Surface Plasmon Resonance

General Introduction

Based on a presentation of Steffen Jockusch; 07/15/07

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Plasmons:

- collective oscillations of the “free electron gas” density, often at optical frequencies.

Surface Plasmons:

- plasmons confined to surface (interface) and interact with light resulting in polaritons.
- propagating electron density waves occurring at the interface between metal and dielectric.

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Surface Plasmon Resonance:

- light (λ) in resonance with surface plasmon oscillation

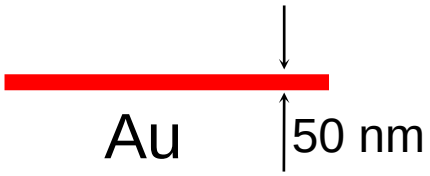
Requirements:

- Material with free electrons:

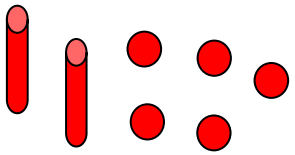
Metals	***plasma frequency***
Pb, In, Hg, Sn, Cd	UV
Cu, **Ag**, **Au**	VIS

- Surface (interface):

flat surfaces



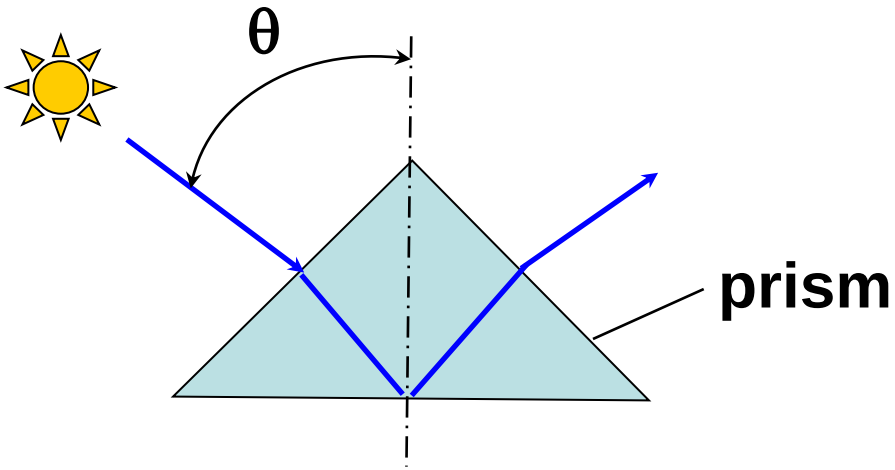
nanoparticles

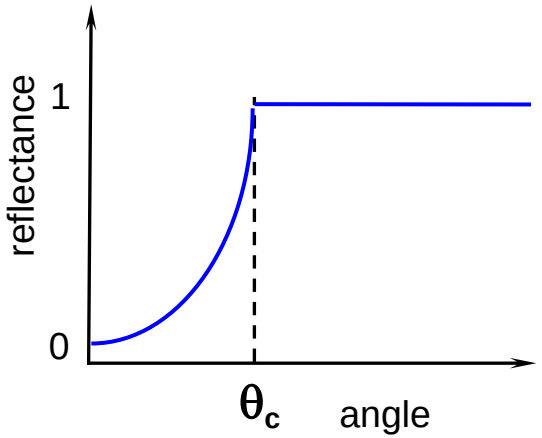


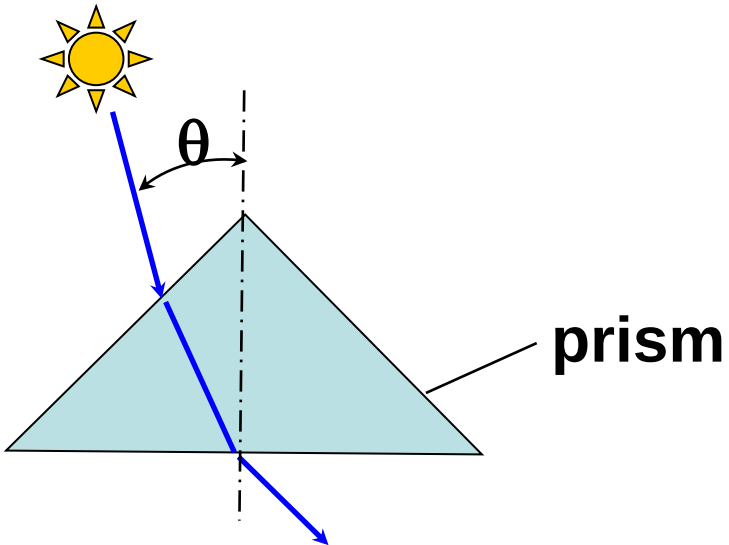
- Light: How to couple the photons to the surface?

Flat surface

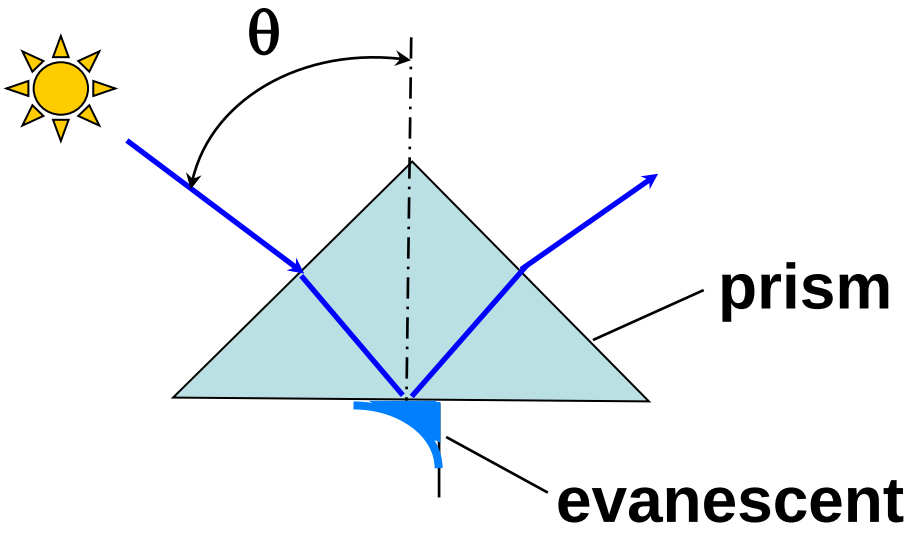
Total reflection on a prism

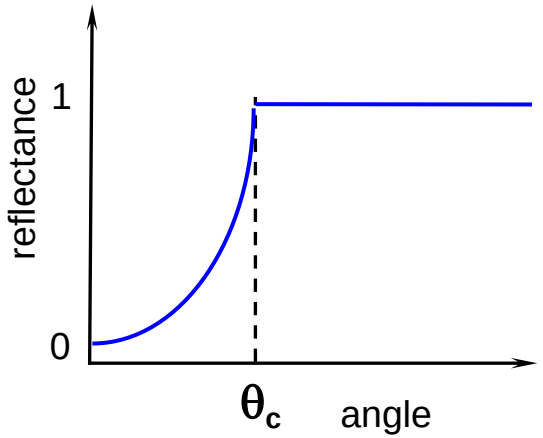






Evanescent Wave

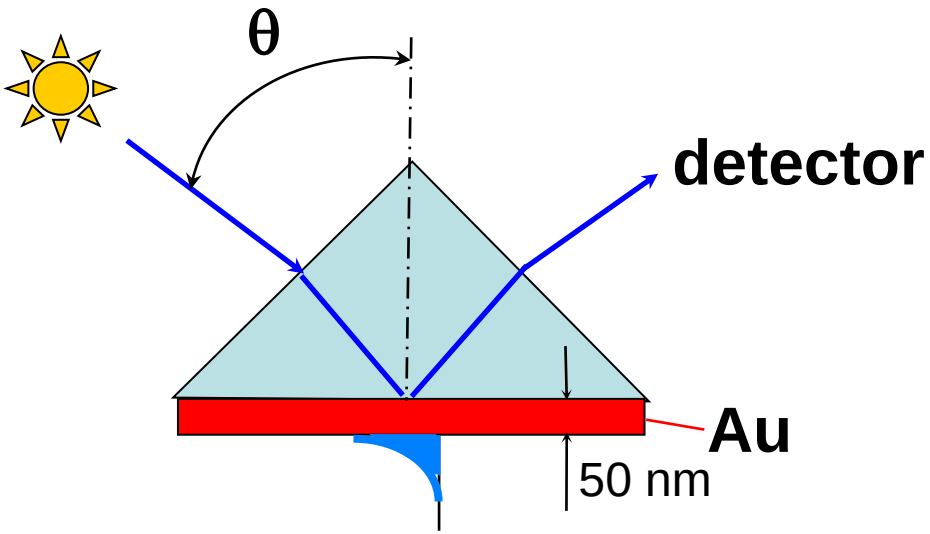


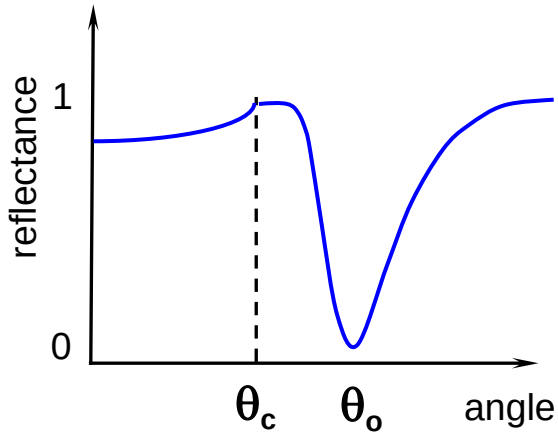


evanescent wave:

- **nearfield standing wave,**
- **extends about 1/2 λ,**
- **decays exponentially with the distance**

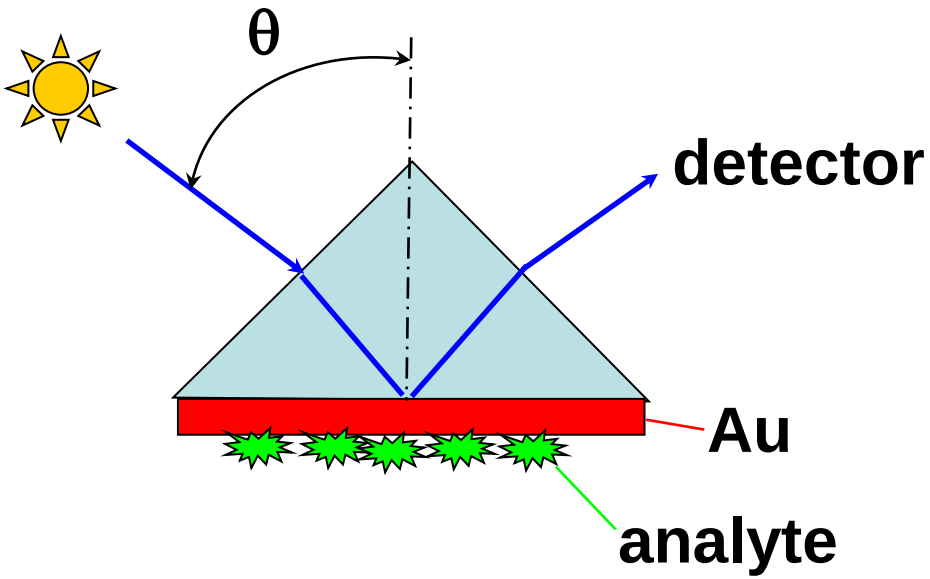
Surface Plasmon Resonance

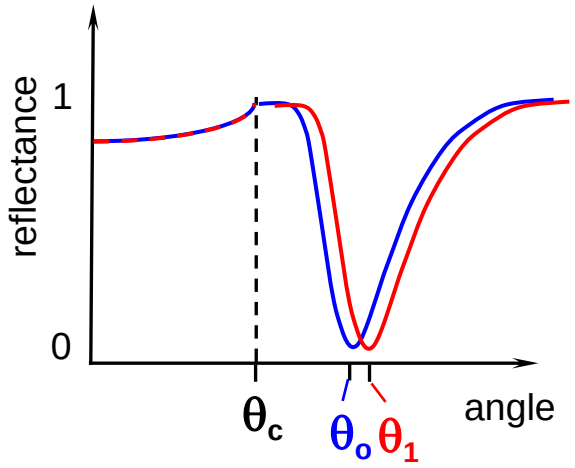




(Kretschmann)

