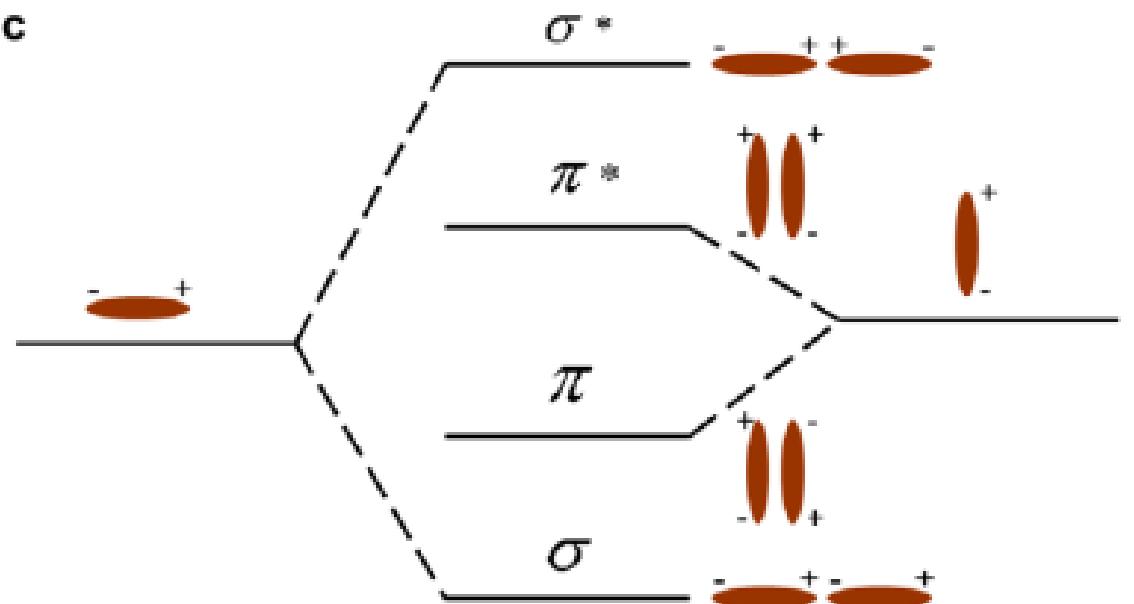
**c**

Fig. 4. The energy level splitting resulting from the dipolar coupling of chromophores in a dimer, showing symmetric (ψ_+) and anti-symmetric coupling (ψ_-) of excitons for (a) ***H-aggregate*** geometry or ***side-by-side*** dimer and (b) ***J-aggregate*** geometry or ***end-to-end dimer***.

(c) Analogy of ***plasmon coupling in nanorod dimers to hybridization of molecular orbitals***. The end-to-end coupling of the nanorod long-axis LSPR is similar to the formation of a bonding σ and anti-bonding σ^* mode. The side-by-side coupling of the nanorod long-axis LSPR is similar to the formation of a bonding π and anti-bonding π^* mode. **Note that the σ^* -like and π -like plasmon modes are optically dark** due to their zero net dipole moment. Reprinted with permission.

APPLICATIONS

- Localized surface plasmons (LSPs) have attracted tremendous interest for a broad range of emerging applications, such as chemical and biomolecular sensing, subwavelength optical imaging, optoelectronic devices such as light emitting diodes (LEDs), solar cells, and photodetectors. LSPs excited by an electric field at a particular incident wavelength where resonance occurs will lead to strong light scattering, intense absorption band and enhancement of the local electromagnetic fields. The oscillation frequency and intensity i. e. coupling efficiency of LSPs can be modulated by the type of metals. They are also highly sensitive to the size, size distribution, shape and the medium which surround/near the metallic nanostructure.
- Gold nanoparticles are common examples of metallic nanoparticles and *have found practical applications as biological and chemical sensors, ‘smart bombs’ for cancer therapy, and optical switching and fluorescent display materials*. Many of these applications are possible owing to the development of techniques to bind photoresponsive chromophores to the surface of the nanoparticles.

- **Gold nanoparticles can be tagged with biomolecules** that afford delivery to specific cells and have found applications as immunoprobes for the early detection of disease.
- Metallic nanoparticles and metallic nanoshells are used as **dielectric sensors** because their optical properties change when they come into contact with different dielectric materials.
- ✓ In particular, **biological sensing** is of interest because biological analytes can bind to the surface of the nanoparticle, *causing a detectable shift* in the plasmon absorption band.
- Nanomaterials have also been used as key electron-transfer agents in a new generation of solar materials that couples photoresponsive π -conjugated, polyaromatic molecules to gold nanoparticle surfaces. Chromophore-functionalized gold nanoparticles afford unique device architectures and flexibility in design as these hybrid materials can be coupled covalently to conductive glass substrates that serve as electrodes, so leading to improved charge transport and photoefficiencies.

Surrounding environment dependence of LSPR

- Generally, NPs are dispersed in a medium, and *interactions* with such a medium can be *classified into two main categories*:
 - (i) media that **alter the refractive index** around metal NPs and
 - (ii) media formed of **molecules that complex** the metal surface.
- Media *not possessing any active functional groups do not directly interact* with metal surface; therefore, *any modification of plasmon band can be safely ascribed only to change in the refractive index* of the surrounding medium. *In these systems, the surface plasmon band of metal NPs gradually shifts toward longer wavelengths* with increasing refractive index of the solvent.
- Conversely, *media chemically interacting with the surface of metal NPs* could alter the position of the plasmon band *due to a different distribution of free electrons*. *In these systems, there can blue-shift or red-shift* of the plasmon wavelength.

- The above two effects that lead to the LSPR peak shift can be explained as follows.
- The *dependence of the wavelength of the LSPR peak on the refractive index of the surrounding environment* is given by the expression ($\varepsilon_{\text{diel}} = (n_{\text{diel}})^2$ where n_{diel} is the refractive index of the (nonabsorbing) medium),

$$\lambda_{\text{max}}^2 = \lambda_p^2(\varepsilon_{\infty} + 2\varepsilon_{\text{diel}})$$

or $\lambda_{\text{max}}^2 = \lambda_p^2(\varepsilon_{\infty} + 2n_{\text{diel}}^2)$ (11)

where $\lambda_p = 2\pi c/\omega_p$ (12)

where λ_{max} is **plasmon wavelength**, λ_p is the bulk plasmon wavelength, ω_p is the bulk plasmon angular frequency, c is the speed of light in free space.

- For bulk metals, the plasmon frequency (ω_p) can be shown to be:

$$\omega_p = \sqrt{\frac{Ne^2}{m_e \varepsilon_0}} \quad (13)$$

- The volume plasma frequency is a property of the metal. Here ***N is the number density of electronic charge***, e is the electronic charge and m_e is the effective mass of the electron.

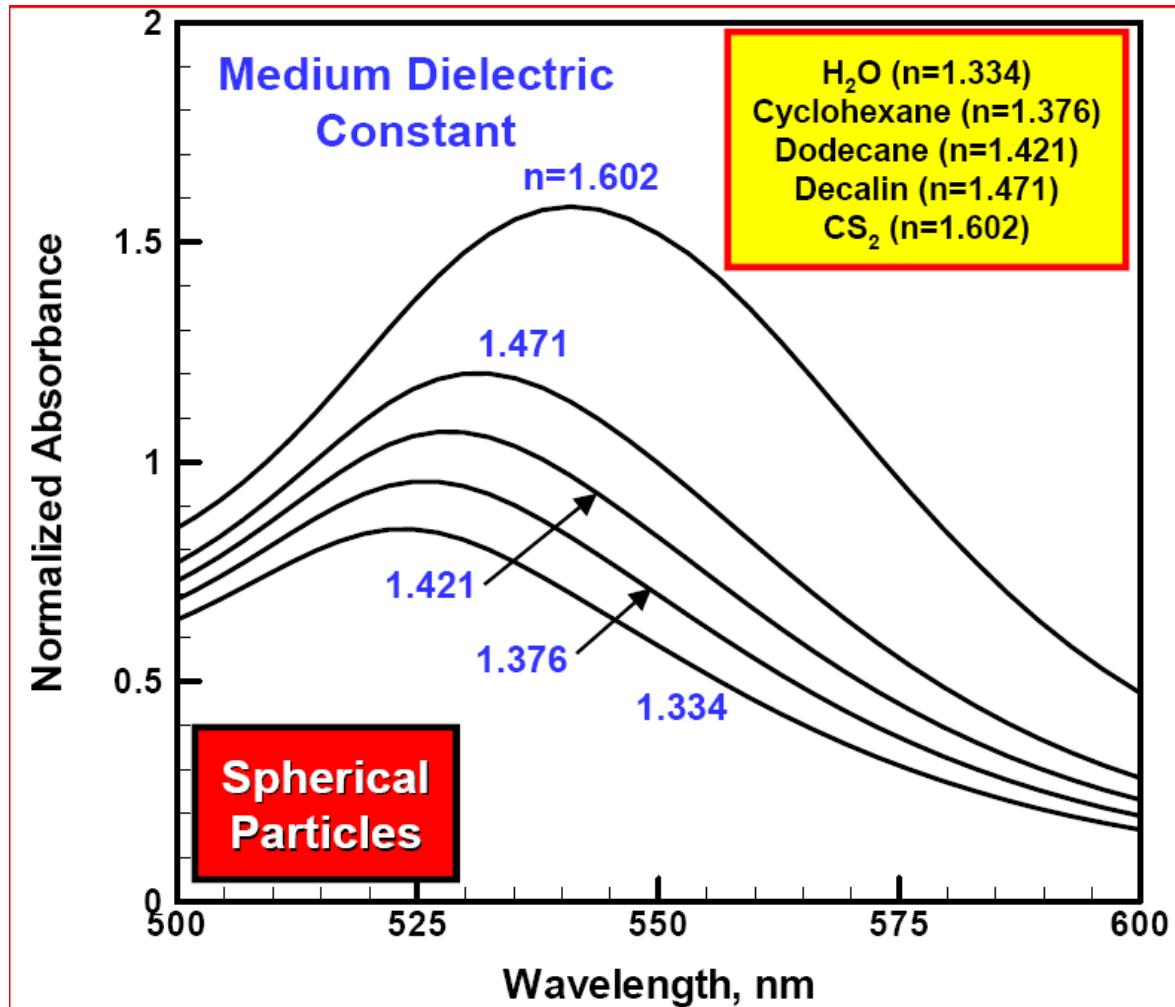
➤ Combining equations 11, 12 and 13, one obtains

$$\lambda_{max}^2 = \frac{4\pi^2 c^2 m_e \epsilon_0}{Ne^2} (\epsilon_\infty + 2n_{diel}^2)$$

which shows that:

- (i) An **increase in the n_{diel} , refractive index**, of the environment (where $n^2_{diel} = \epsilon_{diel}$) increases the plasmon wavelength λ_{max} , i.e., a **redshift** in the LSPR band occurs and *vice versa*.
- (ii) If **electron density (N)** on the nanoparticle **increases**, the plasmon wavelength λ_{max} increases, i.e., then there will be **blue-shift** of the plasmon wavelength and *vice versa*.

(Note: Volume plasmon energy for bulk gold is 9.0 eV and for silver it is 8.9 eV, and it lies in the UV range. However, for nanoparticles the surface plasmon energy is small and lies in the UV-Vis-NIR range.)



Calculated absorption spectra of gold nanoparticles in different solvents.

Figure 5.8 illustrates the media refractive index effect on LSPR of gold nanorods.

(Collect the refractive indices of all these solvents and interpret the observations. Plot the longitudinal plasmon band position with refractive index of the solvent and carry out linear regression of the data. What is the longitudinal plasmon band position for zero refractive index?)

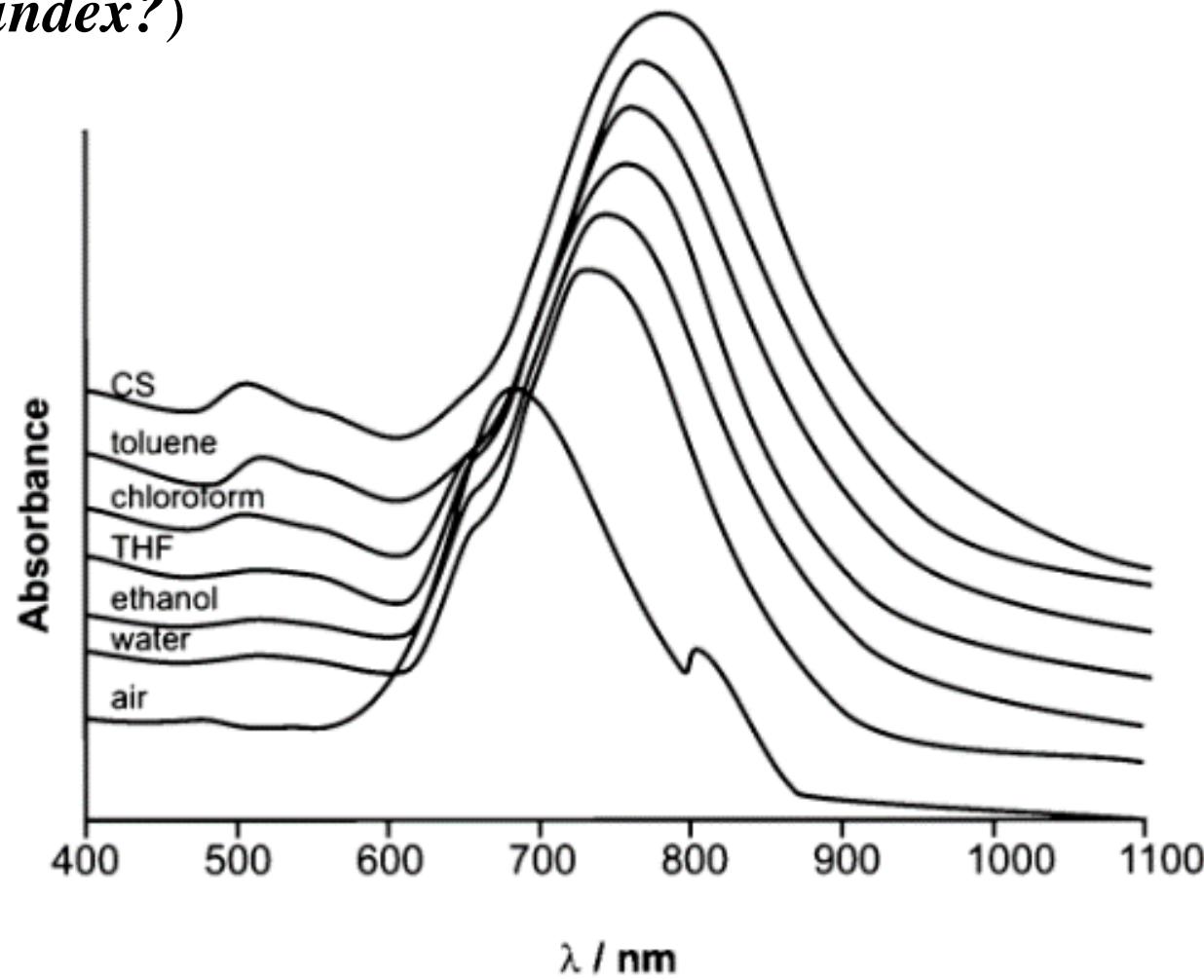
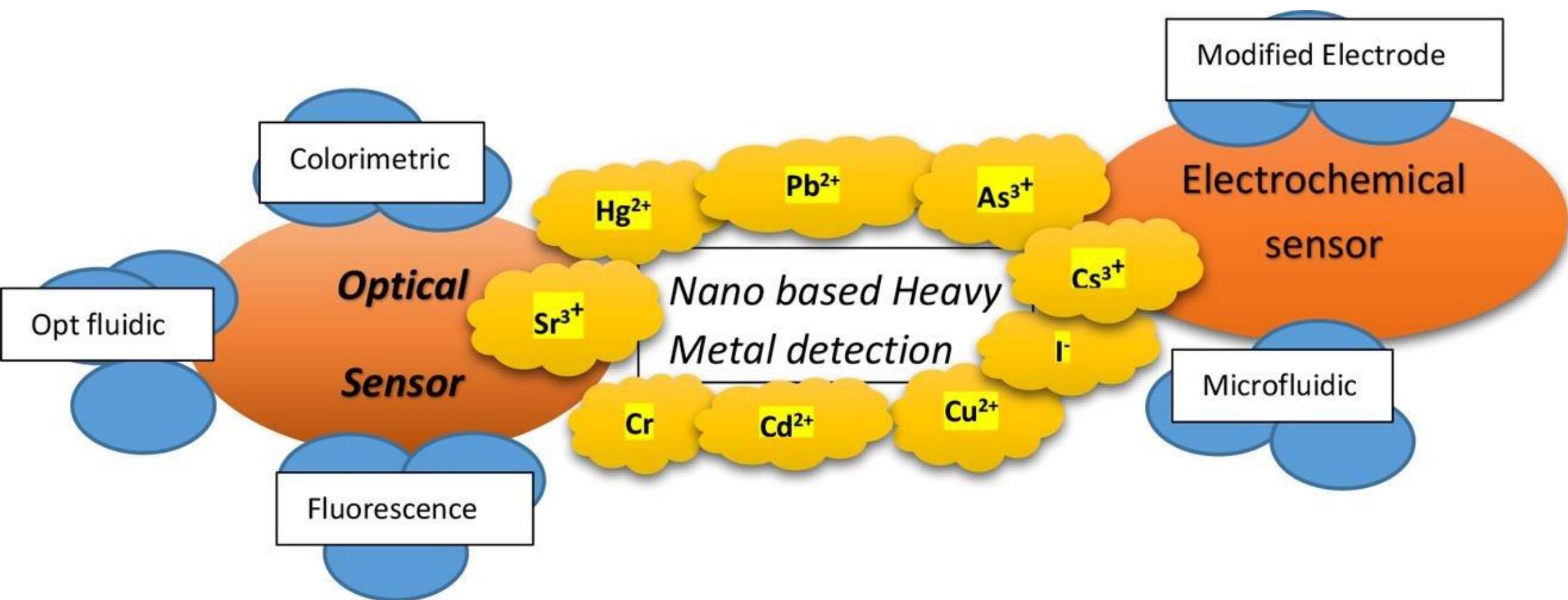