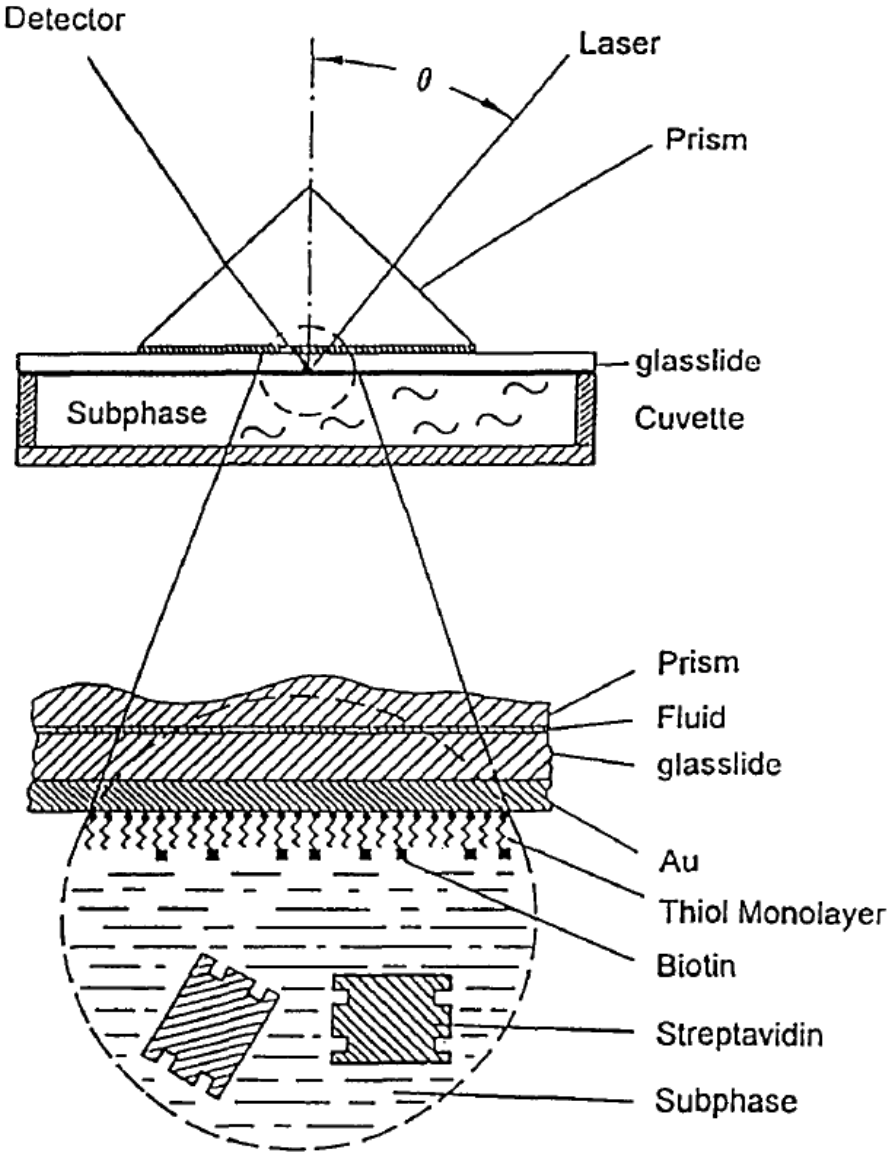
Surface Plasmon Resonance Spectroscopy

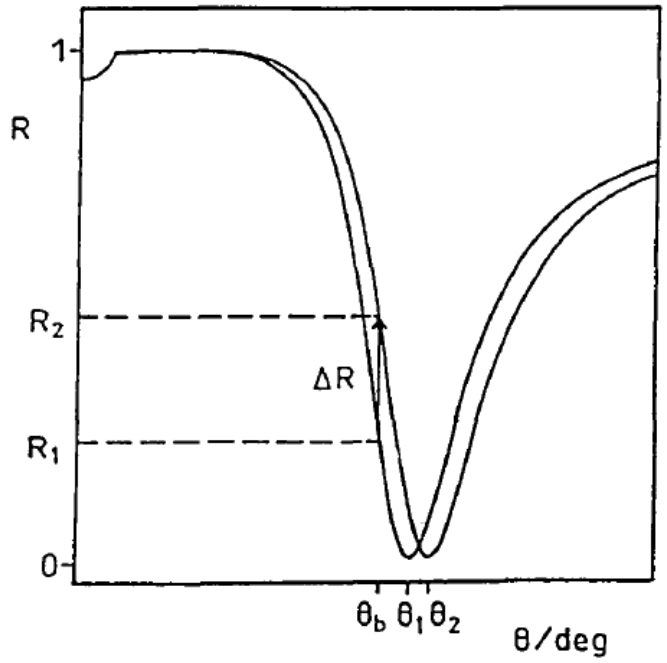


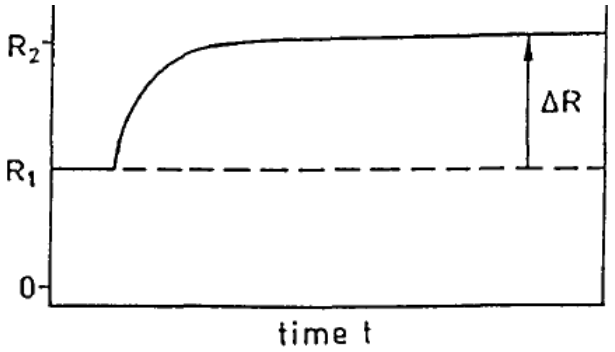


To measure: - thickness changes,
- density fluctuation,
- molecular adsorption

Surface Plasmon Resonance Spectroscopy in Sensors



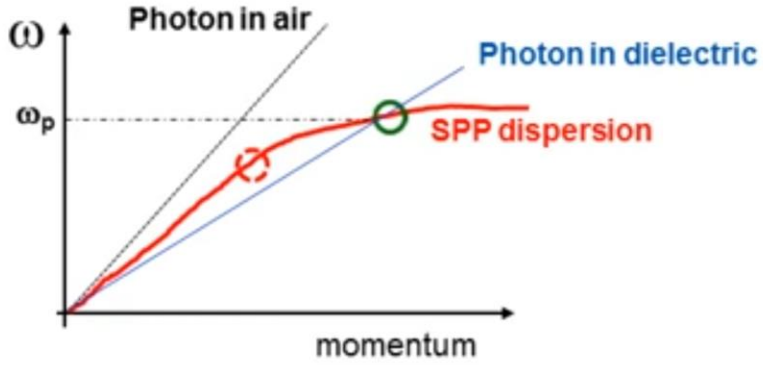


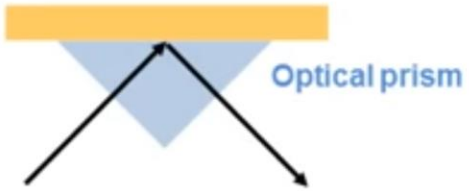


Knoll, et.al. *Biosensors & Bioelectronics*, **1995**, *10*, 903

Mathematical Explanation of the Phenomenon

Resonance in SPR Requires Momentum Conservation: "Photon momentum = Plasmon momentum"





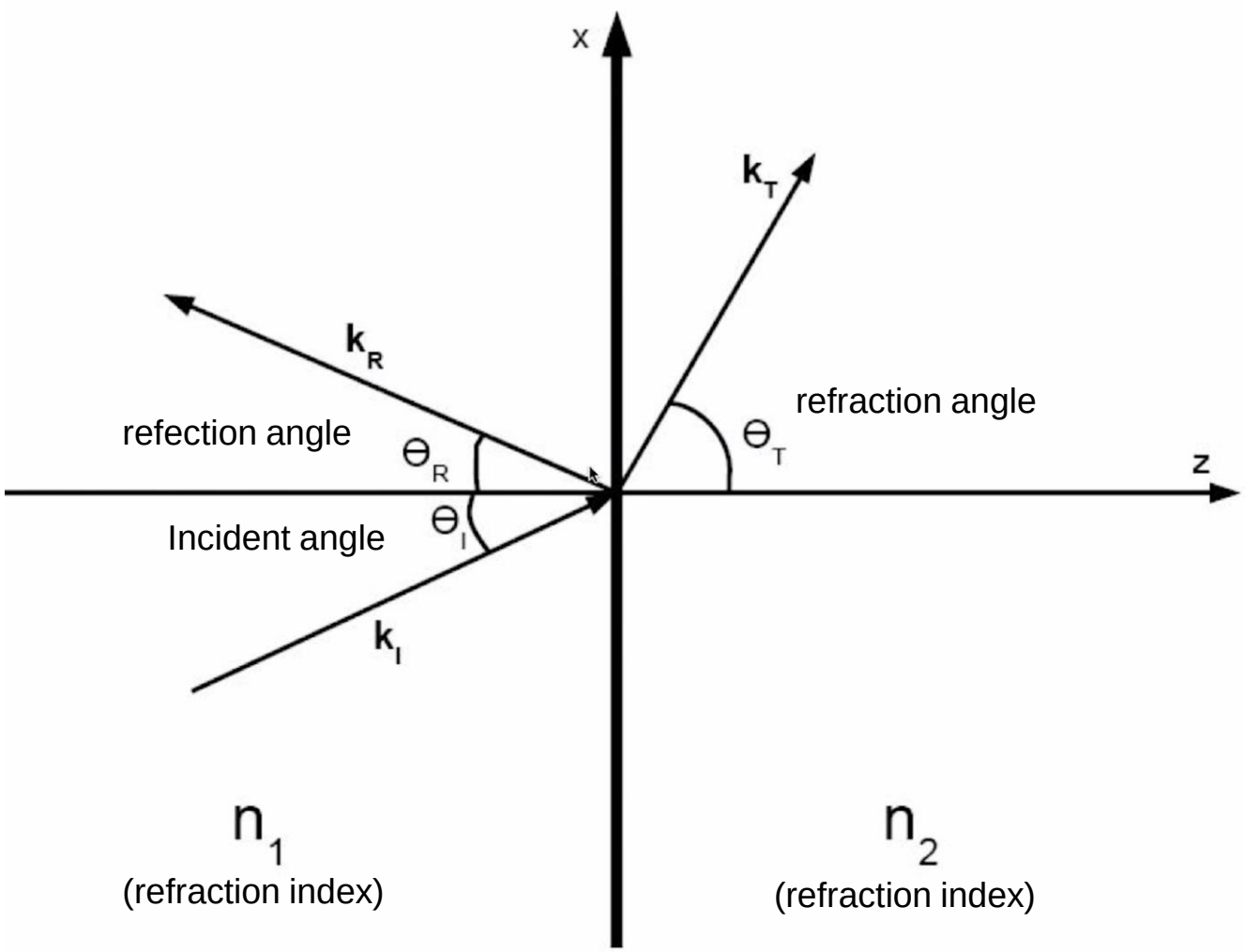
The **momentum of a photon** of energy ω in air is smaller than the **momentum of surface plasmon** of the same energy

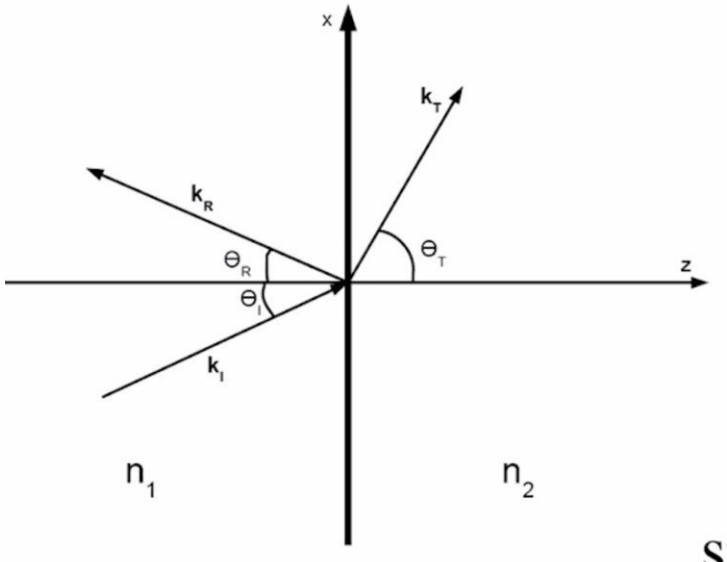
➡ **No excitation of SPP is possible**

In a dielectric, **the momentum of the same photon is increased**

At the wavelength ω_p, **the momentum of the photon is equal to the momentum of the surface plasmon** (i.e. fulfills the resonant condition)

LAMDAGEN CORPORATION


x
z
k_T
k_R
k_I
refection angle
Θ_R
refraction angle
Θ_T
Θ_I
Incident angle
n_1
(refraction index)
n_2
(refraction index)



$$n_1 \sin\theta_I = n_2 \sin\theta_T$$

Snell's law

$$\theta_T = \sin^{-1}\left(\frac{n_1}{n_2}\sin\theta_I\right)$$

$$\sin\theta_I > \frac{n_2}{n_1} \qquad \frac{n_1}{n_2}\sin\theta_I > 1$$

$$\theta_C = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$

Critical Angle

$$\theta_C = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$ Critical Angle

$$\theta_I > \theta_C$$

"Total" Internal reflection

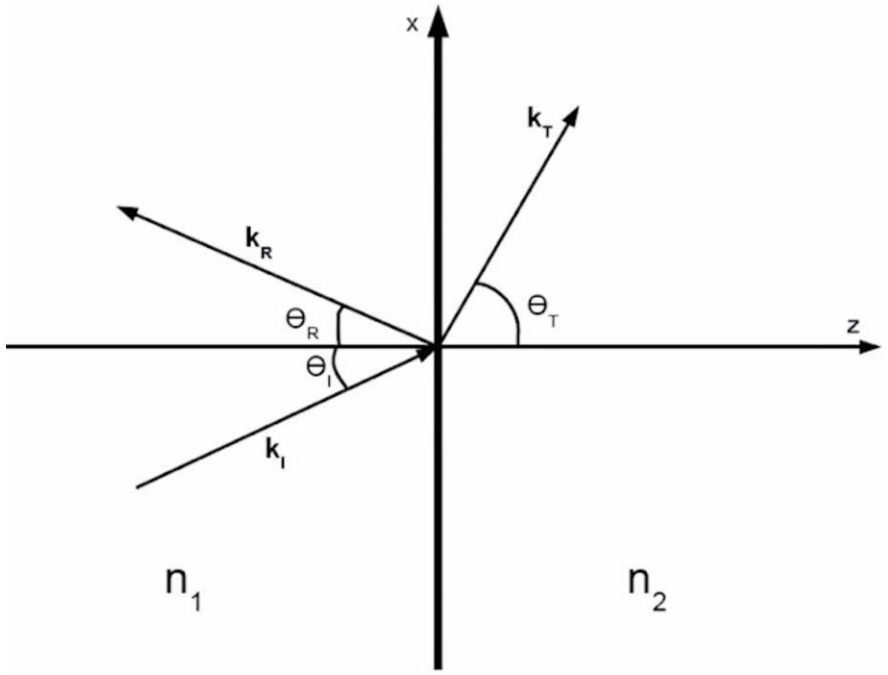
Light incident on surface completely reflects off of it back into the medium from where it came

$$\theta_C = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$

$$\theta_I > \theta_C$$

$$\sin^{-1}\left(\frac{n_2}{n_1}\sin\theta_T\right) > \theta_C$$

$$\sin\theta_T > 1$$



$$\vec{E}_T = \vec{E}_{0T} e^{i(\vec{K}\vec{\gamma} - \omega t)}$$

$$\vec{E}_T = \vec{E}_{0T} e^{i(k_x x + k_z z - \omega t)}$$

$$k_z = k_T \cos\theta_T$$

$$k_x = k_T \sin\theta_T$$

$$\vec{E}_T = \vec{E}_{0T} e^{i(k_T \sin\theta_T)x} e^{i(k_T \cos\theta_T)z} e^{-i\omega t}$$

$$\vec{E}_T = \vec{E}_{0T} e^{i(k_T \sin\theta_T)x} e^{i(k_T \cos\theta_T)z} e^{-i\omega t}$$

$$\cos\theta_T = \sqrt{1 - \sin^2\theta_T} \qquad \sin\theta_T > 1$$

$\cos\theta_T$ imaginary

$k_T = \dfrac{n_2\omega}{c}$ real

$$k_T \cos\theta_T = Ai$$

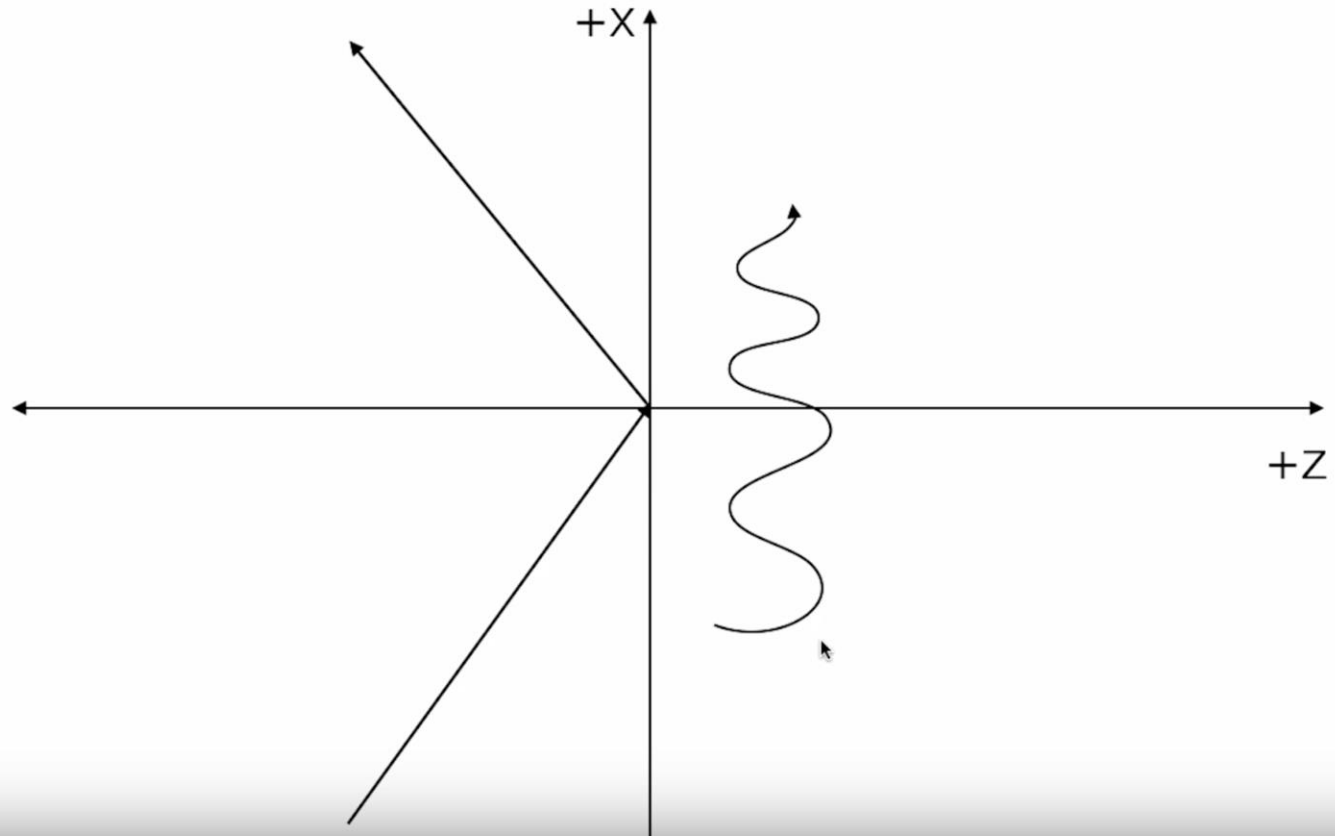
$$\vec{E}_T = \vec{E}_{0T} e^{i(k_T \sin\theta_T)x} e^{i(k_T \cos\theta_T)z} e^{-i\omega t}$$