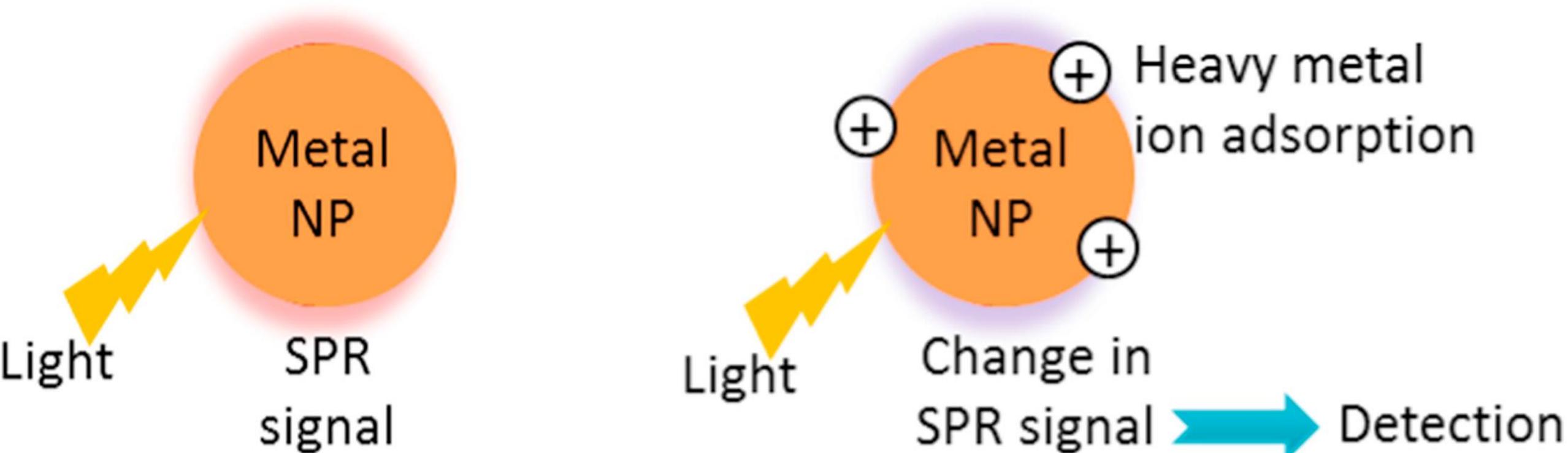
Fig. 5.8. Experimental spectra of gold nanorods in different solvents.
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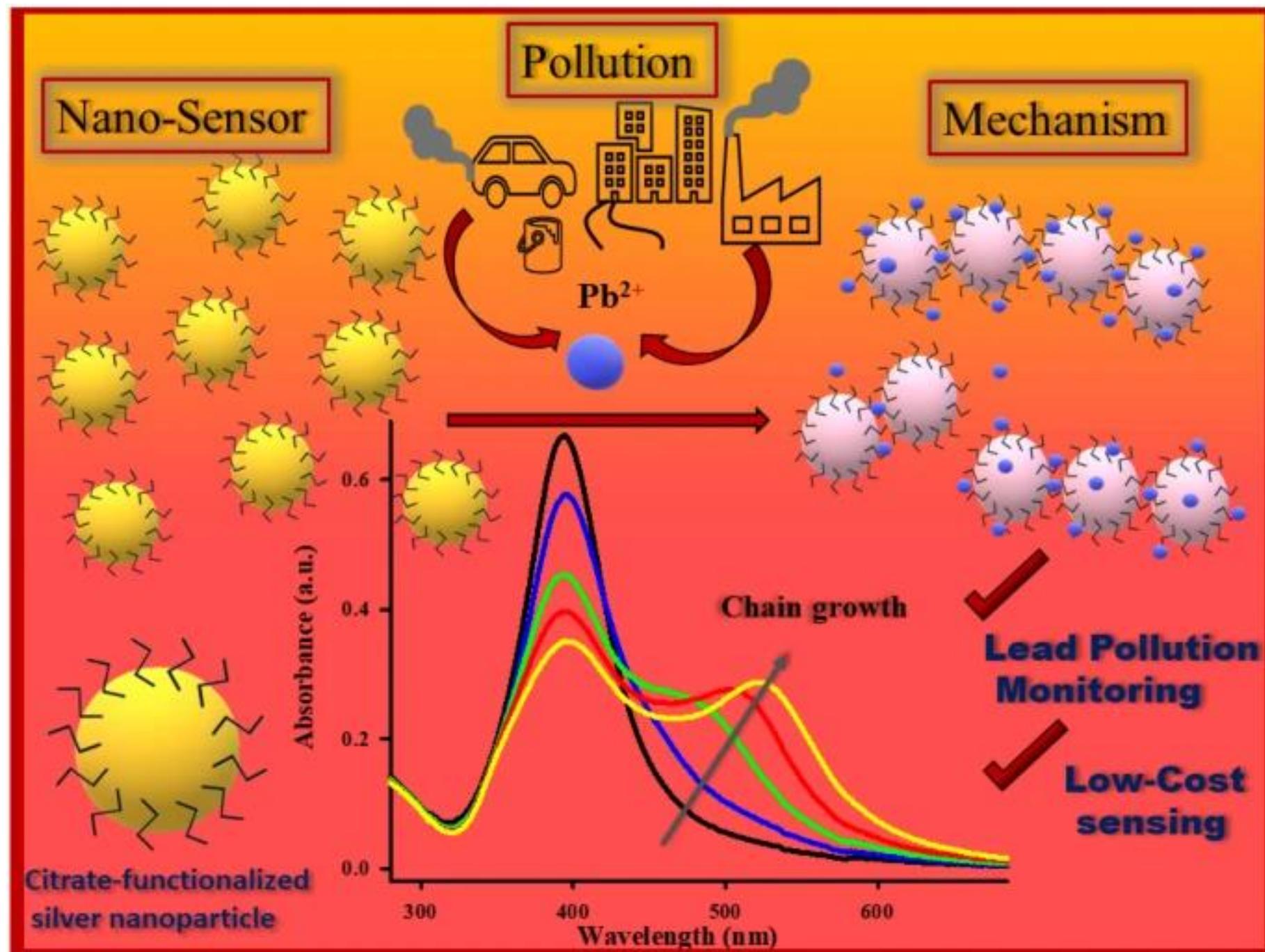
- The color of the semiconductor particles is NOT influenced by the surface plasmon resonance.
- In the case of *semiconductor crystallites*, the free electron concentration (density, N) is orders of magnitude smaller than in metals, even in degenerately doped materials (i.e., $\omega_p = \sqrt{\frac{ne^2}{m\varepsilon_0}}$ is smaller), and as a result *surface plasmon absorption occurs in the infrared (IR) rather than in the visible part* of the spectrum. The color of the semiconductor particles is therefore not influenced by the surface plasmon resonance.
- *Semiconductor crystallites therefore do not change color significantly when the particle size is decreased below the wavelength of visible light*, although the IR spectrum may be affected.
- However, when the size of the semiconductor particles decreases further, the quantum effects appear leading to a change in the electronic band structure of the crystal, which causes the dielectric function of the material itself to change.
- The strong color changes observed when semiconductor crystallites are in the quantum size regime due to the absorption in the visible region leading to electronic transition across the band gap, which emits photons while returning to the ground state.

➤ Heavy metals are one of the major factors which have been degrading our environment at a tremendous rate which unfortunately exploits the natural resources. Among the different heavy metals, arsenic, cadmium, lead, mercury, and chromium (Cr) are highly toxic. Many efforts have been made to quantify and detect heavy metals conventionally and analytically. However, advance technologies always remains in demand to detect heavy metal using user-friendly and sensitive way, for this the Nano based technology came into picture. These Nano (based on inorganic, organic, inorganic–organic hybrid nanoparticles (NPs)) work enhanced the efficiency of analytical devices and were found to be very sensitive, selective, with fast working potential. Nano based are sensors that can be easily incorporated into devices and helpful for on-the-spot detection or on-field detection with high linear range and low detection limit.



SPR Sensor for Heavy Metal Ion Detection





Applications of Nanoshells

Gold nanoshells resonant at 660–980 nm and are available with either polyethylene glycol (PEG) or polyvinylpyrrolidone (PVP) capping agents, or in a dried formulation.

This class of plasmonic nanoparticles has a wide variety of applications, including uses in optical filters, sensing and cancer therapy. For example, one of our most popular nanoshells products has a strong plasmon resonance at 800 nm and the very high absorption in the NIR is the basis for therapies that utilize the localized heating of nanoparticles to eradicate cancer cells.

Further tuning of the nanoshell size results in particles that scatter different portions of the spectrum, which can be readily observed using dark field microscopy. The tunable plasmonic properties make nanoshells of interest for Surface Enhanced Raman Scattering (SERS) applications, or as optical sensors where a shift in color of the nanoshell is indicative of the presence of a target analyte in solution.

Due to the difference in the scattering and absorption properties of the nanoshells, many variants are bichromic: for example, when a solution of 800 nm-resonant nanoshells are viewed in transmission (back lit) the nanoshells solution appears blue, but when viewed with reflected light the same solution can appear a rusty red due to scattering by the particles.

Colorimetry and biosensing

Colorimetric sensing is monitoring changes in the colour of the nanoparticles which act as sensors. Usually gold nanoparticles are used for this purpose and polynucleotides, oligonucleotides and DNA have been detected successfully. Mirkin *et al.* have used gold nanoparticles for detection of DNA. Single strand of DNA was immobilized on gold nanoparticles and used for detection of complementary DNA strand. It is shown that an intense ruby red-colour changes to blue upon agglomeration when complementary DNA was added. Core shell particles can be a better choice for this purpose because of enhanced sensitivity. Core shell particles with highly controlled optical properties are used in several biotechnological applications. It is possible to modify these particles to enhance their integration with biomolecules. This can be achieved by modifying their surface layer for enhanced aqueous solubility, biocompatibility and biorecognition. For such applications, mostly silica core and gold or silver shells have been used because they offer highly favourable optical and chemical properties for biomedical imaging and therapeutic applications. It is possible to attach biomolecules to these core shell assembly and form an immunoassay to detect analytes, cancer cells, tumours, antibodies and microorganisms. These particles offer a sensitive, reliable and rapid detection of biomolecules.

For such kind of detection, it is necessary that nanoshells have an affinity towards the specific analyte which is to be detected. This can be achieved by immobilizing specific antibodies onto the nanoshells. Antibodies can be conjugated on nanoshells via the amino group present in them. Since these antibodies are raised against a particular analyte, they have an affinity for it and bind to it. It is like a lock and key arrangement, which fits perfectly. The detection is carried out by monitoring changes in the UV-Vis extinction spectra. Nanoshells show extinction maxima at a particular wavelength, which can be taken as reference. When analytes are added to it, because of agglomeration or charge transfer interactions or changes in refractive index (or all), shifts are produced in the spectra. These changes to the nanoshell spectra are an indication of the presence of certain biomolecules. A simple detection test has been developed for checking the potability of water. Silver nanoshells can also be used for detection of toxic ions such as Cd, Hg and Pb present in water. The extinction spectrum of silver nanoshells changes when it is mixed with a solution containing these ions.

Figure 11 *a* shows the absorption spectra of silver nanoshells with different amount of Hg ions. This test is sensitive and can detect even small quantities of Hg ions. However, this test lacks specificity. Figure 11 *b* shows variation of intensity with the amount of added Hg ions.