$$k_T \cos\theta_T = Ai$$

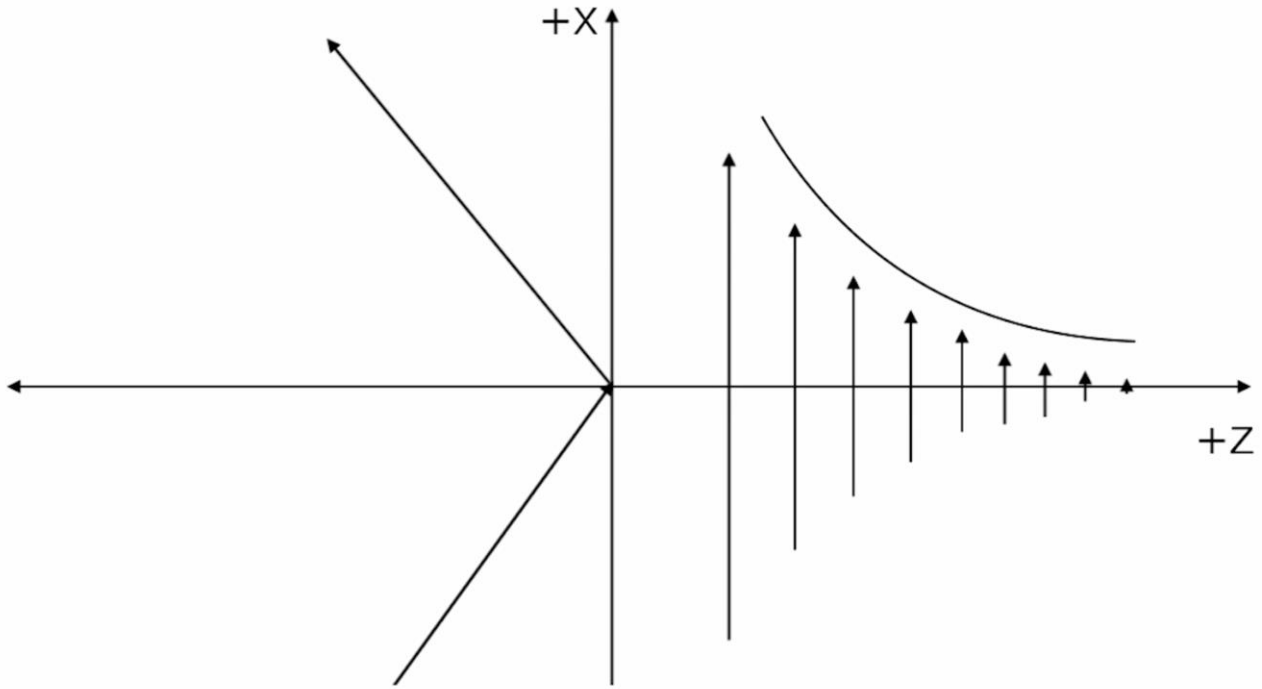
$$\vec{E}_T = \left(\vec{E}_{0T} e^{i(k_T \sin\theta_T)x} e^{-i\omega t} \right) e^{-Az}$$

$$\mathrm{Re}\left(\vec{E}_T\right) = \vec{E}_{0T} \cos\left(\left(k_T \sin\theta_T\right)x - \omega t\right) e^{-Az}$$

$$\mathrm{Re}\left(\vec{E}_T\right) = \vec{E}_{0T}\cos\left(\left(k_T \sin\theta_T\right)x - \omega t\right)e^{-Az}$$



$$\mathrm{Re}\left(\vec{E}_T\right) = \vec{E}_{0T}\cos\left(\left(k_T \sin\theta_T\right)x - \omega t\right)e^{-Az}$$



Evanescent Wave

Therefore:

Evanescent Wave

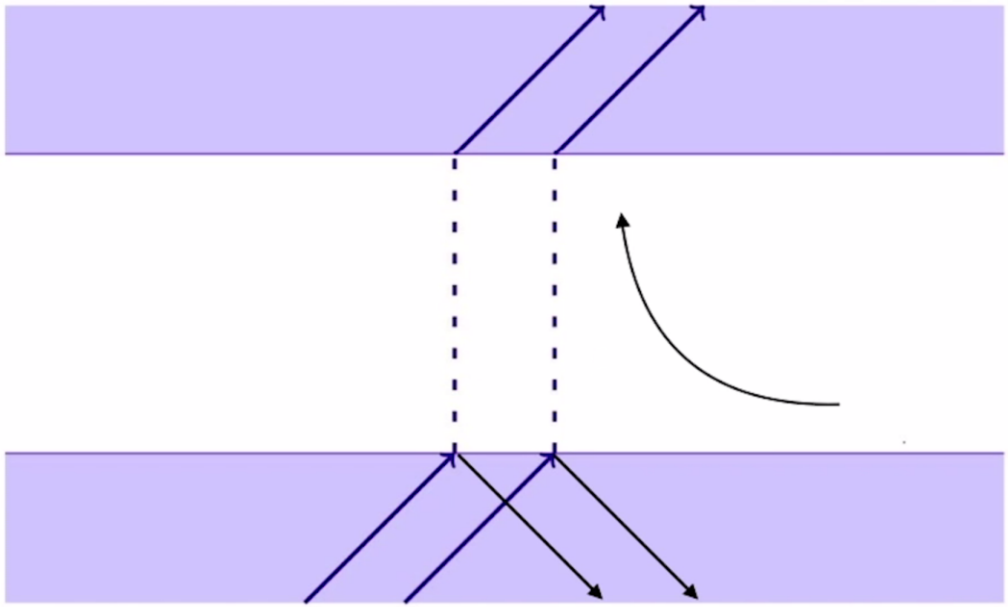
It does not propagate as an electromagnetic wave

Its energy is concentrated spatially in the vicinity of the source, in this case, the boundary between the materials

There is no net energy flow . i.e. The Poynting Vector when averaged algebraically over a complete oscillation results in zero

The physical explanation for the existence of the evanescent waves is that the electric and magnetic fields cannot be discontinuous at a boundary

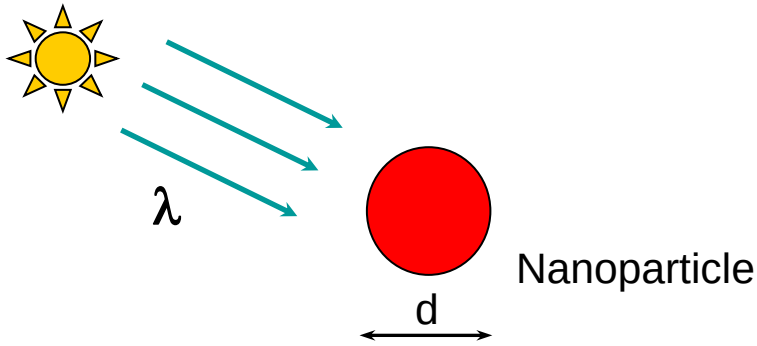
Detection



Frustrated Total Internal Reflection

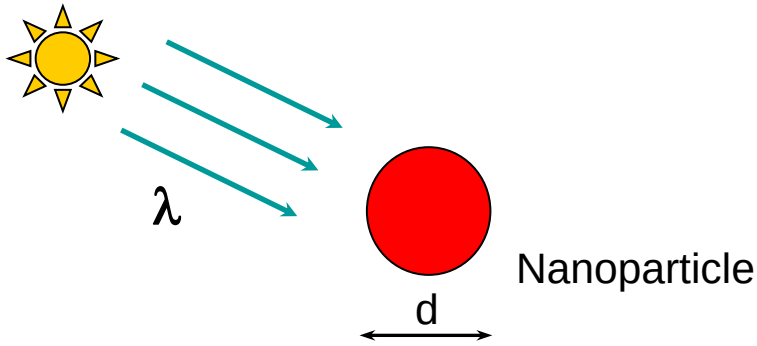
Particle

Nanoparticle Surface Plasmon

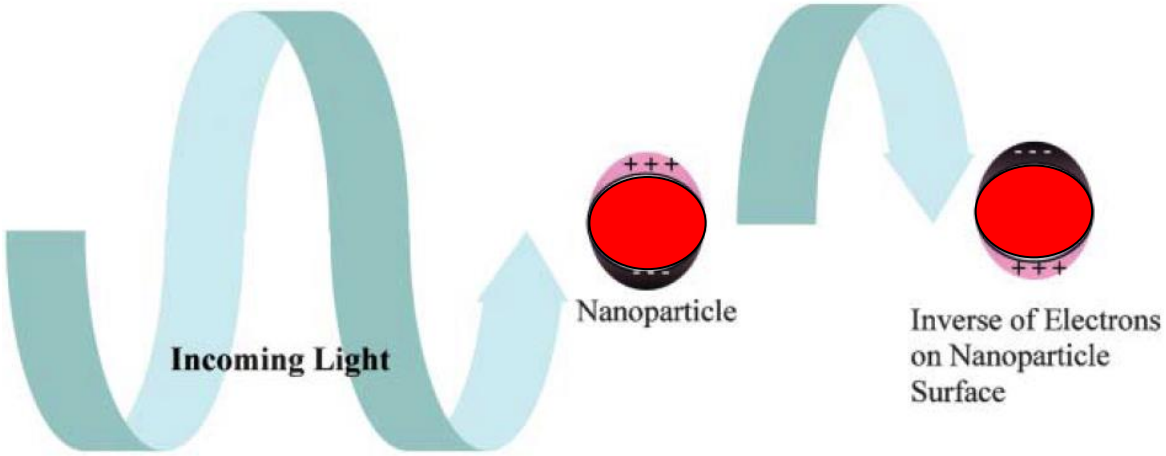


d << λ

Nanoparticle Surface Plasmon



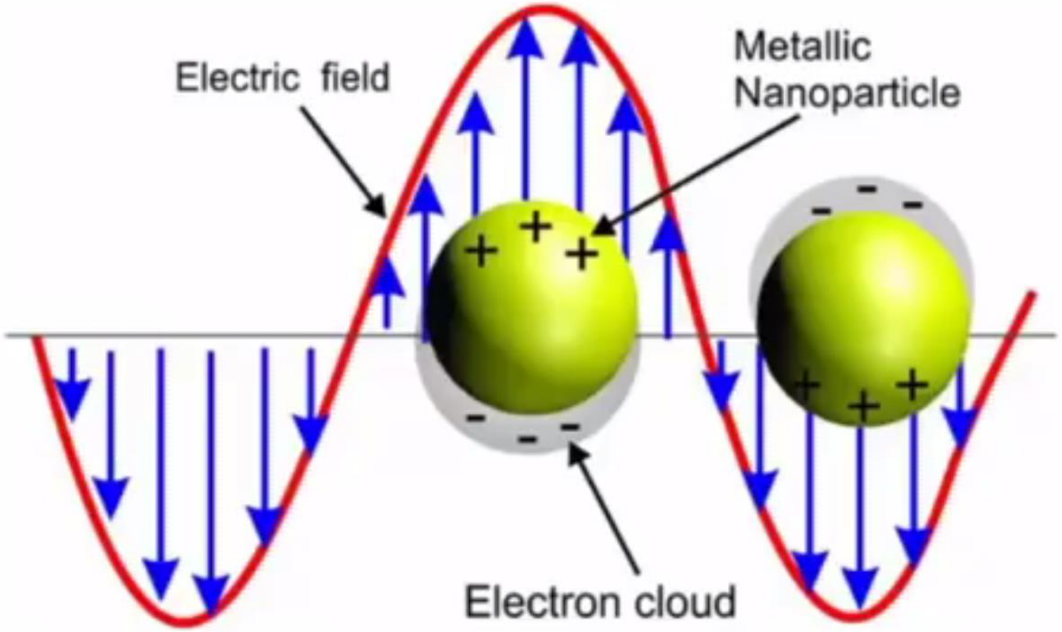
$d \ll \lambda$



Light resonance with the surface plasmon oscillation causes the free electrons in the metal to oscillate.

Eustis and El-Sayed, *Chem. Soc. Rev.*, **2006**, *35*, 209

The wavelengths of the light are larger than the size of the particles….



From: Camacho, A. Focusing nanoplasmonics. *J. Nano Sc. Tech*, 3(2015)10-17

Plasmon energy equation

The plasmon energy is described classically:

$$\omega_p{}^2 = \frac{Ne^2}{m\epsilon_o}$$

Here, ω_p is the plasmon resonance frequency, N is the number density of the electrons ($1/m^3$), e is the electron charge, m is the electron mass, and ϵ_o is the permittivity of free space. So an increased electron density causes an increase in the plasmon resonance frequency (blue-shift). This helps explain why different materials (like Ag vs. Au) have nanoparticles that are different colors, even if they are the same size and shape.

Effect of size and surroundings

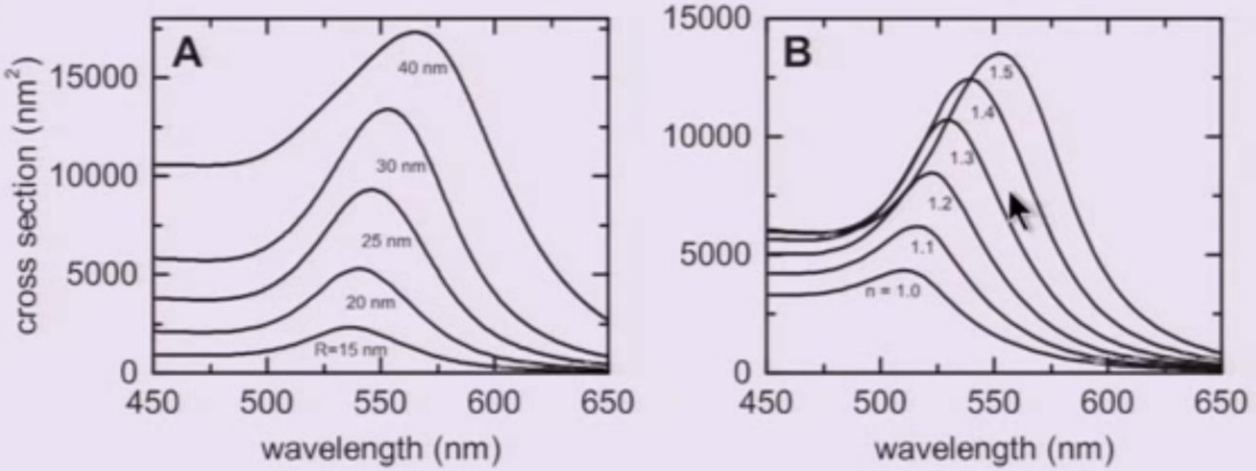
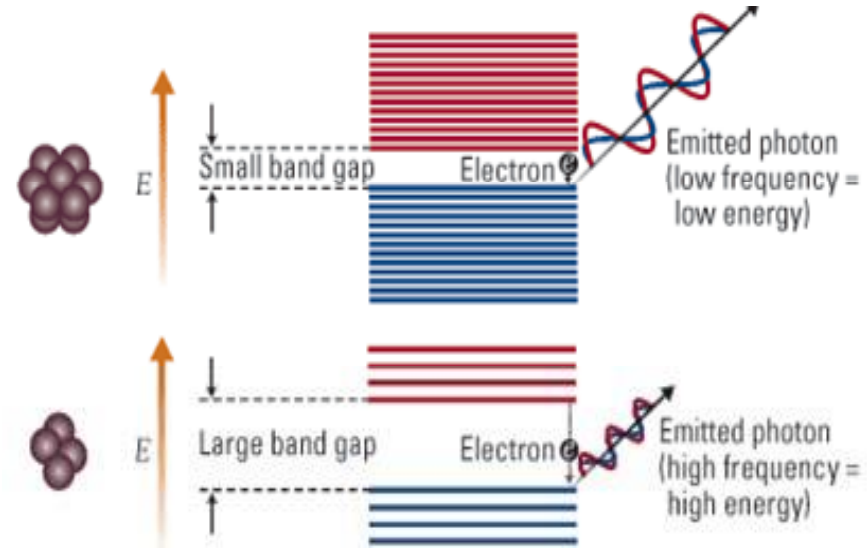


Figure 1.4: Absorption spectra for increasing radius with $n_m = 1.5$ (A), and for increasing refractive index with $R = 30$ nm (B).

Meindert Alexander van Dijk, Nonlinear-optical studies of single gold nanoparticles, Ph.D. Thesis, Leiden University, 2007.



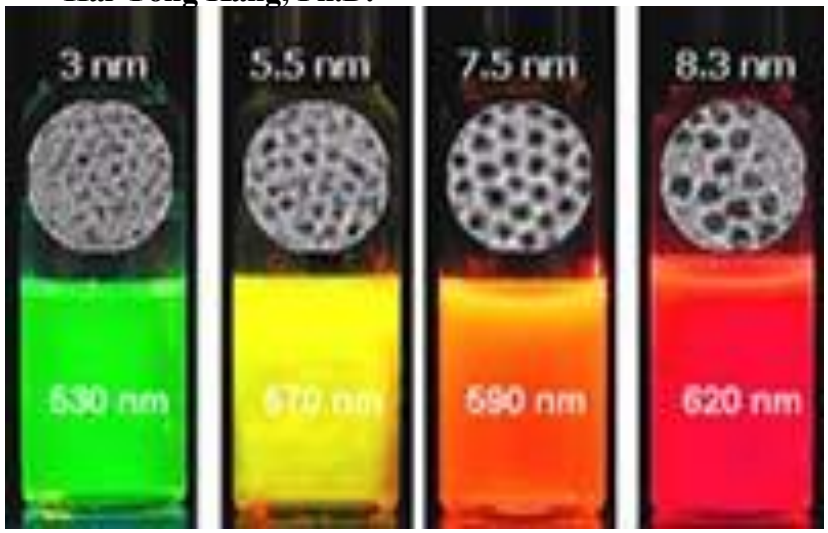
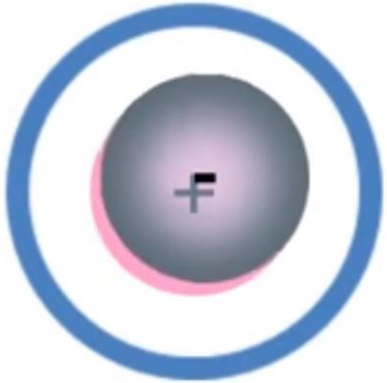


Figure 4.2 Schematic diagrams of band gap and photon energy (Rogers 2008), and changing color of quantum dots according to size of dots (Ocean NanoTech).

Localized Surface Plasmon (LSP)

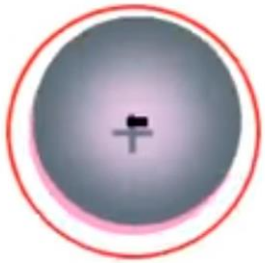
How are Resonance Conditions Met in LSPR?

$\omega_{light} \neq \omega_p$



Natural Oscillation Frequency: ω_p

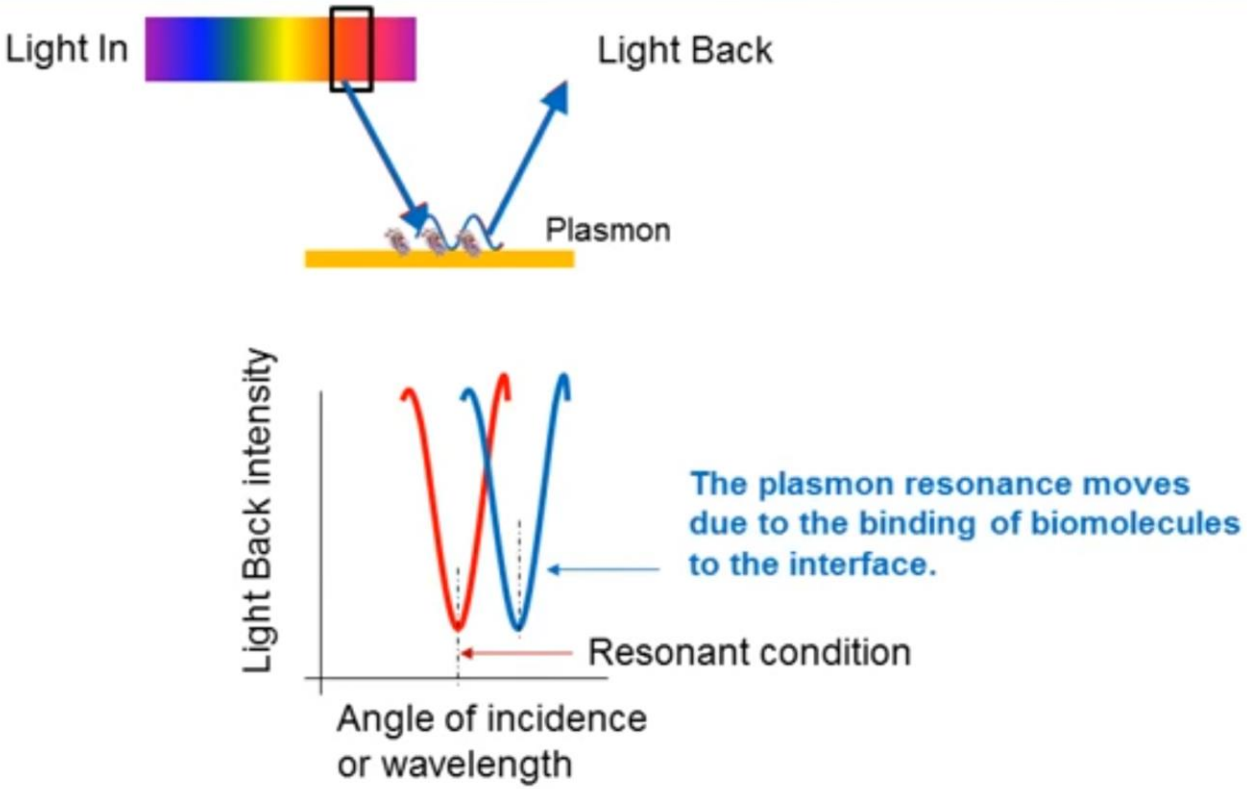
$\omega_{light} = \omega_p$



$$\omega_{light} \sim \frac{1}{\lambda_{light}}$$

https://www.youtube.com/watch?v=QLT1vrnJXWI

SPR and LSPR for Biosensing



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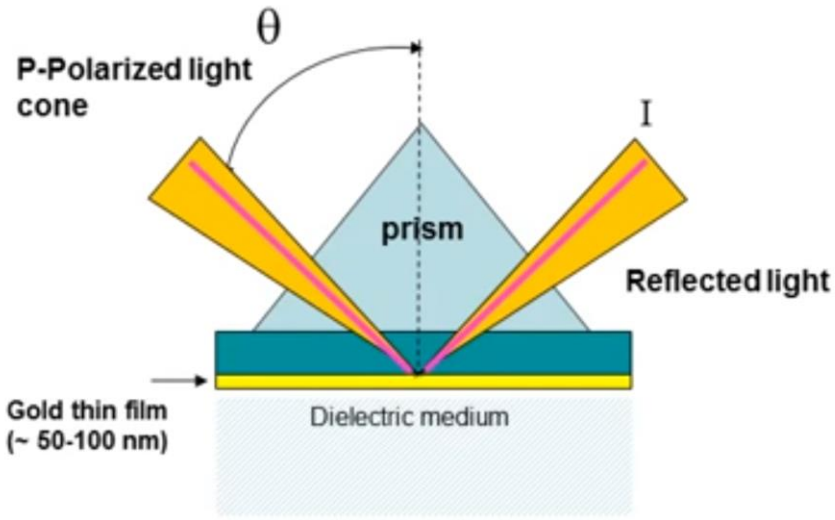
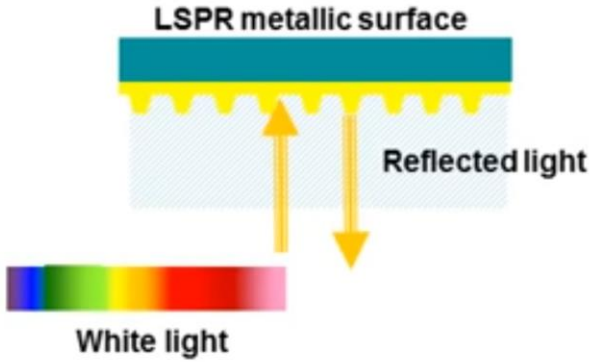
https://www.youtube.com/watch?v=QLT1vrnJXWI