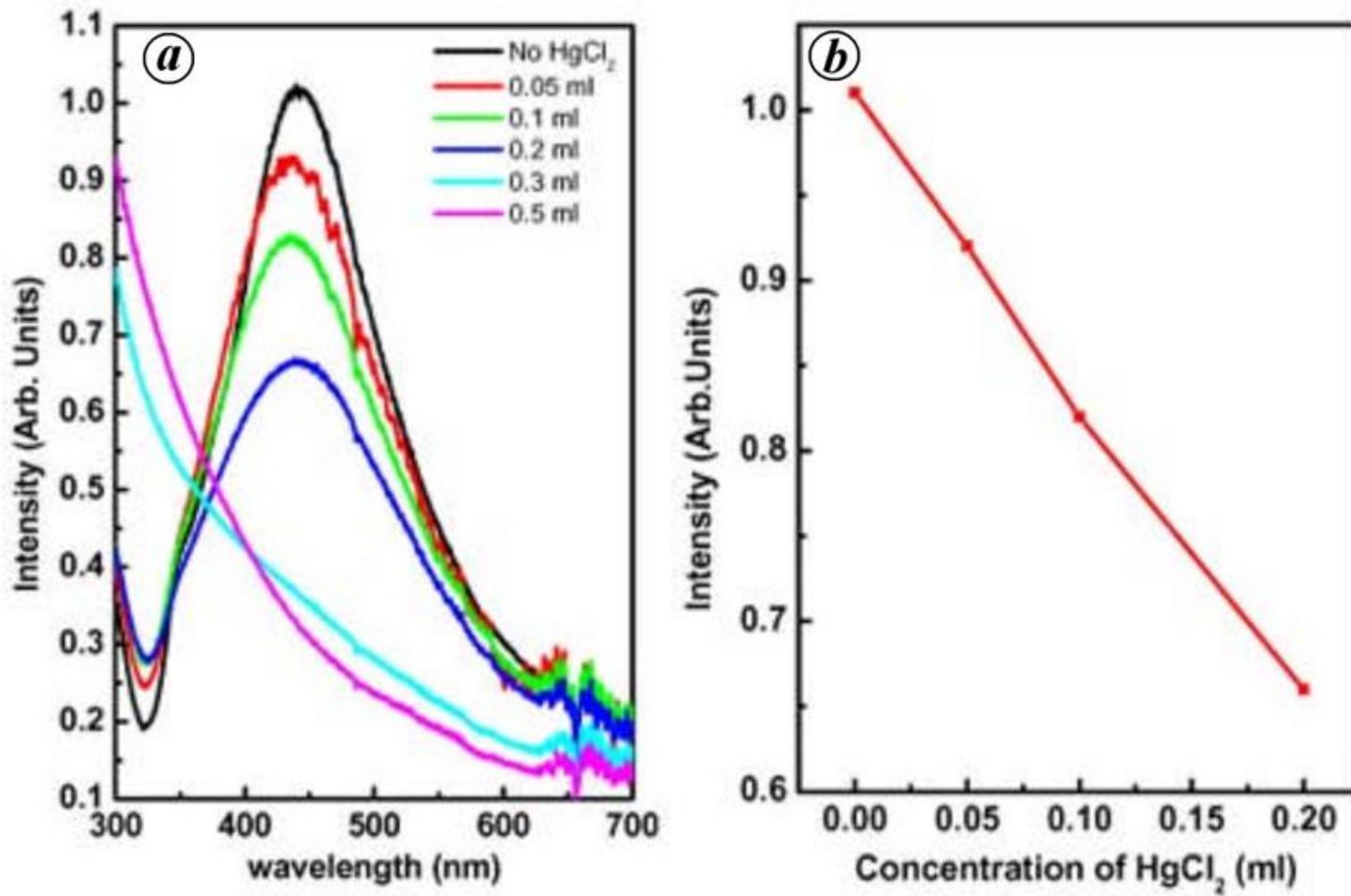
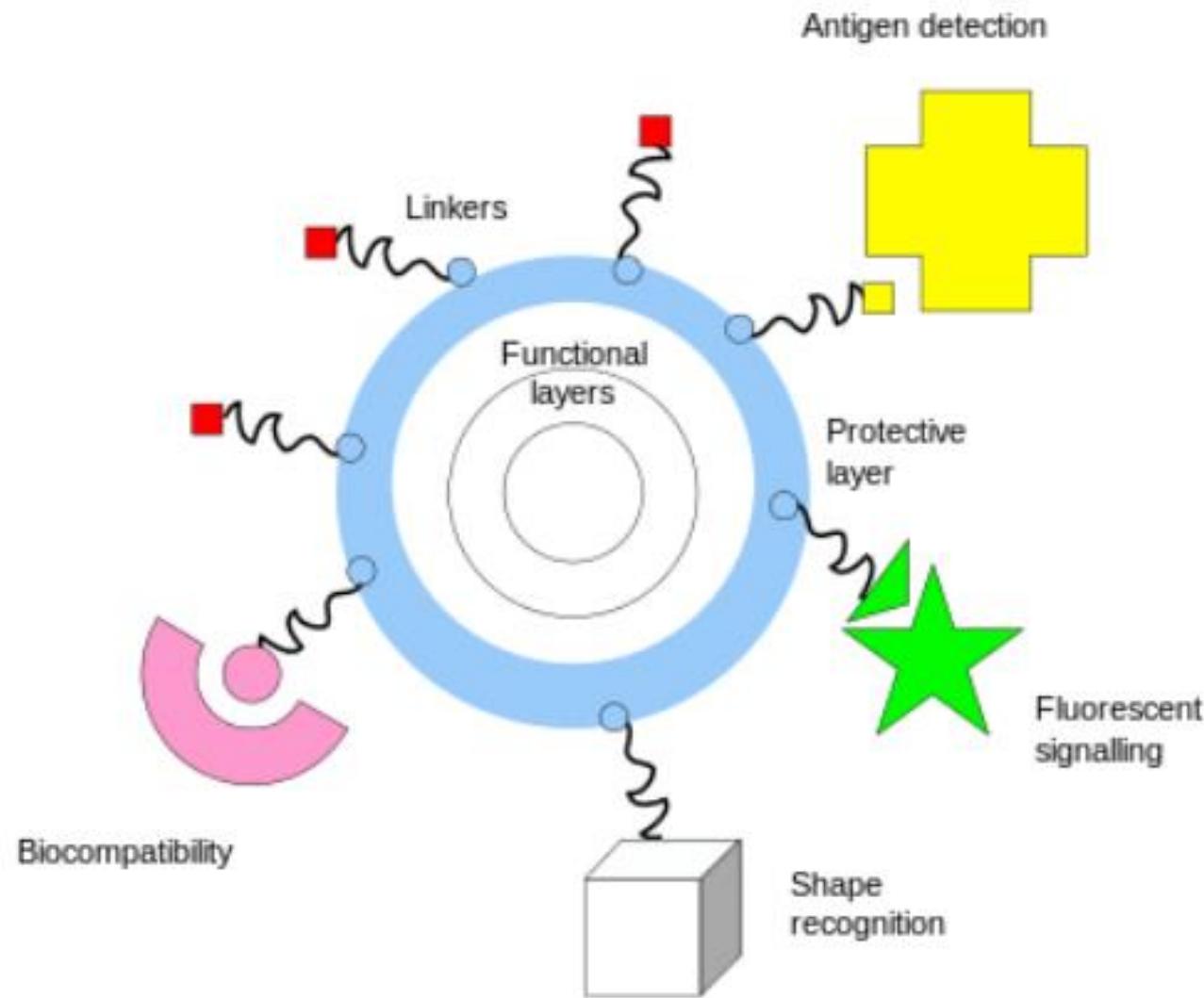


Figure 11 a: ***Effect of addition of HgCl₂ on SPR of silica-silver core shell particles;***
b: Plot of intensity of SPR band as a function of amount of HgCl₂.

❖ The foundation for many biosensing applications

- One of the **key complementary properties of noble metal nanoparticles that is important to their use in biomedicine** is the ease with which they can be **covalently conjugated** with polymers or small molecules, typically via thiol or amine bonds at their surface.
- This imparts biological recognition properties to the particles that enables them to bind to specific biomolecular targets. The figure on the right illustrates some of the functionality that can be imparted to nanoparticles through surface functionalization.



❖ The foundation for many biosensing applications (contd.)

- **Surface plasmons** should be distinguished from **bulk plasmons** (bulk plasma) which have a longitudinal nature and cannot be excited by visible light.
- **LSPR** differs from **SPR** as the induced plasmons oscillate locally to the nanostructure, rather than propagating on the surface.
- ✓ One can also have **surface propagating plasmons** (along the metal-dielectric interface) or **surface plasmon polaritons** in thin films as distinct from the LSPR (plasmons oscillate locally to the nanostructure) which occur at the nanoparticle's surface.
- ✓ It is of great mechanistic importance that surface plasmons are surface electromagnetic waves that propagate in parallel along a metal/dielectric interface.
- ✓ Since the *wave is located on the boundary of the metal and the external medium (or vacuum), these oscillations are very sensitive to any change in the chemical composition of this boundary*, such as the **adsorption** and **exchange** of **ligands** and **macromolecules** (e.g. (bio)polymers) to the metal surface.

❖ The foundation for many biosensing applications (contd.)

- The *decay length* of the electromagnetic field observed in *surface plasmon polaritons* is in the order of 200 nm, whereas the decay length of the electromagnetic field in *LSPR is in the order of 10 nm* (both decaying exponentially).
- The shorter field decay length for LSPR reduces the sensitivity to interference from solution refractive index fluctuations (bulk effect) whilst providing increased sensitivity to refractive index changes on the surface. *This property acts as the foundation for many biosensing applications.*
- These powerful localized sources of light are useful in different areas of science and technology which include *scanning near-field optical microscopy*, *biosensor applications*, *surface-enhanced Raman scattering (SERS)*, *nanophotonics*, *optical data storage*, etc.

- *Chemists and Biologists* are more interested in the following Equation (16.8) what is known as Lambert–Beer’s law. $A(\lambda)$ is the absorbance or optical density of the sample, ε_{abs} ($M^{-1} cm^{-1}$) is the molar absorption coefficient, c (M) is the molar concentration of the light absorbing species, and x (cm) is the optical path length.

$$\➤ A(\lambda) = \varepsilon_{abs(\lambda)} c x \quad \text{Equation (16.8)}$$

- Note that *the molar absorption coefficient is directly related to the absorption and scattering cross-section* by means of Equation (16.10).
- Conventionally, chemists measure the extinction coefficient of a solution in units of $M^{-1} cm^{-1}$, where the colloid concentration is the molar metal atom concentration. For particles of radius R (cm), this quantity is related to σ_{ext} by

$$\➤ \varepsilon(M^{-1} cm^{-1}) = 3 \times 10^{-3} \frac{V_m \sigma_{ext}}{4\pi R^3 \times 2.303} \quad \text{Equation (16.10)}$$

where V_m ($cm^3 mol^{-1}$) is the molar volume of the metal.

- *For small particles* where the *absorption strongly dominates* the scattering, the absorption cross section is $\sigma_{abs} = \sigma_{ext} - \sigma_{sca} \approx \sigma_{ext}$.

- Equation 11.6.5 shows that the extinction cross section varies as R^3 . As the number density decreases as R^3 (Equation 16.10) *for a given amount* of the colloidal material, ***the absorption coefficient is independent of the particle size in the dipolar approximation*** (which itself is valid when the particle size is small, $R \ll \lambda$).
- *The extinction coefficient is found to be size-independent in the size range between approximately 5 nm and 30 nm.*

$$\sigma_{absorption} = \frac{9\omega}{c} \epsilon_{diel}^{\frac{3}{2}} V \frac{\epsilon''_{metal}}{(\epsilon'_{metal} + 2\epsilon_{diel})^2 + (\epsilon''_{metal})^2} \quad (11.6.5)$$

$$\➤ \epsilon(M^{-1}cm^{-1}) = 3 \times 10^{-3} \frac{V_m \sigma_{ext}}{4\pi R^3 \times 2.303} \quad \text{Equation (16.10)}$$

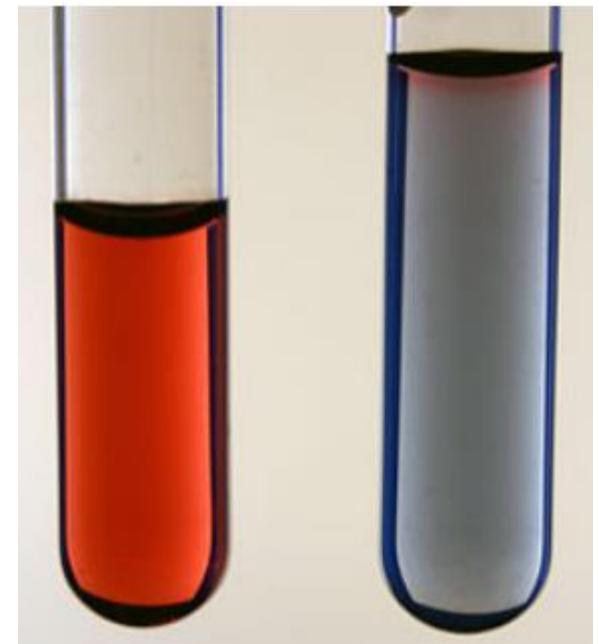
- Metal nanoparticles show **remarkably larger absorption cross-sections** compared to organic dyes and metal complexes. A typical example are the nanospheres that have been used by El-Sayed et al. for the laser-induced photothermal hyperthermia treatment of cancer cells, which feature *an absorption cross-section of $2.93 \times 10^{-15} \text{ m}^2$ ($\epsilon = 7.66 \times 10^9 \text{ M}^{-1} \text{ cm}^{-1}$) at their plasmon resonance maximum of $\lambda = 528 \text{ nm}$* . This is five orders of magnitude larger than that of the commonly used NIR dye indocyanine green ($\epsilon = 1.08 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 778 \text{ nm}$) or the sensitizer ruthenium(II)-tris-bipyridine ($\epsilon = 1.54 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 452 \text{ nm}$) and four orders of magnitude larger than rhodamine-6G ($\epsilon = 1.16 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 530 \text{ nm}$) or malachite green ($\epsilon = 1.49 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 617 \text{ nm}$).
- Metal nanoparticles possess **remarkable light-scattering properties** as well. Gold nano-spheres of **80 nm** in diameter have approximately *the same Mie-scattering characteristics as polystyrene beads of 300 nm* (both feature $C_{sca} = 1.23 \times 10^{14} \text{ m}^2$ at $\lambda = 560 \text{ nm}$, corresponding to a molar scattering coefficient of $3.22 \times 10^{10} \text{ M}^{-1} \text{ cm}^{-1}$). It is noteworthy that this **strong scattering is five orders of magnitude higher than the light emission (fluorescence) from fluorescein** ($\epsilon = 9.23 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 521 \text{ nm}$, emission quantum yield $\Phi = 0.98$ at $\lambda = 483 \text{ nm}$).

- Some studies have suggested that multiple-photon absorption of gold nanostructures can be advantageous, for instance in SERS-microscopy and plasmonic heating (photo-induced hyperthermia).
- It should be noted that noble metal nanostructures (e.g. gold nanorods) can be easily tuned for monophotonic applications in the wavelength range from 600 to 1000 nm. Monophotonic excitation is advantageous, because its absorption cross-section is several orders of magnitude higher!

Gold nanoparticle probes for the detection of nucleic acid targets:

- Functionalization of gold nanoparticles with **thiol-terminated single-stranded DNA** was the basis of one of the first nanoparticle sensors, highly sensitive optical detection of the target sequence, developed by the Mirkin group at Northwestern University.
- The gold nanospheres were functionalized in a programmed scheme such that the presence of a DNA strand with the right DNA sequence would trigger via DNA hybridization and the assembly of the gold nanoparticles. ***This assembly-induced shift for the sensing of trace amounts of sequence-specific DNA strands.***
- **DNA-AuNPs** can be assembled into different structures by designing linker DNA with a *complementary sequence*.
- For example, **AuNPs** modified with either **DNA A** or **DNA B** can be assembled in solution by the addition of a third DNA sequence **A'B'** which is complementary to **A** and **B**, respectively.

- **DNA-coated nanoparticles** have the characteristic **wine-red** plasmonic color of spherical nano-gold. However, when these particles are linked together by *a complementary DNA strand*, the resonance frequency shifts, resulting in a **blue color**. This color change, illustrated in the figure at the right, provides a "litmus test" for the *presence of the target DNA sequence*.
- *The assembly process is marked by a dramatic **red-to-blue** color change and a dampening and red shifting of the surface plasmon* (Fig.).



Aggregation of Au nanoparticles (in this case by adding salt to a colloidal solution) causes a color change from wine red (left) to blue (right). Photo credit: George Lisensky, Beloit College.

- Like DNA duplex formation, the ***DNA-AuNP assembly process is reversible***.
- By ***denaturing the interconnecting DNA duplexes*** within the AuNP assembly, the DNA-AuNPs ***can be redispersed, and a return of the red color is observed***.
- This “***melting***” process can be induced by an ***increase in the temperature*** or a ***decrease in salt concentration***.
- ***"Melting" of the DNA*** - heating it to the temperature at which double stranded DNA dissociates to make single strands - reverses the color change. The DNA hybridization/melting transition is highly cooperative because of the aggregation of many gold particles, so the transition temperature is very sharp. With proper temperature control, the color change can be ***sensitive to a single base mismatch in the target DNA*** that is detected by this method.
- Note that ***the aggregation of (noble) metal nanoparticles (disregarding whether they are ligand-stabilized or not), leads to pronounced changes of their absorption spectra due to plasmonic interaction***. This shift is ideal for the design of optical biosensors.

- The *melting process can be monitored by measuring the intensity of the surface plasmon* as a function of temperature.
- The melting transition exhibited by DNA-AuNP assemblies is remarkably different from unmodified DNA duplex melting transitions in two distinct ways: (1) *the melting transition of the AuNP assembly is significantly sharper*, where *the first derivative displays a full width at half maximum (FWHM) of about 2°*C* to 4°*C* compared to an FWHM of about 12°*C* for DNA duplex*, and (2) the melting temperature (T_m) is significantly higher than the T_m of an analogous DNA duplex under identical conditions.
- Both of these properties are a function of the DNA-AuNP conjugate and are important for the types of applications that will be described later.
- Despite these two notable differences in the melting properties, DNA-AuNPs exhibit other behaviors similar to duplex DNA. For example, *increasing the DNA length, DNA concentration, or salt concentration in the system increases* the stability of the DNA-AuNP assemblies and the T_m .