LSPR is Instrumentally Simple vs. SPR

SPR: Instrumentally Complex



LSPR: Instrumentally Simple



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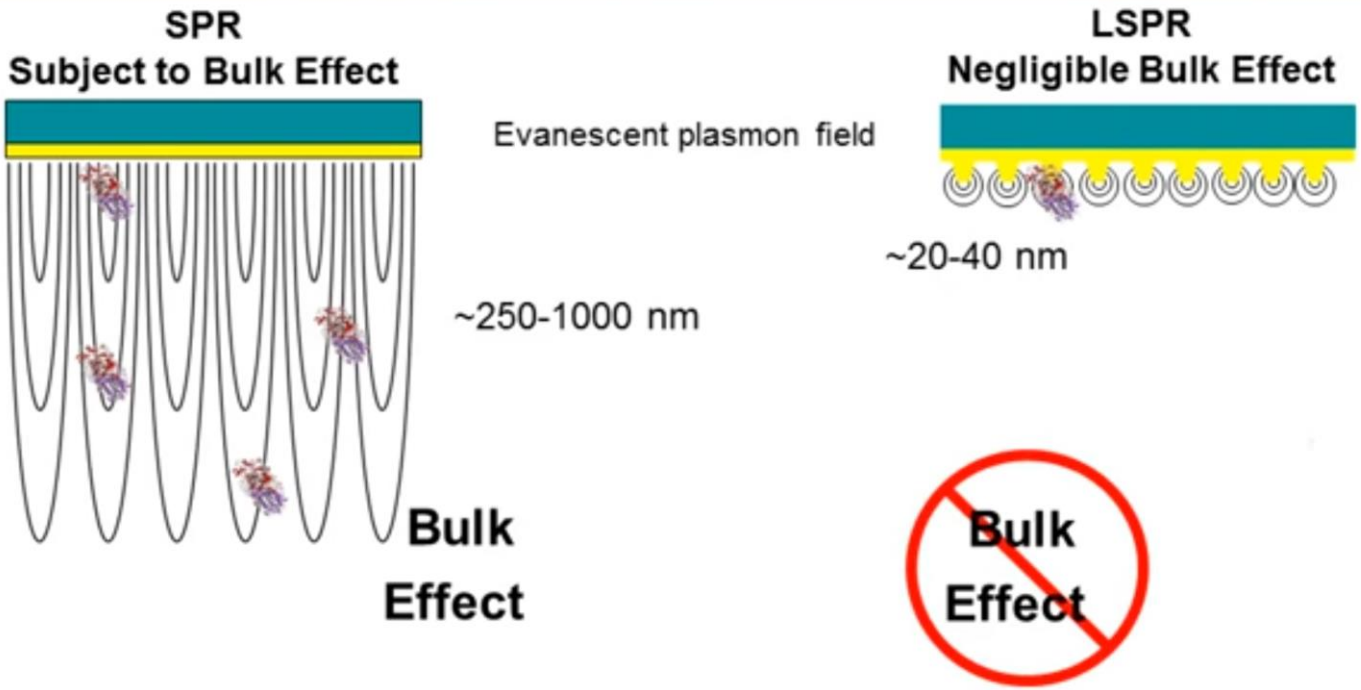
https://www.youtube.com/watch?v=QLT1vrnJXWI

LSRP has Marginal Bulk Effect vs. SPR



https://www.youtube.com/watch?v=QLT1vrnJXWI

LSPR has Unique Advantages for Dx Application

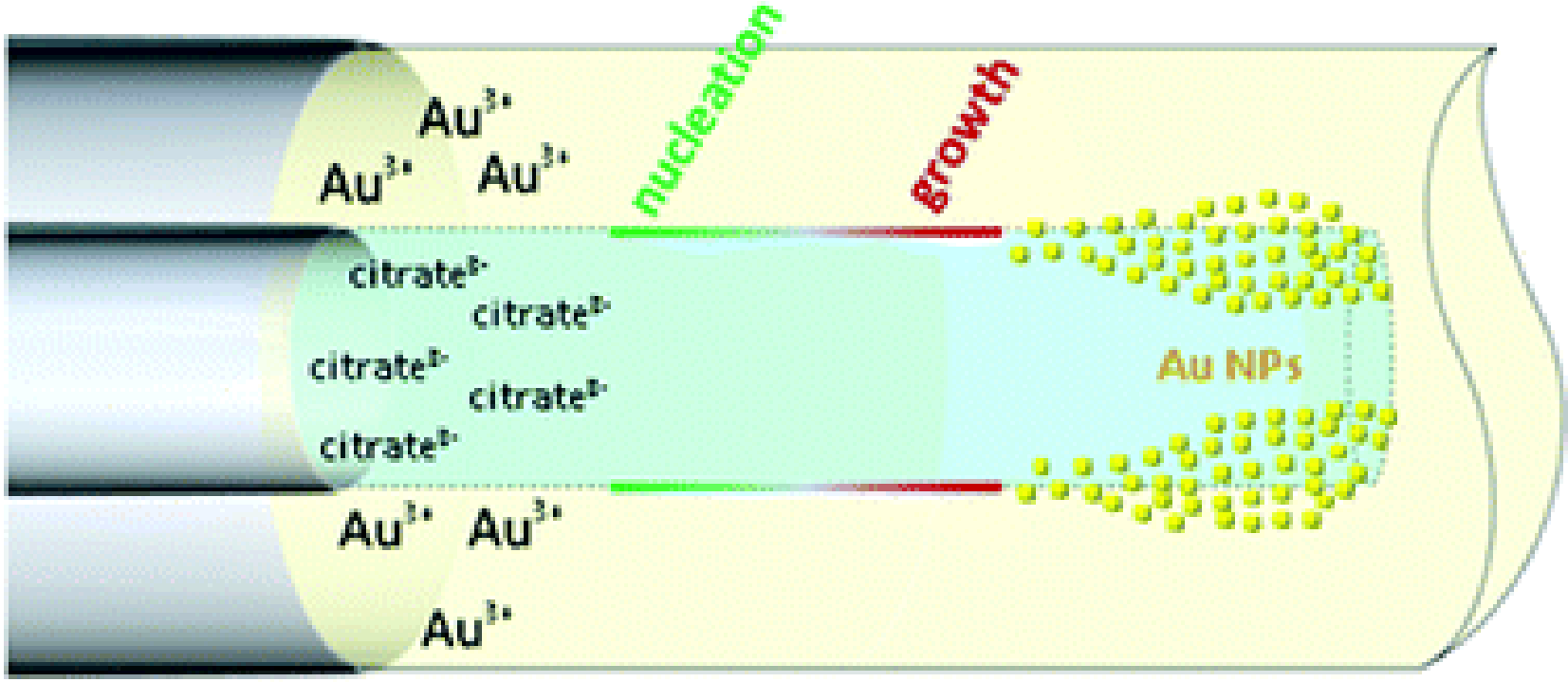
- LSPR and SPR are surface plasmon enabled sensing techniques
- LSPR enjoys inherent advantages over SPR
  - Marginal bulk effect
  - Instrumental simplicity – no adaptive optics or thermal controls needed
  - Amenable to different types of assay enhancements
- LSPR's advantages provide for
  - Design flexibility, scalability and low cost
  - Miniaturization and mobility
  - Robustness for high-sensitivity diagnostic application

Synthesis

An engineering approach to synthesis of gold and silver nanoparticles by controlling hydrodynamics and mixing based on a coaxial flow reactor.

Nanoscale, Issue 37, 2017; Razwan Baber,[a] Luca Mazzei,[a] Nguyen Thi Kim Thanh*[bc] and Asterios Gavriilidis*[a]

In this work we present a detailed study of flow technology approaches that could open up new possibilities for nanoparticle synthesis. The synthesis of gold and silver nanoparticles (NPs) in a flow device based on a coaxial flow reactor (CFR) was investigated. The CFR comprised of an outer glass tube of 2 mm inner diameter (I.D.) and an inner glass tube whose I.D. varied between 0.142 and 0.798 mm. A split and recombine (SAR) mixer and coiled flow inverter (CFI) were further employed to alter the mixing conditions after the CFR. The 'Turkevich' method was used to synthesize gold NPs, with a CFR followed by a CFI. This assembly allows control over nucleation and growth through variation of residence time. Increasing the total flow rate from 0.25 ml min^{-1} to 3 ml min^{-1} resulted initially in a constant Au NP size, and beyond 1 ml min^{-1} to a size increase of Au NPs from 17.9 ± 2.1 nm to 23.9 ± 4.7 nm. The temperature was varied between 60–100 ° C and a minimum Au NP size of 17.9 ± 2.1 nm was observed at 80 ° C. Silver NPs were synthesized in a CFR followed by a SAR mixer, using sodium borohydride to reduce silver nitrate in the presence of trisodium citrate. The SAR mixer provided an enhancement of the well-controlled laminar mixing in the CFR. Increasing silver nitrate concentration resulted in a decrease in Ag NP size from 5.5 ± 2.4 nm to 3.4 ± 1.4 nm. Different hydrodynamic conditions were studied in the CFR operated in isolation for silver NP synthesis. Increasing the Reynolds number from 132 to 530 in the inner tube created a vortex flow resulting in Ag NPs in the size range between 5.9 ± 1.5 nm to 7.7 ± 3.4 nm. Decreasing the inner tube I.D. from 0.798 mm to 0.142 mm resulted in a decrease in Ag NP size from 10.5 ± 4.0 nm to 4.7 ± 1.4 nm. Thus, changing the thickness of the inner stream enabled control over size of the Ag NPs.



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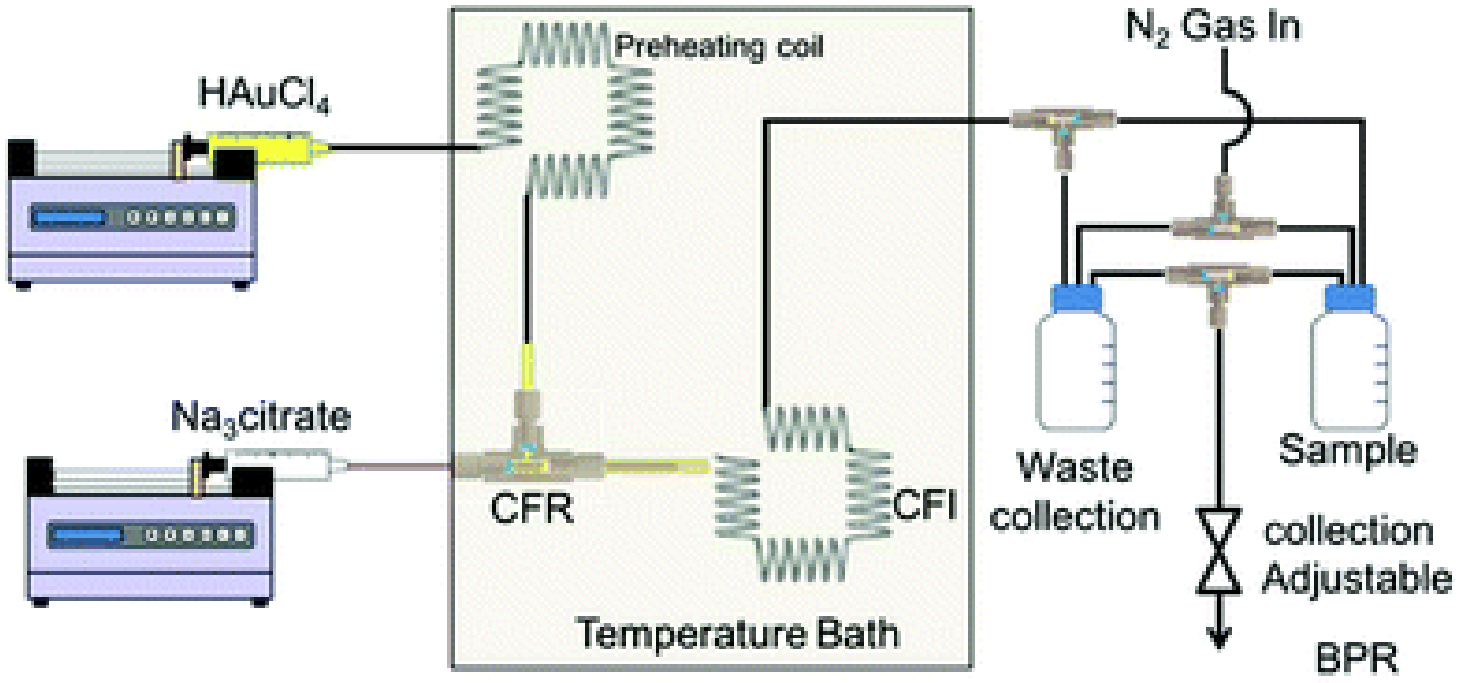
Nanoscale, Issue 37, 2017; Razwan Baber,[a] Luca Mazzei,[a] Nguyen Thi Kim Thanh*[bc] and Asterios Gavriilidis*[a]



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CdSe/CdS core shell structure

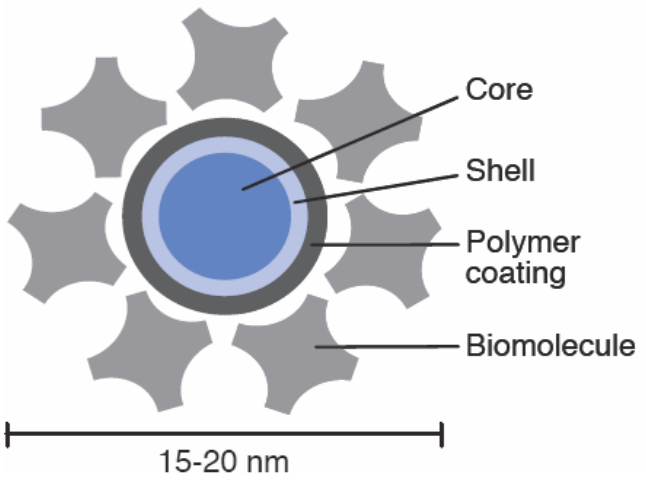


Figure 4.3 The schematic diagram of polymer coated core/shell quantum dot (Invitrogen).

structurally related, the emission intensity and stability are enhanced. For example, the CdSe/CdS core/shell structure quantum dots enhance the property of plain CdSe quantum dots (Li 2003).

However, these core/shell quantum dots are not soluble in water, which limits their biological usages. To overcome this, an outer coating, such as a polymer layer[6], is added to make the quantum dot water-soluble and allow for conjugation to the biomaterial (Invitrogen). Figure 4.3 shows the schematic diagram of a polymer-coated core/shell quantum dot for conjugation to biomaterials.

Based on : "A Review of the Emrging nanotechnology Industry: Materials, Fabrications and Applications" by Hai-Yong Kang (2010)

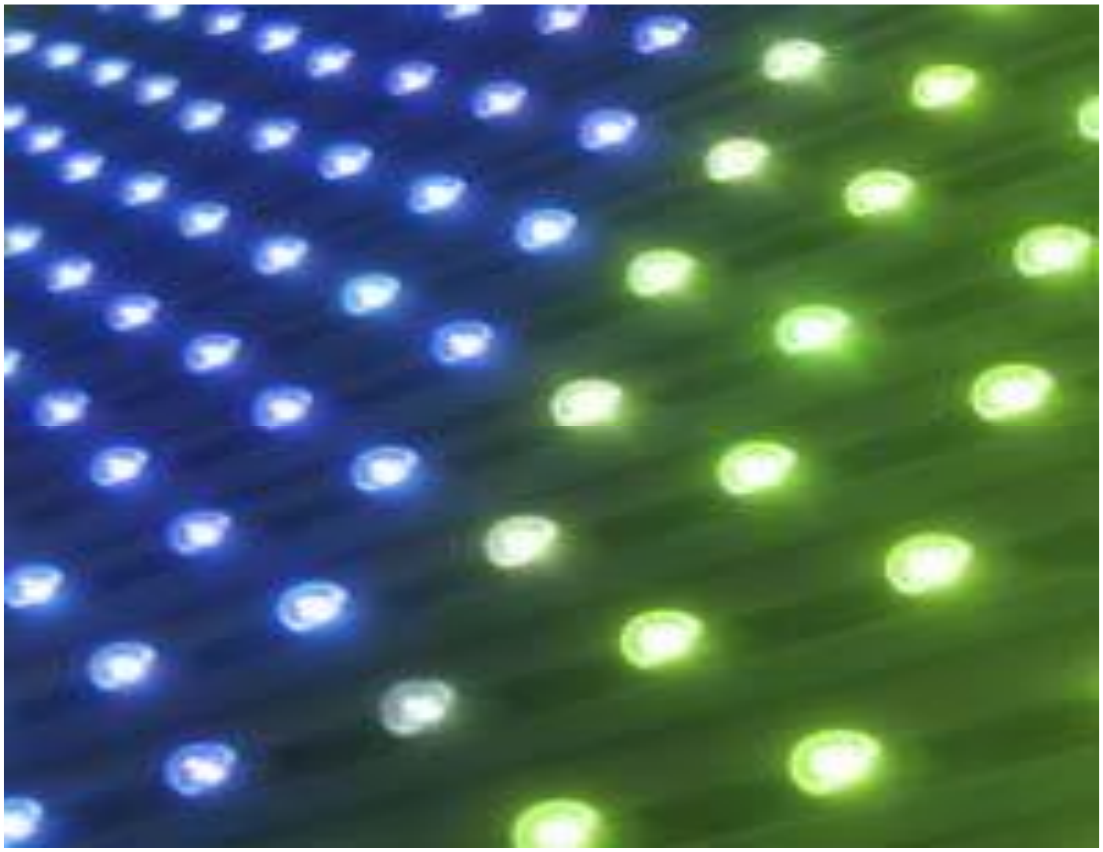
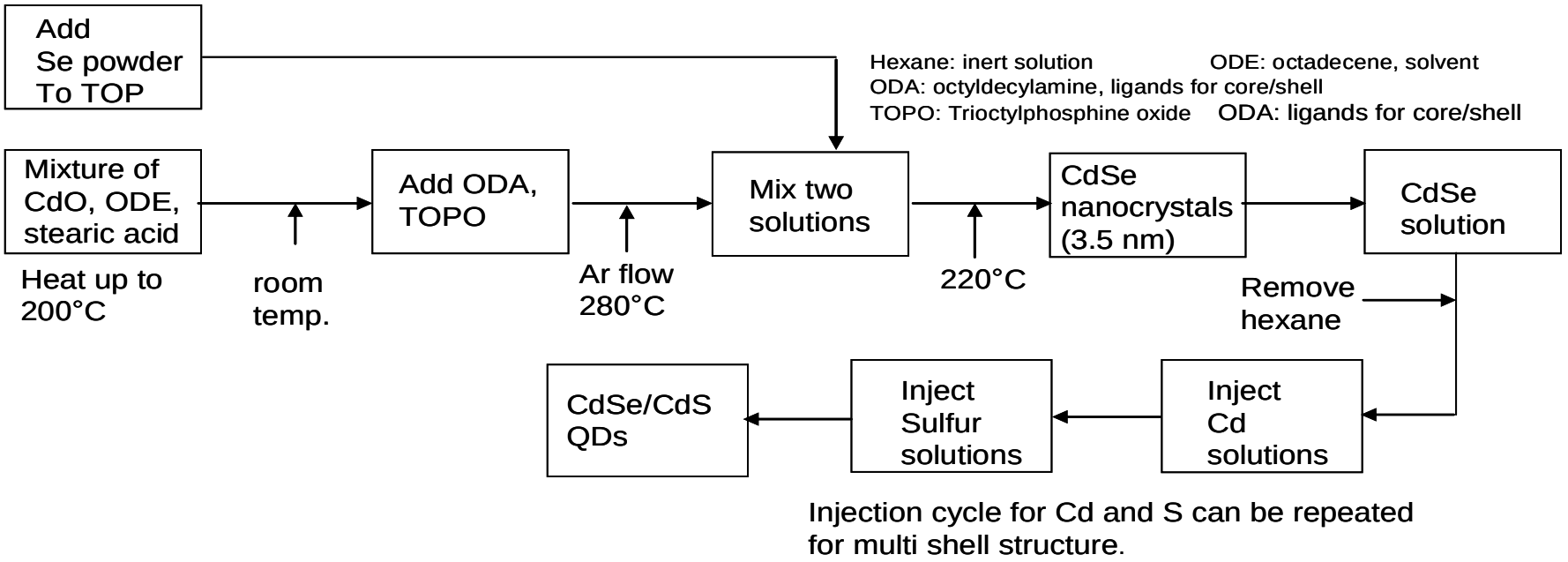