- A mixture of gold nanoparticles with surface-immobilized non-complementary DNA sequences (a, b) appears red in color (absorbance at 520 nm). When a complementary DNA sequence ($a'b'$) is added to the solution, the particles are reversibly aggregated causing a red shift in the surface plasmon absorbance to 574 nm, thus, appearing purple in color.
- A representative example is shown in the lower left (Fig. 12.1) where monodisperse particles (red) are aggregated using a complementary DNA linking sequence (purple).
- Heating the aggregates above the melting temperature of the DNA strands mediating aggregation results in a return to the red color.
- This melting transition is strikingly sharp as demonstrated in the lower right where gold nanoparticle-linked DNA is compared to unmodified DNA.
- At any given temperature, a small aliquot of the reaction mixture can be spotted on the surface of a reverse-phase TLC plate to monitor the degree of hybridization as determined by the temperature, as shown in the bottom right.

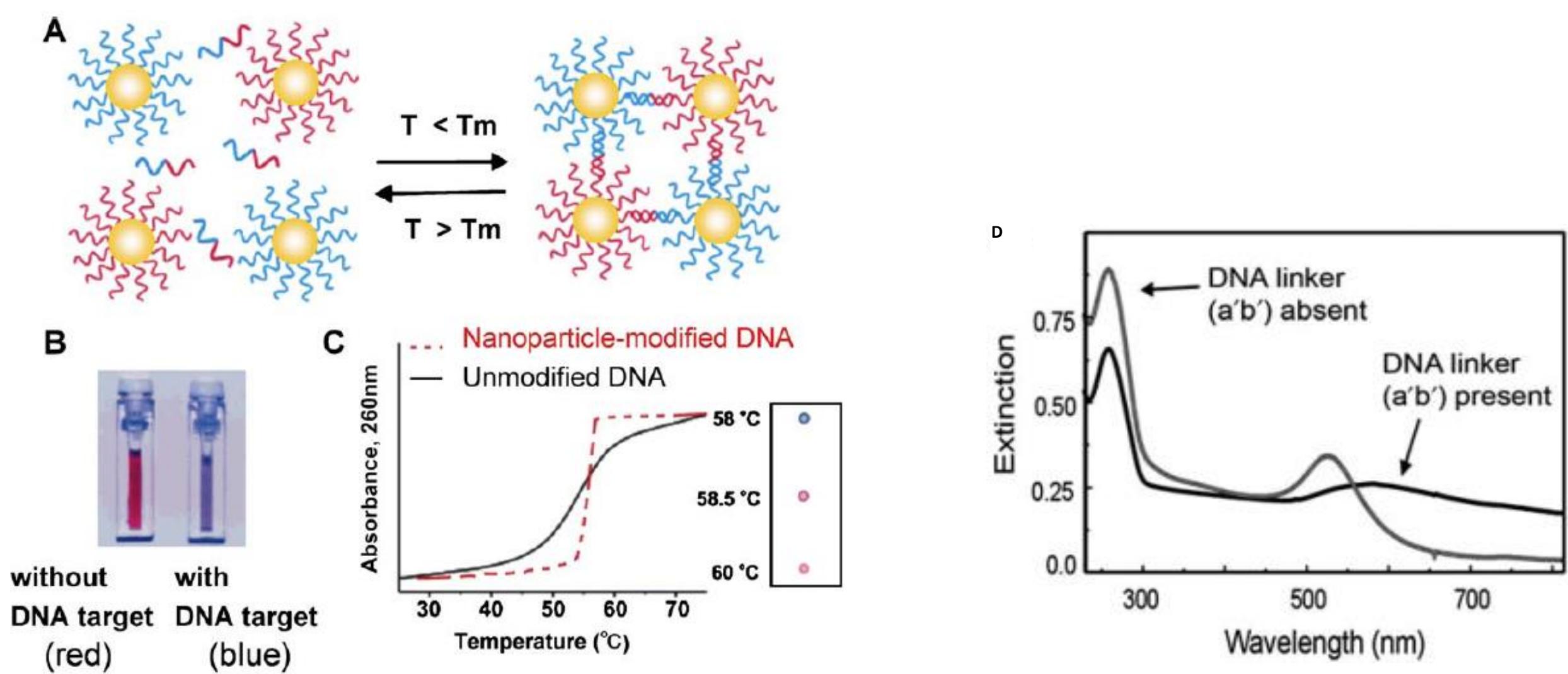


Fig. 12.1 (A) DNA-AuNPs assembled using a complementary DNA linker. (B) 13 nm DNA-AuNPs appear red in color without linker DNA and turn blue when linker DNA induces nanoparticle assembly. (C) Melting transition of unmodified duplex DNA (black) and DNA linked DNA-AuNPs (red). (D) Extinction spectrum of dispersed and assembled DNA-AuNPs.

(Reproduced with permission from C. A. Mirkin et al., *Nature* 1996, 382, 607–609.) (Adapted from N. L. Rosi and C. A. Mirkin, *Chem. Rev.* 2005, 105, 1547–1562.) **C.S. Thaxton et al., *Clinica Chimica Acta* 363 (2006) 120–126.**

□ **Molecular plasmonic ruler.** (Alivisatos' group (UC Berkeley) demonstrated the use of plasmonic ruler.)

- ❖ Color effect on directed assembly of DNA-functionalized gold and silver nanoparticles.
- (a) First, nanoparticles functionalized with streptavidin are attached to the glass surface coated with BSA-biotin (left).
- Then, a second particle is attached to the first particle (center), again via biotin-streptavidin binding (right). The biotin on the second particle is covalently linked to the 3' end of a 3-3 base pair long ssDNA strand bound to the particle via a thiol group at the 5' end. Inset: principle of transmission darkfield microscopy.
- (b) Single silver particles appear blue (left) and particle pairs blue-green (right). The orange dot in the bottom comes from an aggregate of more than two particles.
- (c) Single gold particles appear green (left), gold particle pairs, orange (right). Inset: representative transmission electron microscopy image of a particle pair to show that each colored dot comes from light scattered from two closely lying particles, which cannot be separated optically.

- (d) Representative scattering spectra of single particles and particle pairs for silver (top) and gold (bottom).
- Silver particles show a larger spectral shift (102 nm) than gold particles (23 nm), stronger light scattering, and a smaller plasmon line width.
- Gold, however, is chemically more stable and is more easily conjugated to biomolecules via –SH, –NH₂ or –CN functional groups.
- When *DNA hybridization takes place* the *inter-particle bond becomes rigid/stronger* and the *inter-particle distance increases* compared to the flexible single DNA strand connecting the two particles.
- As *the interparticle distance increases only a few nm*, there is *a clear blue shift* of the SPR band.
- *By measuring this SPR band shift, one could measure small (a few nm) changes in the distance during an interaction process or between two species.*

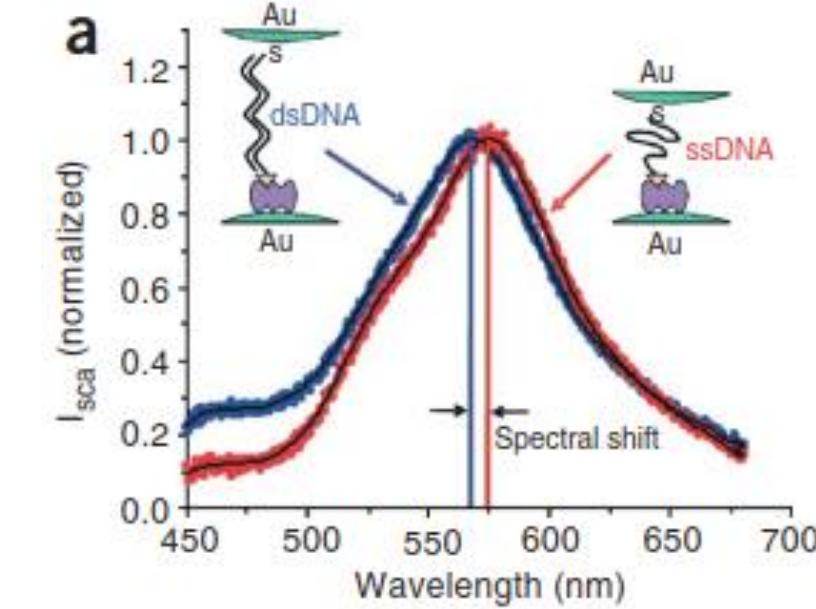
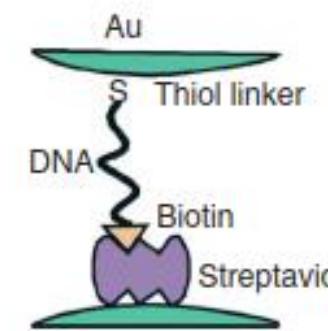
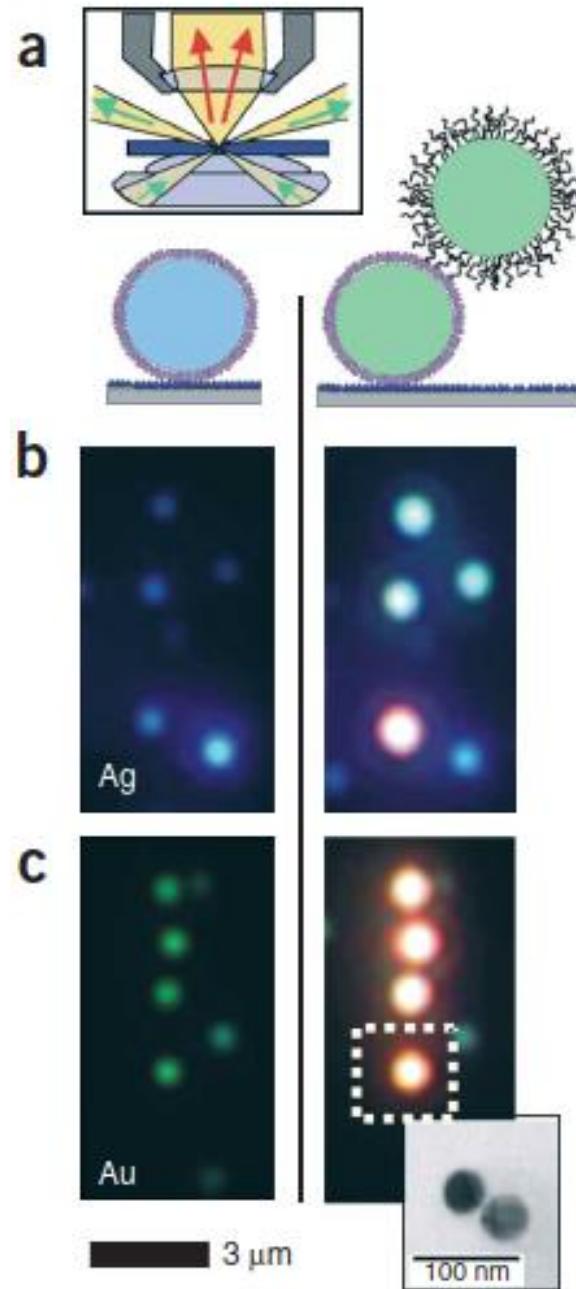
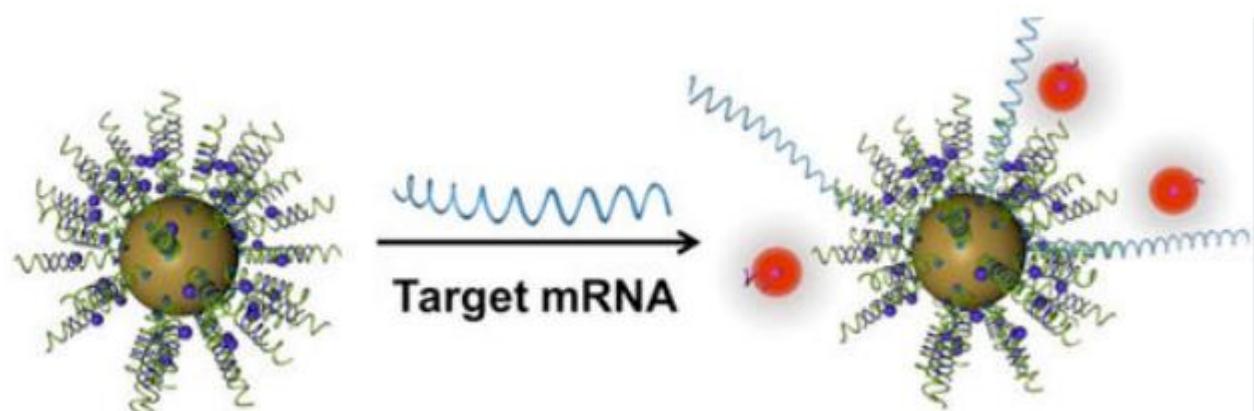


Figure 3. Spectral shift upon DNA hybridization.

(a) Example of a spectral shift between a gold particle pair connected with ssDNA (red) and dsDNA (blue). The shift is clearly visible.

- Subsequent research has developed sophisticated **diagnostic and therapeutic ("theranostic")** applications for these spherical nucleic acid particles. These particles easily penetrate cell membranes and can report on the chemistry happening inside living cells.
- An important property of gold nanoparticles in these applications is their ability to quench the fluorescence of reporter molecules that are near their surface. Nucleic acid strands that contain a hairpin loop can position fluorescent molecules near the gold surface, where their ***fluorescence is turned off by nanoparticle quenching***.
- Hybridization of these sequences to target RNA or DNA causes the ***fluorescence to turn on by moving the fluorescent molecule away from the nanoparticle surface***. These so called "nanoflares" can thus signal the up- or down-regulation of specific genes inside cells.
- Nanoflares are the basis of the Verigene System, developed and commercialized by Nanosphere, Inc. to detect markers for infectious diseases and cancers.

General schematic of nanoflare-based detection.



Plasmonic photothermal therapy (PPTT)

The use of heat has become one of the major methods for tumor therapy since its ancient usage in 1700 BC when a glowing tip of a firedrill was used for breast cancer therapy. Later heating sources ranging from radio-frequency to microwaves as well as ultrasound waves were introduced to induce moderate heating in a specific target region, which is termed as **hyperthermia**.

Hyperthermia is commonly defined as heating tissue to a temperature in the range 41–47°C for tens of minutes.

Tumors are selectively destroyed in this temperature range because of their reduced heat tolerance compared to normal tissue, which is due to their poor blood supply.

Hyperthermia causes irreversible cell damage by loosening cell membranes and denaturing proteins. But the applications of the heating sources conventionally employed for hyperthermia are limited because of their damage to surrounding healthy tissues.

A revolution in cancer therapy has taken place by the emerging use of laser light to achieve controlled and confined thermal damage in the tumor tissue. Laser, the acronym for light amplification by the stimulated emission of radiation, is an optical source that emits photons in a coherent and narrow beam.

The use of lasers, over the past few decades, has emerged to be highly promising for cancer therapy modalities, most commonly the **photothermal therapy** method, which employs light absorbing dyes for achieving the photothermal damage of tumors, and the **photodynamic therapy**, which employs chemical photosensitizers that generate singlet oxygen that is capable of tumor destruction.

However, recent advances in the field of nanoscience have seen the emergence of noble metal nanostructures with unique photophysical properties, well suited for applications in cancer phototherapy.

Noble metal nanoparticles, on account of the phenomenon of **surface plasmon resonance**, possess strongly enhanced visible and near-infrared light absorption, several orders of magnitude more intense compared to conventional laser phototherapy agents.

The use of plasmonic nanoparticles as highly enhanced photoabsorbing agents has thus introduced a much more selective and efficient cancer therapy strategy, viz. **plasmonic photothermal therapy (PPTT)**.

The synthetic tunability of the optothermal properties and the bio-targeting abilities of the plasmonic gold nanostructures make the PPTT method furthermore promising.

The usefulness of the PPTT method with gold nanospheres coupled with visible lasers and gold nanorods and silica–gold nanoshells coupled with near-infrared lasers have been shown both *in vitro* and *in vivo*.

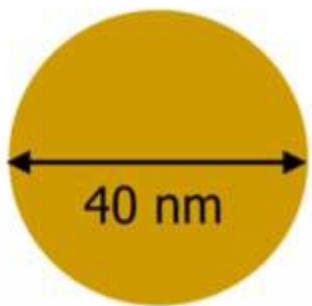
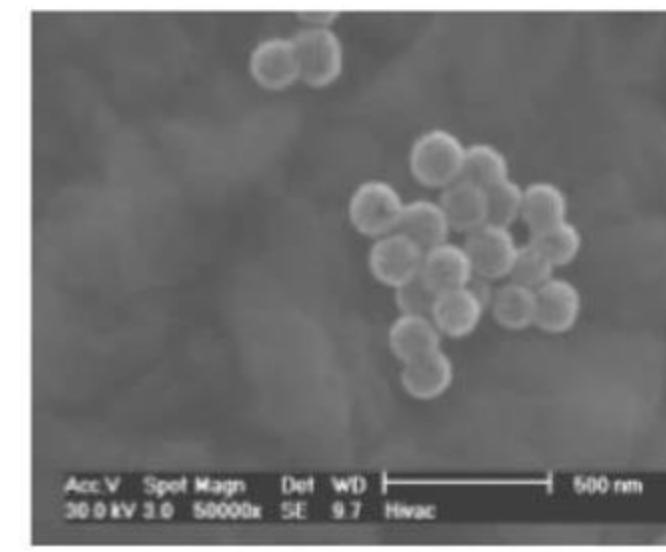
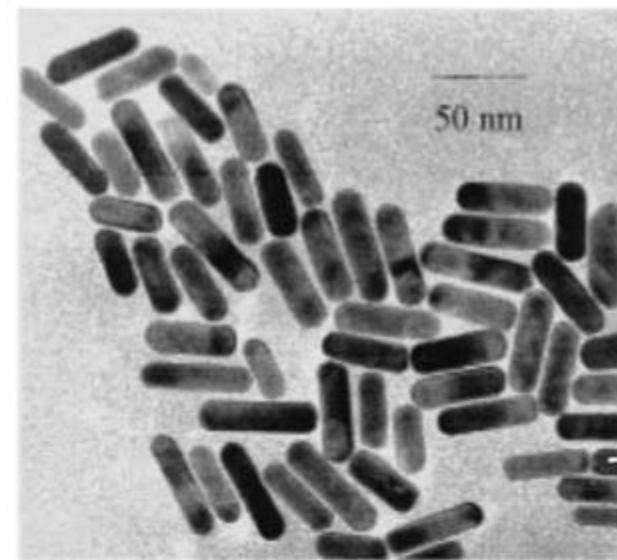
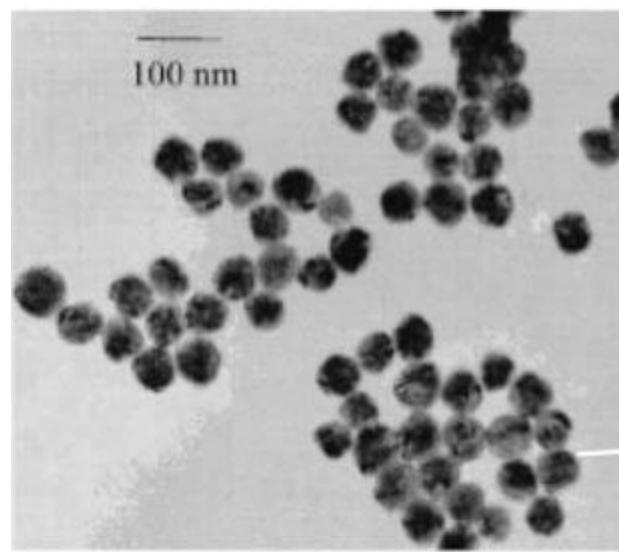
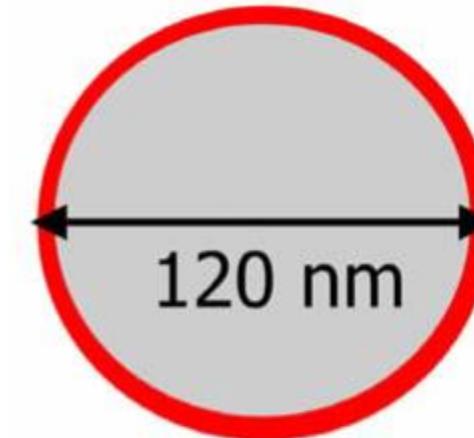
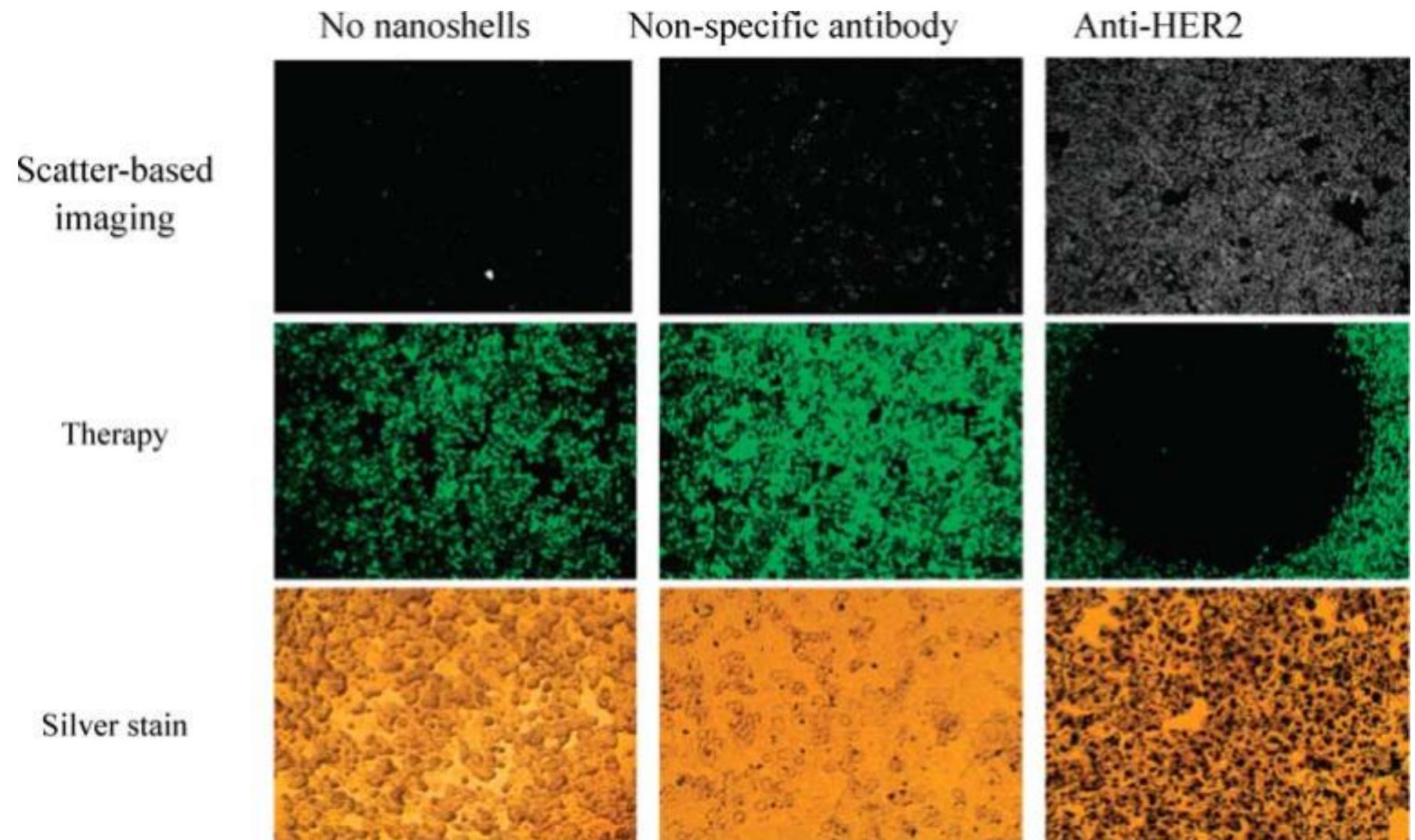
a**b****c**

Fig. 1 Plasmonic gold nanostructures commonly used for PPTT. (a) Nanospheres (transmission electron microscopy [TEM] image); (b) nanorods (TEM image); (c) Nanoshells (TEM image)

Fig. 6 Selective PPTT for cancer cells by using anti-Her2 antibody conjugated gold nano-shells. Only the cells incubated with anti-Her2 anti-body conjugated gold nano-shells are damaged under NIR Irradiation. Here an active targeting done using antibody-conjugated nanoshells. In the antibody case, gold nanoshells conjugated through PEG linkers to anti-Her2 antibodies were employed for targeting breast cancer cells. A diode laser at 820 nm was used for photothermal heating (7 min) of the labeled cells.



Only the cancer cells incubated with the antibody conjugated gold nanoshells were damaged under the laser irradiation. It was shown that NIR light of 820 nm at 4 W/cm^2 caused irreversible tumor tissue damage. Most notably, these studies show that laser dosages required to induce tissue damage using the plasmonic gold nano-structures are 10- to 25-fold lower than those used in studies employing photoabsorbing dyes such as indocyanine green dye.

□ Enhanced Local Field and Surface-enhanced Spectroscopies

- In the dipole approximation, the Mie theory also predicts that the incident radiation induces a constant electric dipole moment inside the sphere, proportional to the amplitude of the light electromagnetic field (E_0). As a consequence, the local electric field on the sphere surface (i.e., located within a few nanometers from the sphere) becomes equal to:

$$E_{loc} = \frac{3\epsilon}{\epsilon + 2\epsilon_m} E_0$$

where ϵ is the complex dielectric constant of the metal and ϵ_m is the dielectric constant of the surrounding medium ($\epsilon_m = n_m^2$ where n_m is the refractive index of the (nonabsorbing) medium).

- ***Under the resonance condition***, when $\epsilon = -2\epsilon_m$, E_{loc} is strongly enhanced with respect to the far field. This ***huge increase in the local field around metal nanoparticles*** (or metal nanostructures) is the basis of the surface-enhanced sensing applications, such as ***surface-enhanced Raman scattering (SERS)*** and surface-enhanced fluorescence (SEF) spectroscopy, which will be described later.

Local Field Effect on Raman Scattering and Fluorescence

- In the surface-enhanced Raman spectroscopy, the *scattering of incoming light by an analyte molecule is significantly increased by the plasmon resonance*.
- SEF involves the *increase of fluorescence emission of suitable chromophores in the presence of a plasmonic structure*. This is also called *metal-enhanced fluorescence (MEF)*, and devices based on such phenomenon are called MEF sensors.

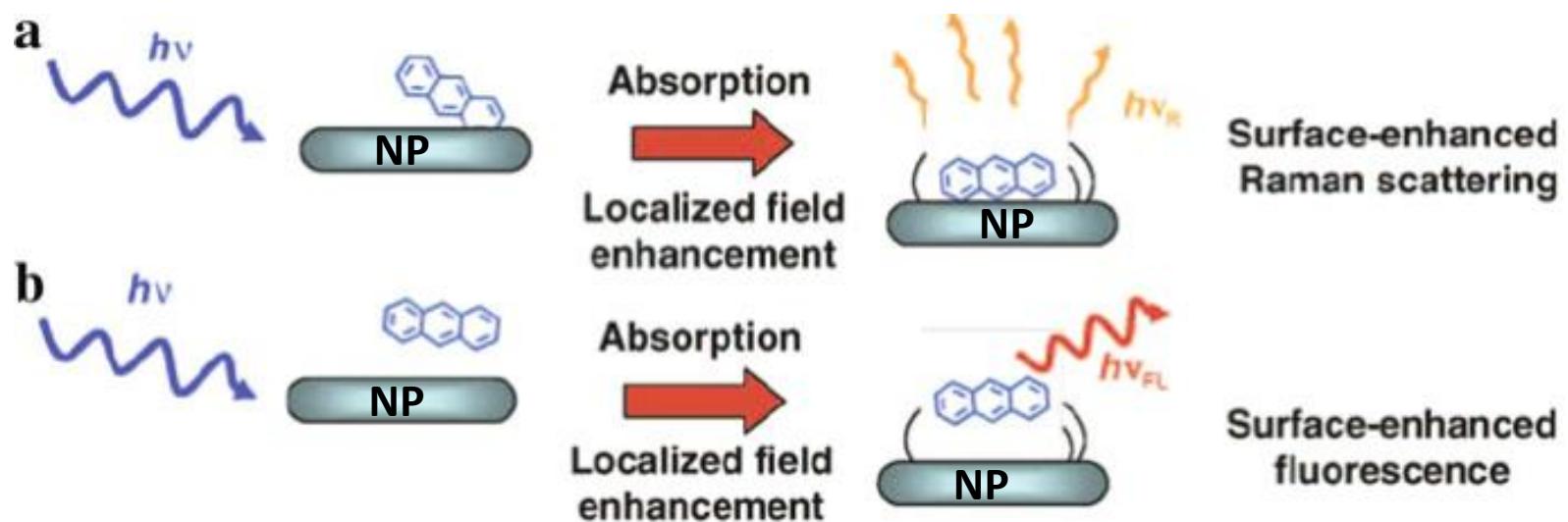


Fig. 7.27 Schematic showing surface-enhanced Raman scattering $h\nu_R$ and surface-enhanced fluorescence $h\nu_{FL}$. Photons are indicated by $h\nu$. (Reprinted with permission. © 2005 Elsevier)

- Raman spectrometry is a technique in which a much higher energy radiation is applied to the sample, so molecules initially in both upper and lower energy levels are promoted, and then fall back. If they fall back to the higher level, a lower frequency radiation is emitted, called *Stokes Raman scattering*, whereas if they fall back to the higher level it is *Anti-Stokes Raman scattering*.
- If the exciting radiation is **re-emitted unchanged**, this is **Rayleigh scattering**.
- As shown in Figure 12.24, the difference or Raman shift corresponds to ΔE .
- The electrical field associated with the electromagnetic radiation will interact with the molecule to change its electrical properties. Some molecules (for example, HCl) have **a dipole moment due to charge separation** and will interact with the field. Others may acquire a dipole when they vibrate. For example, methane, CH_4 , has no dipole, but when one of the CH bonds stretches, the molecule will develop a temporary dipole.
- Even if the molecule does not have a dipole, the electric field, E , may **distort the electron distribution and polarize** the molecule: $\mu_{\text{ind}} = \alpha E$ where μ_{ind} is the dipole induced by the field, E , and α is the polarizability of the molecule.
- The rules governing transitions in the infrared region of the spectrum require that, **in order to absorb**, the dipole moment of the molecule must change during the vibration. Such vibrations are said to be **IR active**.
- For transitions to be **active in the Raman** region, it is required that **the polarizability must change** during the vibration. The transitions are then **Raman active**, or **R active**.

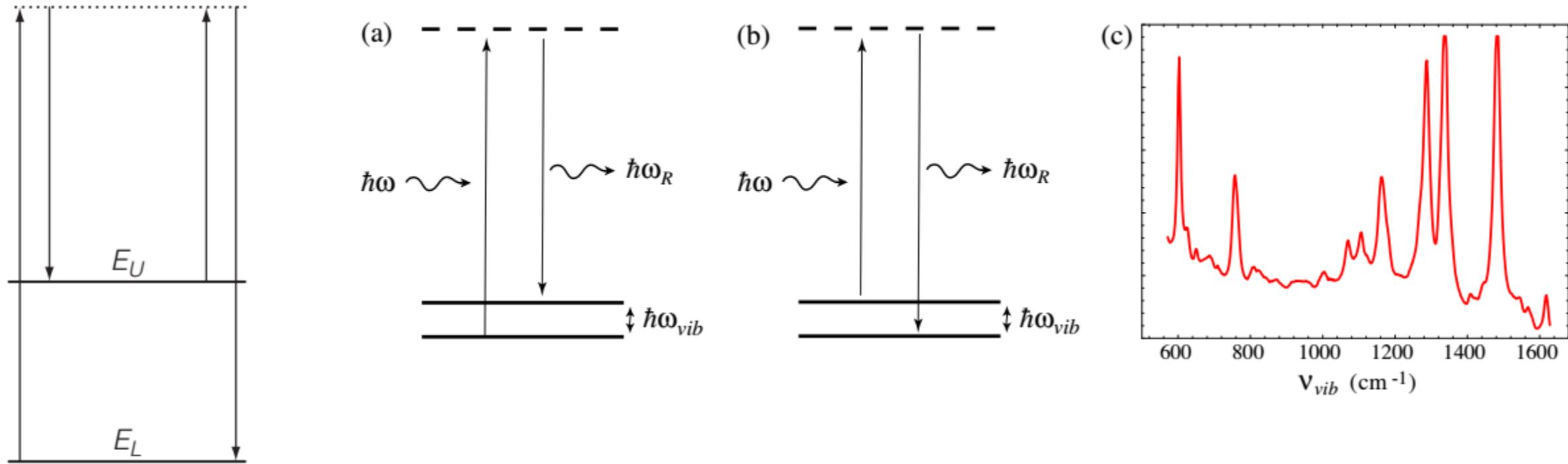


Figure 12.24: Raman scattering refers to the spectroscopic process in which a molecule absorbs a photon with frequency ω and subsequently emits a photon at a different frequency ω_R which is offset with respect to ω by a vibrational frequency ω_{vib} of the molecule, i.e. $\omega_R = \omega \pm \omega_{vib}$. Absorption and emission are mediated by a virtual state, i.e. a vacuum state that does not match any molecular energy level.

(a) If $\omega > \omega_R$ one speaks of **Stokes** Raman scattering, and (b) if $\omega < \omega_R$ the process is designated as **anti-Stokes** Raman scattering. (c) Raman scattering spectrum representing the vibrational frequencies of Rhodamine 6G. The spectrum is expressed in wavenumbers $\nu_{vib}(\text{cm}^{-1}) = [1/\lambda(\text{cm})] - [1/\lambda_R(\text{cm})]$, with λ and λ_R being the wavelengths of incident and scattered light, respectively.

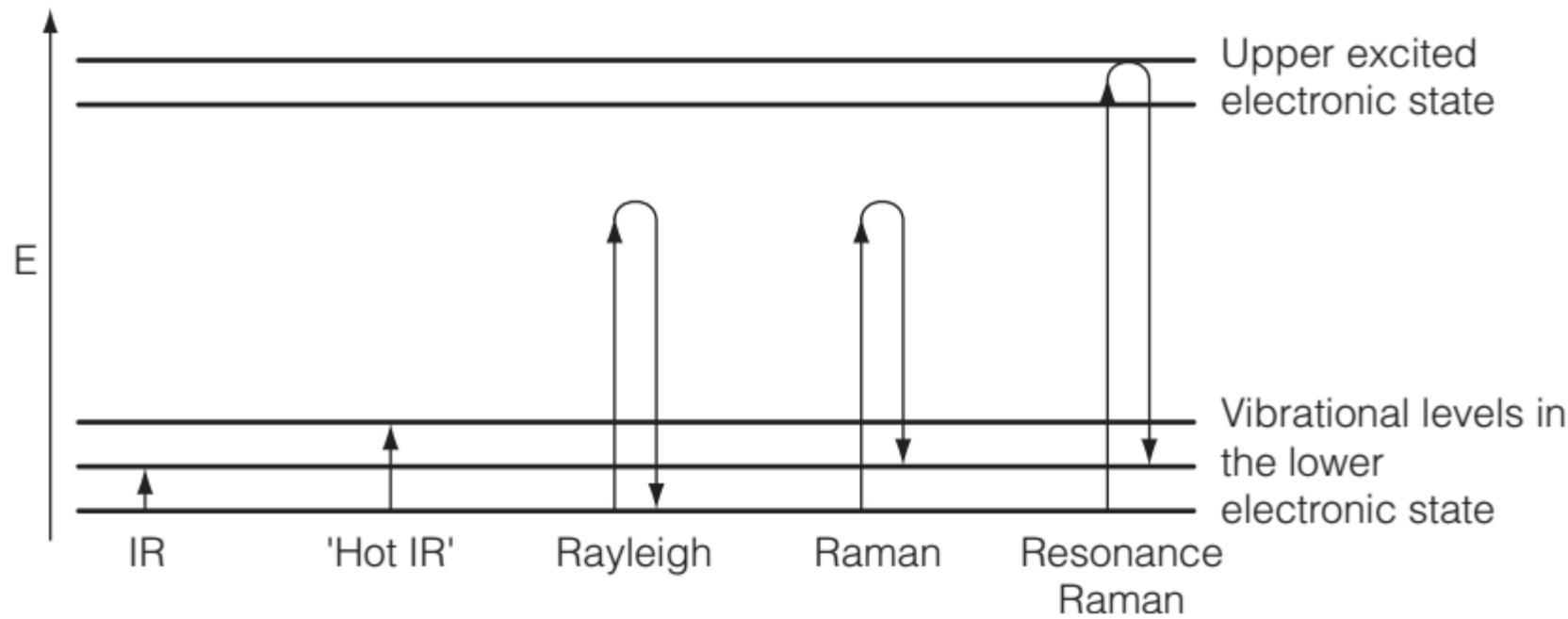


Fig. 1. Energy levels for IR and R transitions.

Raman scattering and Surface-enhanced Raman scattering

- The energy spectrum of molecular vibrations can serve as an unambiguous characteristic fingerprint for the chemical composition of a sample. Due to its sensitivity to molecular vibrations, *Raman scattering spectroscopy is a very important tool* for the analysis of materials. Raman scattering is named after Sir Chandrasekhara V. Raman who first observed the effect in 1928.
- *According to classical theory, a vibration is Raman active if the polarizability is changed during the vibration.*
- Although the *classical theory of Raman* scattering explains the *origin of the Stokes and anti-Stokes line*, they do *not account for their differences in intensities*.
- The quantum mechanical theory will provide this information and forms the basis for a complete treatment of all aspects of Raman scattering.
- The most important feature of quantum theory of radiation is that a concept of virtual energy can be introduced, which represents *an intermediate quantum state occupied by the combined system of the photon field and the medium* (Fig. 12.24).
- Raman scattering can be viewed as a mixing process similar to amplitude modulation used in radio signal transmission: the time-harmonic optical field (the carrier) is mixed with the molecular vibrations (the signal). This mixing process gives rise to scattered radiation that is frequency-shifted from the incident radiation by an amount that corresponds to the vibrational frequencies of the molecules (ω_{vib}).

- The vibrational frequencies originate from oscillations between the constituent atoms of the molecules and, according to quantum mechanics, these oscillations persist even at ultralow temperatures. **Because the vibrations depend on the particular molecular structure the vibrational spectrum constitutes a characteristic fingerprint of a molecule.**
- Fig. 12.24 shows the energy level diagrams for Stokes and anti-Stokes Raman scattering together with an experimentally measured spectrum for Rhodamine 6G.
- *According to quantum mechanics, a vibration is Raman active if the polarizability is changed during the vibration.*
- The Raman scattering intensity is proportional to *the number of molecules illuminated*, the *intensity of incident light* and to $(\nu_0 - \nu)^4$.
- *The Raman intensity can therefore be increased by increasing the incident light intensity or by using incident light of higher frequency, ω_0 (shorter wavelength).*
- It is indeed the development of more sensitive and cost-effective Raman instruments that was delayed until the advancements in laser and detector technology.
- This detection sensitivity was significantly improved in the early 1960s, when the laser was invented and then used as an ultra-intense light source for Raman spectroscopy.
- With the recent advances in laser and detector technology and optics, the cost and size of Raman spectrometers have significantly reduced without the sacrifice of sensitivity.

- It is not the purpose of this section to go into the details of Raman scattering but it is important to emphasize that **Raman scattering** is an *extremely weak effect*. The Raman scattering cross-section is typically 14 – 15 orders of magnitude smaller than the fluorescence cross-section of efficient dye molecules.

□ **Raman Scattering vs. SERS: WHY SERS?**

- In infrared spectroscopy, it can be shown that the intensity of a mode is proportional to the square of the scalar product of the **electric field (E)** vector of the incident wave with the derivative of the **dipole moment (μ)** vector:

$$I \propto \left(\frac{\partial \mu}{\partial q} \cdot E \right)^2 = \left(\frac{\partial \mu}{\partial q} \right)^2 E^2 (\cos \theta)^2 , \quad (9.51)$$

where θ is the angle between the exciting electric field and the direction of the vector $\partial \mu / \partial q$.

- A mode will be *more intense* as the term $\partial \mu / \partial q$ increases, but also as the electric field becomes more closely aligned with the direction of the derivative of the dipole moment.
- Owing to the sensitivity of vibrational spectroscopy to the force constants between atoms, these *methods are often used to characterize molecules*, but also to *observe the changes they undergo when they interact with their surroundings*.
- Moreover, in ordered systems, these methods can be used to *determine the orientations* of molecular groups.

□ WHY SERS? (contd.)

- Because *Raman scattering refers directly to typical vibrational frequencies of the molecule, each Raman spectrum determines in a univocal way a specific molecule.*
- For this reason, the *employment of Raman spectroscopy is very interesting in sensing.*
- Unfortunately, the *Raman scattering intensity is very low with respect to the incident light.*
- *Raman scattering intensity depends on the incident laser intensity and the number of the probed molecule (N), on the analyte Raman cross section (σ_R):*

$$I_R(v_s) \propto NI(v_0)\sigma_R \quad (7.12)$$

where v_s is the Stokes (or anti-Stokes) line frequency.

- Raman scattering is a two-photon process occurring at a time scale of ca. 10^{-12} s; and σ_R is usually very low, ranging between 10^{-25} and 10^{-30} cm^{-2} .
- The σ_R (Raman cross-section) of a molecule for such a process is about 10^8 and 10^{10} times smaller than those of **infrared (IR)** and **fluorescence processes**, respectively.
- When compared to a *fluorescence cross-section*, whose typical value is between 10^{-17} and 10^{-16} cm^2 , Raman scattering is rather weak.

□ WHY SERS? (contd.)

- This optical quality is not enough for lower detection limits in analytical applications.
- Since *Raman scattering is inherently weak*, therefore, *a large number of molecules* in Raman experiments are necessary to achieve the *same signal level in fluorescence*.
- As *Raman technique presents low sensitivity*, the *measurement of Raman scattering requires a huge quantity of analyte, a powerful light source and very sensitive detectors*.
- The *LSPR of the nanoparticles can boost the Raman signal intensity* dramatically for molecules of interest near the surface of the nanoparticle. *In order to maximize this effect, a nanoparticle should be selected with its resonant wavelength falling in the middle of the incident and scattered wavelengths*.
- ✓ The overall intensity enhancement of SERS can be as large as a factor of 10^6 , with the *surface plasmon resonance responsible for roughly four orders of magnitude of this signal increase*. The other two orders of magnitude have been attributed to *chemical enhancement* mechanisms arising from charge interactions between the metal particle and the adsorbate or from resonances in the adsorbate alone, as discussed above.
- ✓ The *field enhancement associated with surface plasmons*, as described above, has hence been extensively explored *for increasing the interaction-strength between a molecule and optical radiation*. The most prominent example is **surface enhanced Raman scattering (SERS)**.

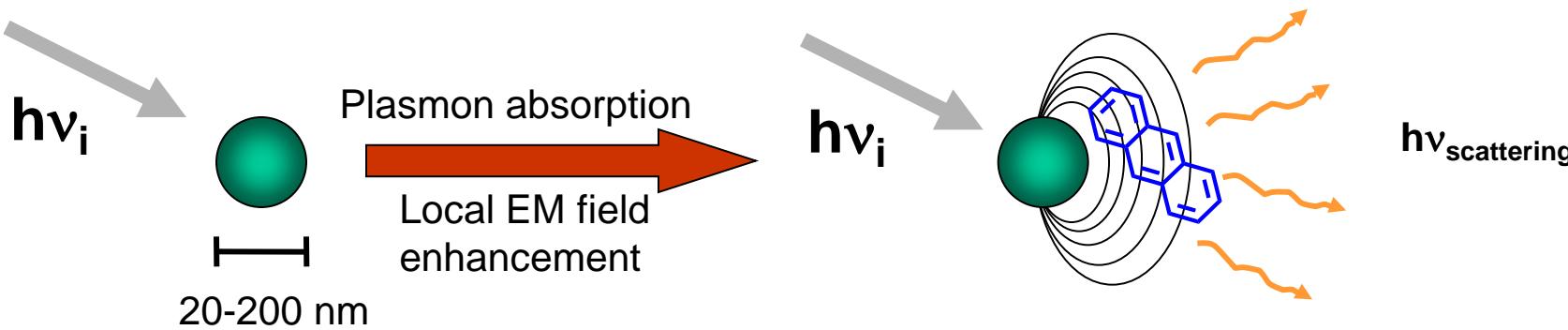
□ **Surface-enhanced Raman scattering (SERS)**

- The **major breakthrough with using Raman scattering** as a characterization and detection technique came with the discovery of ***the enhancement in scattering on roughened noble metal surfaces***.
- A discovery was made that the ***Raman cross-section of a material may be increased by a factor of 10⁷ or more*** by the presence of *metal colloid* or *roughened metal surface*. This effect is called ***surface-enhanced Raman scattering (SERS)***.
- In 1974, Fleischman observed the enhancement in Raman scattering of pyridine molecules on silver electrode surfaces. However, this enhancement was first explained with the increased pyridine concentration on a roughed electrode surface that resulted with an increased surface area. In 1977, Jeanmarie and Van Duyne and Albrecht and Creighton proposed two separate mechanisms, electromagnetic (EM) and charge transfer, respectively, to explain the increased Raman scattering. In 1978, Moskovits proposed a relationship between enhancement in Raman scattering and surface plasmons.

- In the following years, it was demonstrated that enhancement in Raman scattering did not occur only on the surface of silver, gold, and copper but also on other conductors, such as aluminum, indium, platinum, and transition metals.
- It is *now commonly accepted* that the *enhancement mechanism has two components* — *electromagnetic* (EM), which is related to the surface plasmons, and *chemical*, which is related to the charge transfer between the metal surface and adsorbed molecule.
- The contribution of the *EM enhancement* is much larger than the charge transfer that depends on the chemical structure of the molecule adsorbed onto the nanostructured noble metal surface.

Surface Enhanced Raman Scattering

SERS substrates: Roughened Au, Ag, Cu surfaces or Plasmonic NPs are mainly used



Incident electric field, E
Polarizability, α

$$I_{\text{Raman Scattering}} \propto (E^2 \cdot \alpha^2)$$

Enhanced local electric field (EM enhancement) and molecular polarizability (CHEM enhancement) contribute to the surface-enhanced Raman scattering (SERS)

- Enhancement Factor $\sim 10^{14} - 10^{15}$ reported.

SERS: *Enhancement Mechanisms*

- The intensity of normal Raman scattering from free molecules is determined by the first-order transition electric dipole, which depends on the **transition polarizability** of the molecule and the **electric field strength** of the exciting radiation.
- The origin of surface enhanced Raman scattering (SERS) must therefore be sought in enhancement either of the transition polarizability or of the electric field strength experienced by the molecules when adsorbed on certain types of surface.
- Classical electromagnetic theory indicates that the *molecule at the metal surfaces will experience a local electromagnetic field that is larger than that of the incident radiation.*
- The **extent of the enhancement depends** on a number of factors, including the **dielectric properties of the metal, the distance of the molecule from the surface, the orientation of the molecule, the wavelength of the exciting radiation, the morphology of the surface and the size and geometry of the nanostructure.**
- The **polarizability can also be changed as a result of electronic interaction between the molecule and the metal.**
- In some cases, **charge transfer may be observed**, leading to resonances different from that of the target molecule.
- The **optical response of a chemisorbed molecule may differ from that of a free molecule**, which may result in wavenumber shifts of those modes involving atoms bound to the metal surface. **The maximum enhancement will be expected with SERRS, when the wavenumber of exciting radiation approaches both an electronic transition of the molecule and the plasmon absorption wavenumber of the metal for LSPR to be excited.**
- Surface-enhanced Raman scattering (SERS) is based on the localized surface plasmon resonance phenomenon, which can greatly increase the Raman scattering cross-section of molecules located in the vicinity of a metallic nanostructure. This enormous signal amplification can be explained by an electromagnetic (EM) mechanism of SERS that is the defining feature of the effect and can provide enhancement of several orders of magnitude.

In the dipole approximation, the Mie theory also predicts that the incident radiation induces a constant electric dipole moment inside the sphere, proportional to the amplitude of the light electromagnetic field (E_0). As a consequence, the local electric field on the sphere surface (i.e., located within a few nanometers from the sphere) becomes equal to:

$$E_{loc} = \frac{3\epsilon}{\epsilon + 2\epsilon_m} E_0$$

Under the resonance condition, E_{loc} is strongly enhanced with respect to the far field. This huge increase in the local field around metal nanoparticles (or metal nanostructures, in a more general point of view) **is the basis for the sensing applications, which will be described in later Sections.**

The SERS phenomenon is a direct correspondence with the localized surface plasmon resonance (LSPR) producing an intense local electromagnetic (EM) field on the SERS-active nanostructures. SERS is primarily a phenomenon associated with the enhancement of the electromagnetic field surrounding a small metal objects optically excited near an intense and sharp dipole resonance. The enhanced re-radiated dipolar fields excite the adsorbate, and if the resulting molecular radiation remains at or near resonance with the enhancing object, the scattered radiation will again be enhanced. So, under appropriate circumstances, accumulated two-fold of electromagnetic enhancement will scale as E^4 .

The total SERS enhancement, E_{SERS} is then given by:

$$E_{SERS} = N \cdot \sigma_{ads}^R / A(v_L)^2 \cdot / A(v_S)^2 \cdot I(v_L)$$

where, σ_{ads}^R is the Raman cross-section of the molecule in contact with the nanostructure, and N is the number of molecules involved in the SERS process, $A(v_L)$ and $A(v_S)$ represent the *enhancement factors* for an excited source of intensity $I(v_L)$ and Raman scattered fields, respectively.

We can therefore identify two separate origins for the modification of the Raman signal: a change in Raman polarizability α , which we will refer to as a “**chemical Enhancement**”, and/or a change in local field E_{loc} , which corresponds to the ‘**electromagnetic (EM) enhancement**’!

In the case of surface-enhanced resonance Raman scattering, where both of these resonance (plasmon and molecular) conditions are fulfilled, the two enhancement mechanisms are multiplicative and can lead to large enhancement factors that often make it easier to detect a single molecule.

Such enhanced field can be exploited for any field dependent property study..... Particularly in the field of Raman spectroscopy this can result in enormous sensitivity enhancements. The enhancement factor (EF) (i.e., by how much the Raman signal can be amplified) can be large enough to allow, in many cases, the observation of single molecules — an interesting subfield of SERS in its own right.

The enhancement factor (*EF*) may be defined experimentally by the following relationship:

$$EF = \frac{I_{SERS}/C_{SERS}}{I_{RS}/C_{RS}}$$

where, I_{SERS}/C_{SERS} is the Raman scattering intensity per unit concentration due to SERS results and I_{RS}/C_{RS} is the normal Raman scattering intensity per unit concentration.

Because LSPR critically depends not only on the nature of the metal but also on architectures of metal nanostructures; and the preparation of substrates is central to gain a higher SERS activity. Different types of nanoparticles give rise to different Raman enhancement characteristics, as the amplification of Raman signals depends on the molecular coupling with localized electromagnetic excitation on the surface of metal nanostructures. Hence, optimizing and tuning of the SERS characteristics require an appropriate control of SERS substrates: size, shape, spacing between nanoparticles, functionalization of nanoparticles and the dielectric environment.

Nanoparticle optical properties are also sensitive to the *proximity* of other plasmonic materials. When two or more plasmonic nanoparticles are near each other (with edge-to-edge separations of one particle diameter or less) their surface plasmons couple as the conduction electrons on each particle surface collectively oscillate. This effect is similar to molecular orbital theory in that plasmon coupling results in the oscillating electrons assuming the lowest energy state, causing the plasmon resonance wavelength of the coupled particles to red-shift to longer wavelengths (lower energies). This coupling effect is responsible for the dramatic changes in the visible color of plasmonic nanoparticle solution when nanoparticles aggregate and also the basis of many different types of plasmonic nanoparticle sensors.

The Raman enhancement can be considerable, arising essentially from the creation of very strong electric fields at the interface of metal particles due to the *coupling of the fields between neighboring particles*. For this reason, surfaces must be prepared in a perfectly controlled way with regard to particle size and interparticle distances.

Figure 7 shows the near field coupling between NPs. Here, the restoring force acting on the oscillating electrons of each NP in the chain is either increased or decreased by the charge distribution of neighboring particles. Depending on the polarization direction of the exciting light, this leads to a blue-shift of the plasmon resonance for the excitation of transverse modes, Figure 7 (a), and a red-shift for longitudinal modes, Figure 7 (b).



Figure 7. Schematic of near-field coupling between metallic NPs for two different polarizations.

It is believed that the greatest enhancements ($\sim 10^{10}$) that enabled single-molecule detection only occurred at specific sites (junctions or gaps between two or more closely spaced nanoparticles) termed hot spots.

The finding that individual nanoshells can vastly enhance the Raman effect opens the door for biosensor designs that use a single nanoshell, something that could prove useful for engineers who are trying to probe the chemical processes within small structures such as individual cells, or for the detection of very small amounts of a material, like a few molecules of a deadly biological or chemical agent. Nanoshells are already being developed for applications including cancer diagnosis, cancer therapy, testing for proteins associated with AD, drug delivery, and rapid whole-blood immunoassays.

Although LSPR sensors can be used to monitor the binding of molecules to functionalized nanoparticle surfaces, extinction spectroscopy does not allow for specific identification of the chemical entity.

Vibrational spectroscopy, on the other hand, is capable of revealing molecular characteristics of the analyte. SERS shows a 10^6 - 10^{14} enhancement in effective Raman cross-section when the analyte is bound or close to the surface of plasmonic nanoparticles. SERS, similar to Raman scattering, is an inelastic scattering process in which photons incident on a sample transfer energy to or from the sample's vibrational or rotational modes. Individual bands in a SERS spectrum are characteristic of a specific molecular motion. As a result, each chemical entity has its own unique Raman signature.

SERS is an important technique that can display intrinsic interfacial sensitivity and selectivity.

There is an enormous interest to utilize surface-enhanced Raman scattering (SERS) in a variety of applications. This is mostly due to its sensitivity and power to provide very specific chemical information about the molecule or molecular structure of interest in a short time without significant sample preparation steps. Due to the fact that this information can be used for detection and identification besides characterization, it has become an important analytical technique in recent years and it is considered one of the most sensitive diagnostic tools available to the scientist.

Silver and gold are usually used because they yield the largest enhancement. SERS has also been demonstrated using copper and several other metals like indium and the alkali metals. Both visible and near-infrared excitation can be used for SERS on silver. Red or near-infrared excitation is required for SERS on gold or copper. By combining SERS enhancement with resonance enhancement (surface enhanced resonance Raman scattering - SERRS), Raman cross section has been increased by a factor of 10^{11} , making single molecule Raman scattering possible. In 1997, by using SERS, single molecules on nanoparticles were successfully detected.

SERS has been used to study quantitative and qualitative study in biological systems. Recent years have seen an explosion in the use of Raman spectroscopy for biological purposes such as blood analyte detection and cellular examination, pharmaceutical product design and production processes. In addition, in forensic sciences for the unambiguous identification of unknown substances, it has also biomedical applications to demonstrate the sensitivity to distinguish between cancerous, pre-cancerous and normal tissues; and its sensitivity to changes in cell metabolites and protein structures etc., which elevate it above competing spectroscopic techniques.

By combining SERS and LSPR spectroscopy, the binding of molecules can be confirmed on the nanosensors.

In the mid-1970s, SERS was discovered which impacted surface science and spectroscopy because of its extremely high surface sensitivity. Most chemical sensors rely on properties such as mass, fluorescence, or a refractive index, which are often not specific for the substance in question. In contrast, Raman spectroscopy offers rich molecular information, and thus provides unequivocal identification of chemical and biological materials of interest. The discovery of SERS has triggered many highly sensitive detection technology development in analytical chemistry, biomedical engineering, and life sciences.

Another important source of Raman signal enhancement is the molecular resonance effect, which is employed by laser excitation that falls within the envelope of an electronic transition of the molecular system, called resonance Raman scattering (RRS). In SERS experiments, enhancements typically up to 10^6 in the Raman signal can be obtained for molecules adsorbed on nanostructures of copper, silver, and gold.

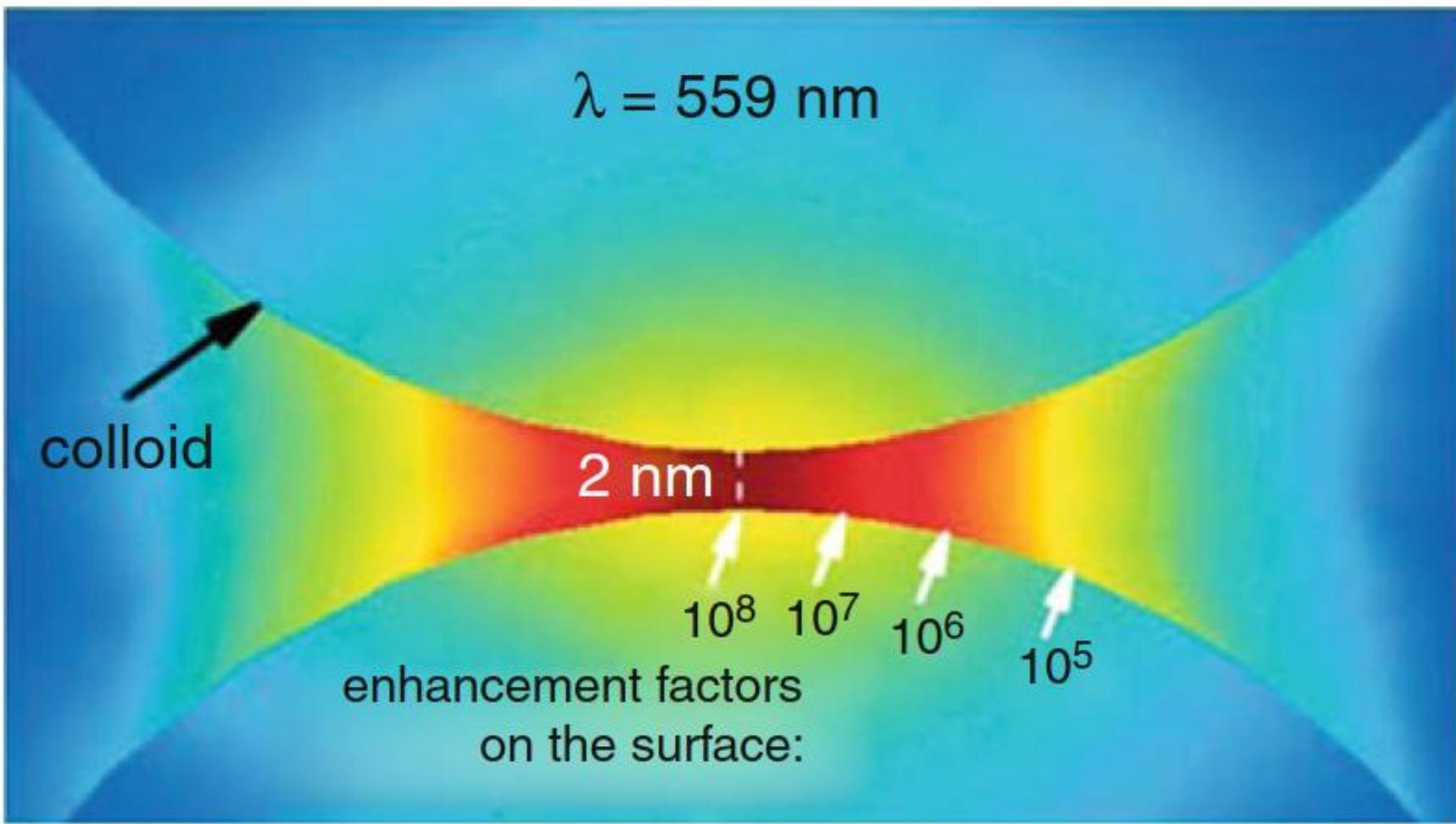
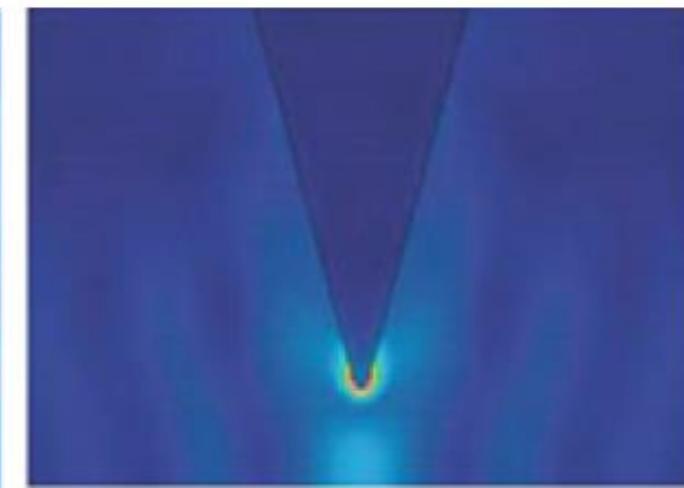
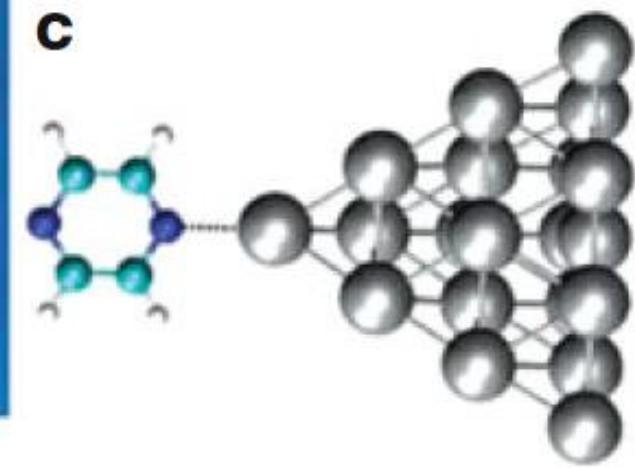
a**b****c**

Fig. 10.1 Examples of different types of generic hot spot: (a) The hot spot formed between two closely placed nanoparticles resulting from a coupled plasmon resonance, (b) The hot spot formed at a sharp geometrical feature and (c) surface complex formed when a molecule adsorbs strongly onto a metal surface.

Figure 10.1 summarizes the different types of generic hot spots that have been proposed in the literature. ***These include (a) those formed between two closely spaced nanoparticles by the coupled plasmon, (b) hot spots formed at sharp nanoscale geometrical features through the “lightening rod” effect, and (c) highly enhancing chemically active binding sites.***

The ambiguity in the exact enhancement mechanism at work within the observed hot spots and the number of active molecules, the magnitude of hot spot enhancement, and the lack of a robust method to define the single molecular signature have led to much debate within the literature. However, it is clear that the properties of any SERS active substrate where hot spots contribute to the observed signal will be completely dominated by them in the low concentration limits important for many proposed applications.

There is an enormous interest to utilize surface-enhanced Raman scattering (SERS) in a variety of applications. This is mostly due to its **sensitivity and power to provide very specific chemical information** about the molecule or molecular structure of interest in a short time without significant sample preparation steps. Due to the fact that this information can be used for detection and identification besides characterization, it has become an important analytical technique in recent years and it is considered one of the most sensitive diagnostic tools available to the scientist.

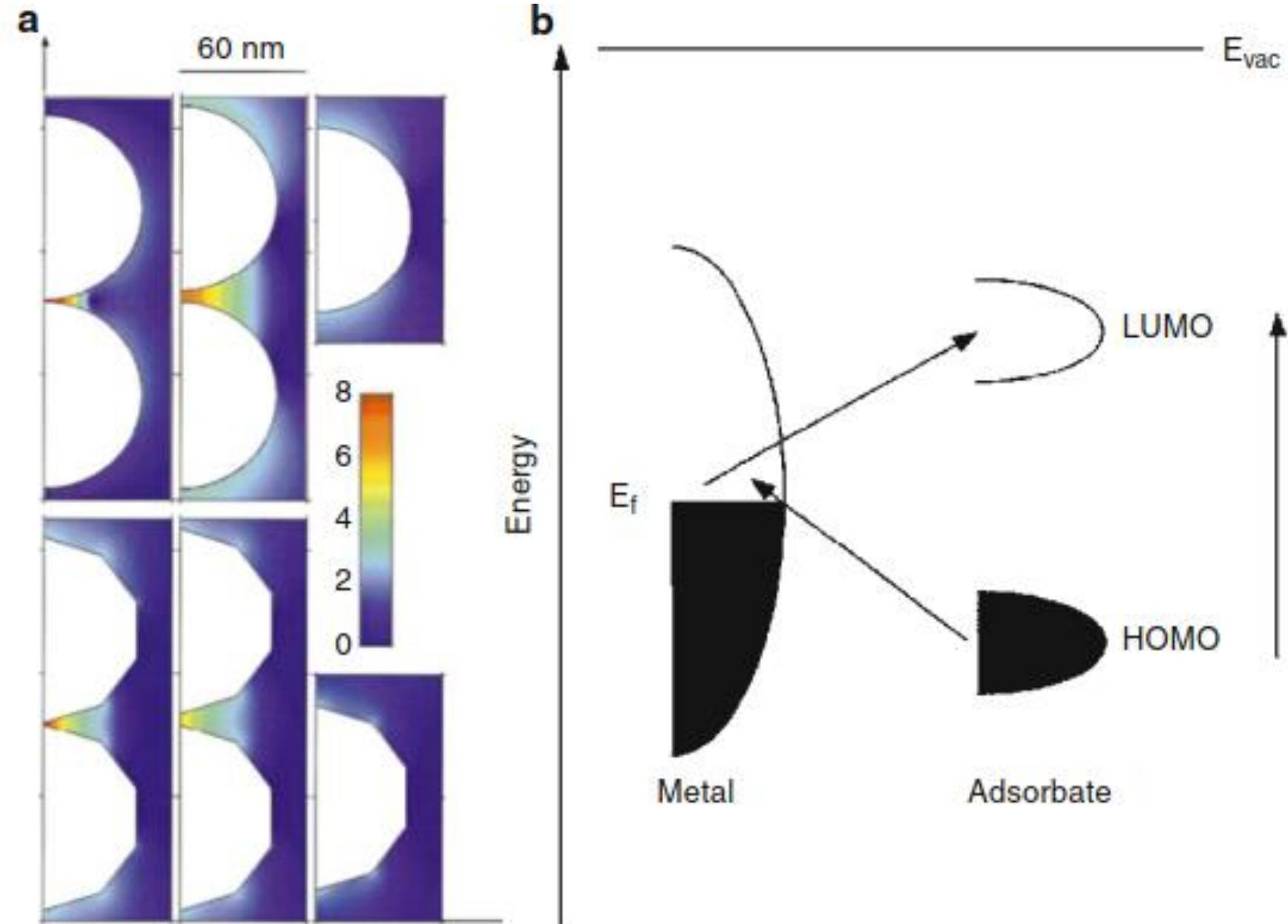
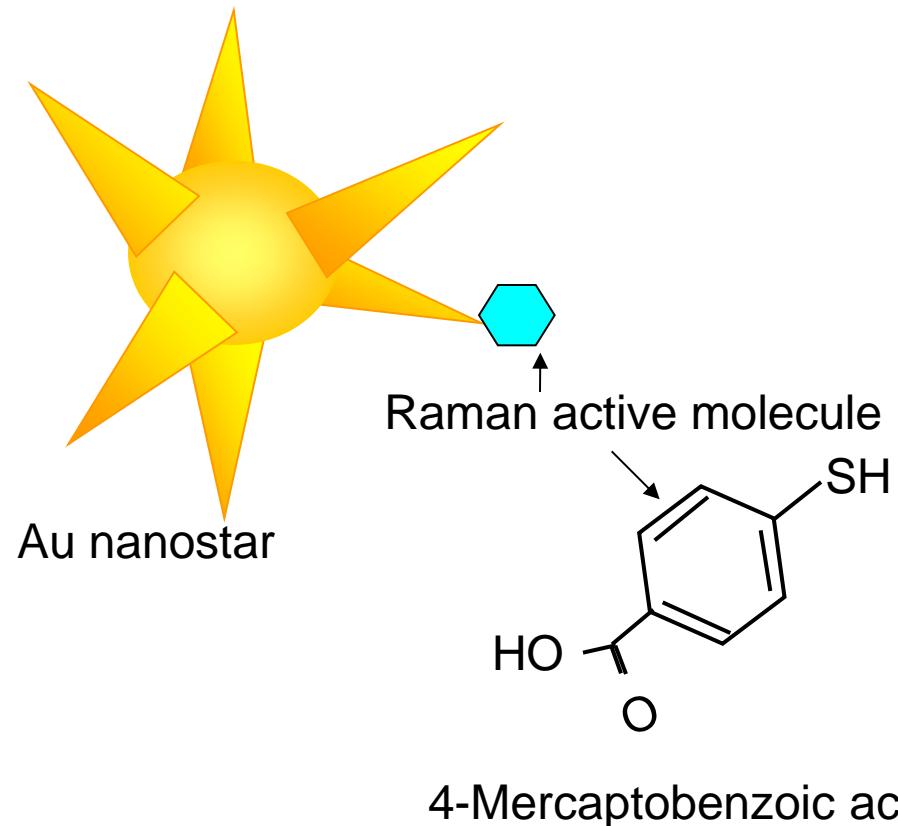


Fig. 11.4 Schemes demonstrating two SERS mechanisms. (a) Local field concentration near the gap between two particles. The white spheres and polygons are silver, and the color scale bar indicates the electro-magnetic field enhancement. The separation distance is 1 and 5.5 nm for the first and second columns, respectively. The wavelength of the incident field is 514.5 nm with vertical polarization, and (b) Possible charge transfer excitations between molecule and metal. The occupied and unoccupied molecular orbitals are broadened by the molecule-metal interactions. Metal-to-molecule and molecule-to-metal charge transfers are indicated by arrows.

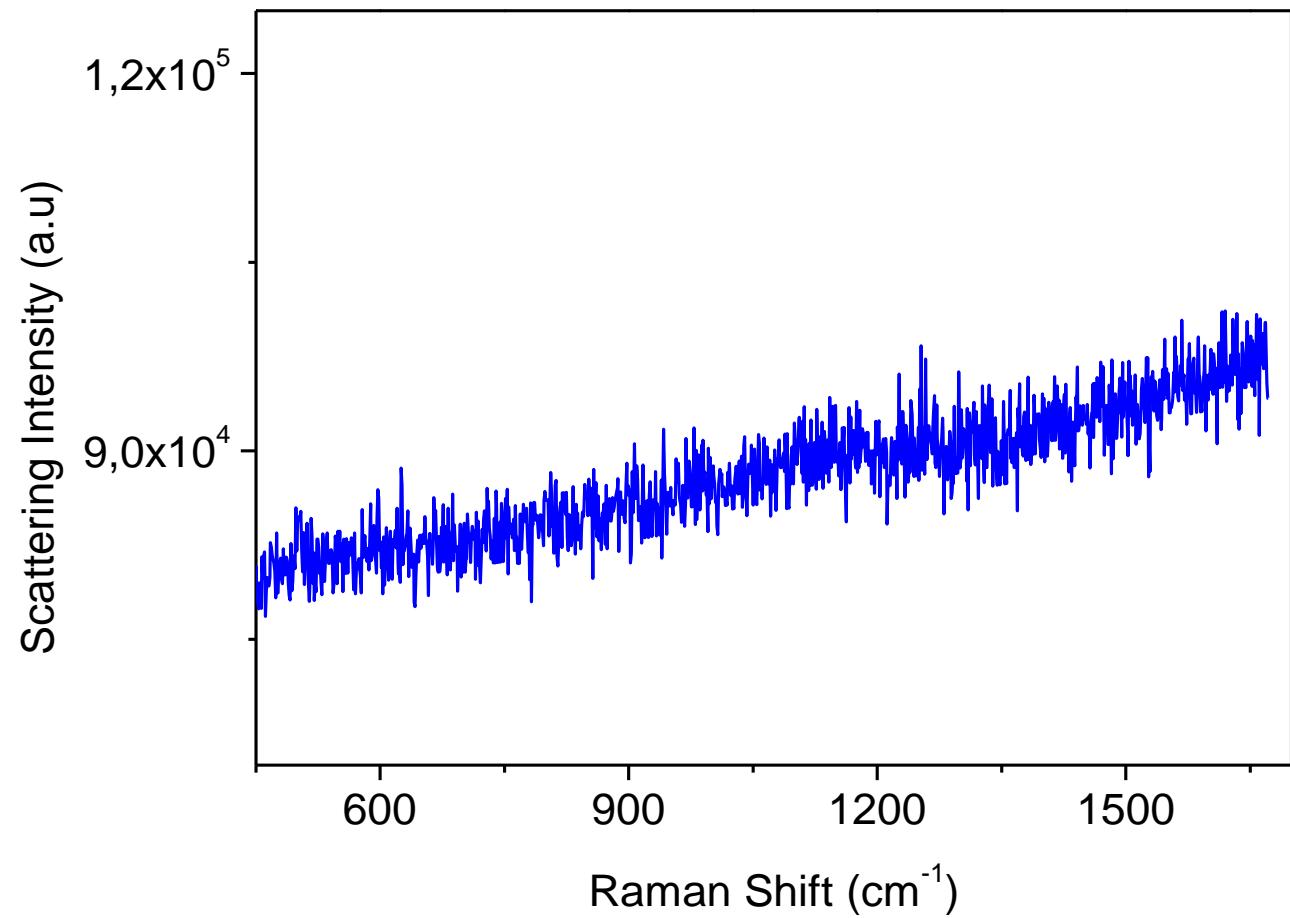
Surface Enhanced Raman Scattering (SERS)



SERS: Au Thin Film

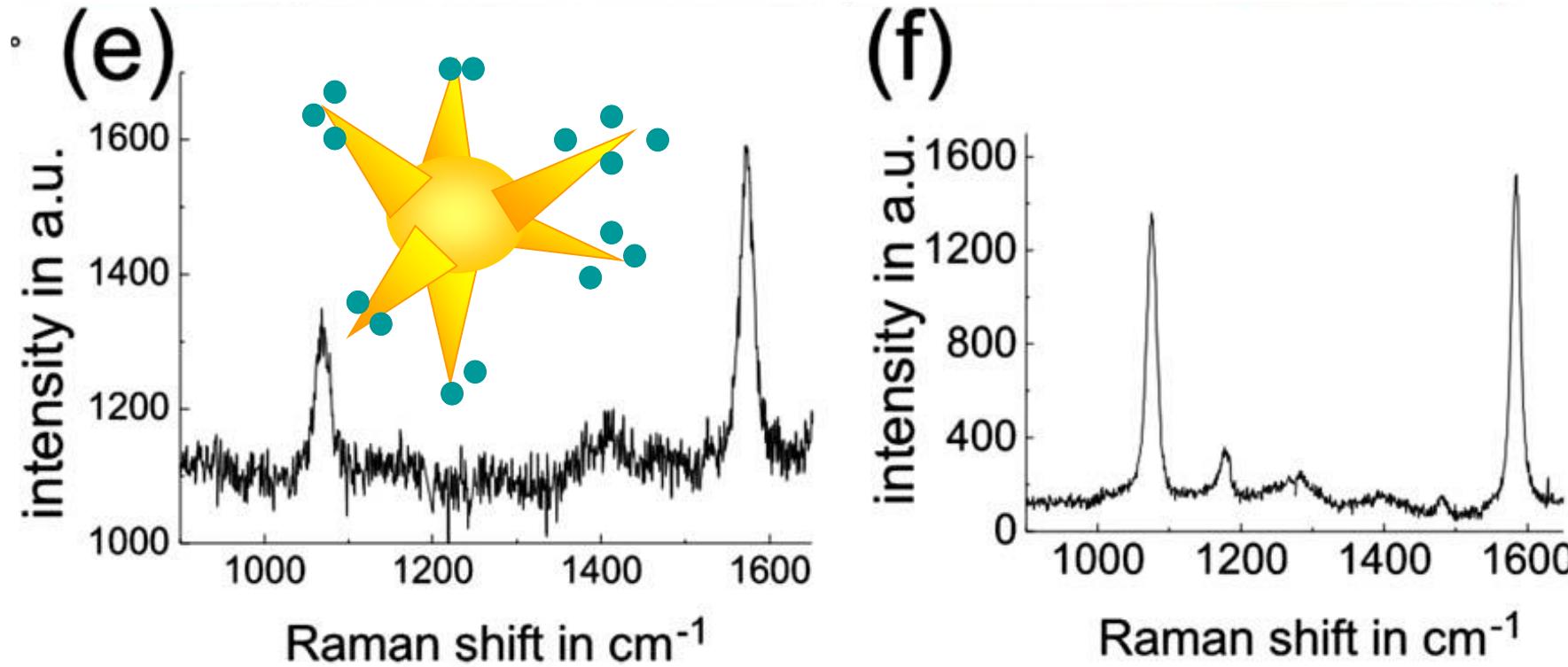


Au THIN FILM With 4-MBA



➤ Au Film **did not** enhance Raman Signal of 4-MBA!

Single Nanostar Enhances Raman Signal of 4-MBA !



(e) Raman spectrum from the **single** gold nanostar.

(f) Raman spectra of a thin multilayer film of ***densely packed nanostars*** coated with MBA SAMs.Raman Intensity (compare from the base) more for aggregated nanostar particles than the single nanostar.

SERS and the Detection of HIV-1 Virus

Ag nanoparticle-surface enhanced Raman scattering:

A DNA-detection SERS probe operating similar to the working principle of molecular beacons. Fig. 4.4 summarizes the working principle of the SERS probe.

The probe is composed of two parts — a stem and a loop.

While the stem part is complementary to each other, the loop is complementary to the target DNA.

The whole structure consisted of a 42-base-long hairpin and a 7-base-pair stem.

The stem was modified with rhodamine 6G (fluorophore) and hexanethiol at the 3' end and the 5' end, respectively.

When the oligonucleotide gets chemically attached to citrate-reduced silver nanoparticles through an Ag-S bond, the rhodamine 6G is brought close to the surface of silver nanoparticles since the stem part is in a naturally hybridized form. ***In the absence of the target DNA, a SERS signal from rhodamine 6G is recorded.*** However, when a *target DNA is present, the stem part is forced to open because the loop part is complementary to the target DNA; rhodamine 6G is removed from the silver surface as the stem part is opened and there is no SERS signal generated.*

The researchers demonstrated the detection of HIV-1 virus with this approach.

Figure 4.4 Detection of HIV-1: The SERS spectrum from the detection system.

(a) No target DNA sequence, higher Raman signal (top curve);

(b) a complementary HIV-1 DNA target, reduced Raman signal (positive diagnostic: middle curve);

(c) in the presence of a noncomplementary DNA target sequence (negative diagnostic: bottom curve).

Raman scattering intensity of Rhodamine 6G (RH-6G) molecule increases near the surface of the plasmonic nanoparticle. The Raman intensity signal reduces when RH-6G molecule moves away from the particle surface due to loop opening.