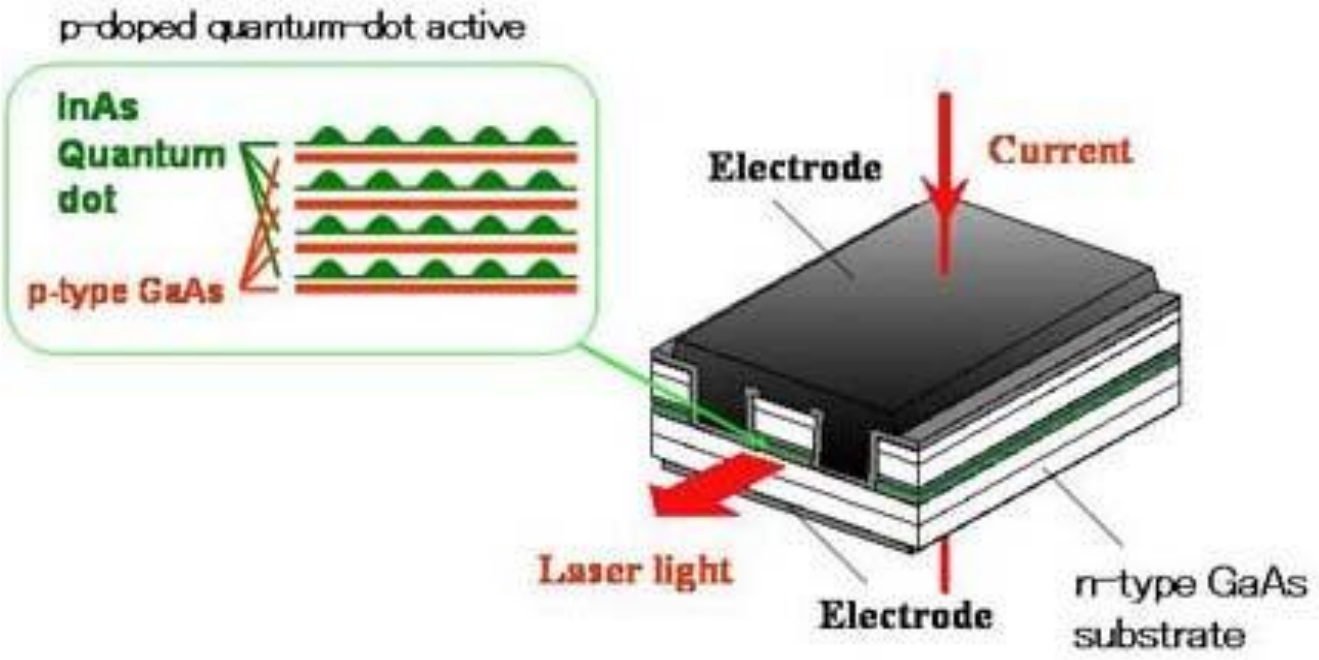
Figure 4.7 Quantum dots application for display device (Evident).

Based on : “A Review of the Emrging nanotechnology Industry: Materials, Fabrications and Applications” by Hai-Yong Kang (2010)

Process flow for the synthesis of CdSe/CdS core shell structure



Nanodot Based Digital Laser



Structure of proposed quantum dot laser.

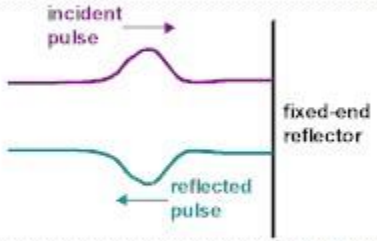
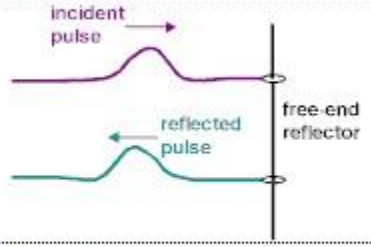
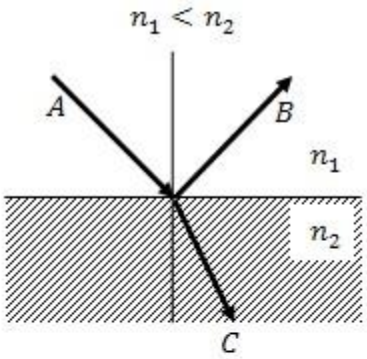
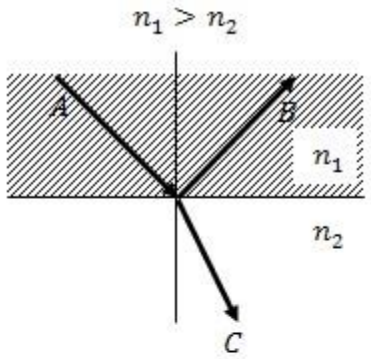
Based on : "A Review of the Emrging nanotechnology Industry: Materials, Fabrications and Applications" by Hai-Yong Kang (2010)

A surface modifying technology

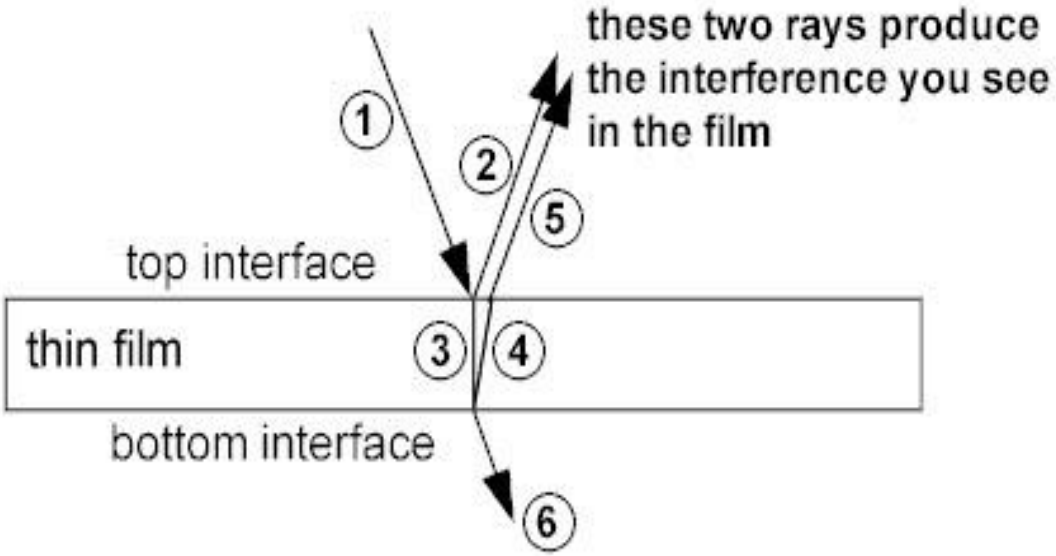
Chunlei Guo: Using femtosecond lasers to create new material properties

https://www.youtube.com/watch?v=FLnKgXWlO_Y&t=10s

More about colors (and thickness)

Fixed-end Reflection:	Free-end Reflection:
Pulses Along the Rope	
	
Light Waves (n = refractive index)	
	
• The reflected ray is **inverted** • This reflection produces a **phase difference** of ½λ from the original wave • A and C are in-phase • B and C are out-of-phase	• The reflected ray is **not inverted** • This reflection produces **no phase difference** with the original wave • A, B, C are in-phase

These reflective properties are critical to our understanding of the colors in such thin films as soap bubbles, coatings on camera lenses, colors in a butterfly's wings or peacock's feathers, or oil spills.



When ray 1 strikes the top interface, some of the light is partially reflected, ray 2, and the rest is refracted, ray 3.

When ray 3 strikes the bottom interface, some of it is reflected, ray 4, and the remainder is refracted, ray 6.

When ray 4 strikes the top interface from underneath, some is reflected (not shown) and some is refracted, ray 5.

It is the interference between rays 2 and 5 that produces a thin film's color when the film is viewed from above.

Step 1

Find the shift for the wave reflecting off the top surface of the film, Δ_a

$$n_1 > n_2 \rightarrow \Delta_a = 0$$
$$n_1 < n_2 \rightarrow \Delta_a = \lambda/2$$

Step 2

Find the shift for the wave reflecting off the film's bottom surface, Δ_b

$$n_2 > n_3 \rightarrow \Delta_b = 2t$$
$$n_2 < n_3 \rightarrow \Delta_b = 2t + \frac{\lambda}{2}$$

Step 3

Calculate the relative shift by subtracting the individual shifts: $\Delta = \Delta_b - \Delta_a$

Step 4

Set the relative shift equal to the condition for constructive interference, or the condition for destructive interference.

$$\Delta = m\lambda$$

Constructive Interference:

Destructive Interference:

$$\Delta = \left(m + \frac{1}{2}\right)\lambda$$

wit h $m = 0, 1, 2, 3...$

Step 5

Rearrange the equation

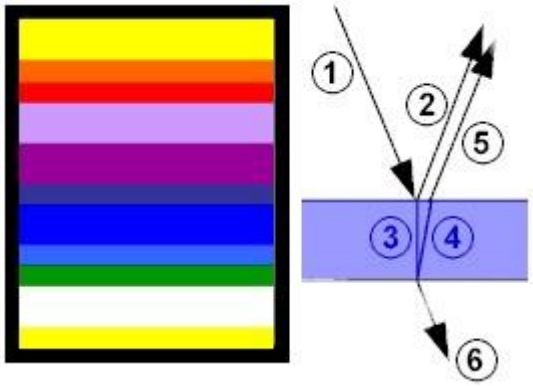
Step 6

Since we are dealing with the behavior of the light in the thin film, we must ALWAYS use the light's wavelength IN THE FILM, λ_n.

The wavelength in a medium whose refractive index, *n* is :

$$\lambda_n = \frac{\lambda}{n}$$

A thin soap film is formed by dipping a plastic rectangular wand into a solution of soapy water which has a refractive index of 1.4. When viewed in daylight, one portion of the film reflects blue light of wavelength 475 nm. Estimate the minimum thickness of that section of the film.



Will ray 2 be in-phase or out-of-phase with ray 1?

Air to Soap, $n_{air} < n_{soap} \rightarrow$ fixed-end reflector $\rightarrow$ rays 1 and 2 out-of-phase with a phase inversion of $\lambda/2$

Will ray 5 be in-phase or out-of-phase with ray 1?

Ray 5: Soap to Air, $n_{soap} > n_{air} \rightarrow$ free-end reflector, in-phase with ray 2, also with 3 and 4.

Since refracted rays remain in-phase with their initial rays, it means ray 1 is also in-phase.

Thus, rays 1 and 5 are in-phase with no phase inversion.

To find minimum thickness, $t_{\min}$

?

To find minimum thickness, $t_{\min}$

Step 1.

Air to Soap, $n_a < n_s \rightarrow \Delta_a = \lambda/2$

Step 2.

Soap to Air, $n_s > n_a \rightarrow \Delta_b = 2t$ (no phase difference)

Step 3.

$$\Delta = \Delta_b - \Delta_a = 2t - \frac{\lambda}{2}$$

Step 4.

Blue light $\rightarrow$Constructive Interference, $\Delta = m\lambda$

Step 5.

$$m\lambda_s = 2t - \frac{\lambda_s}{2} \rightarrow 2t = \left(m + \frac{1}{2}\right)\lambda$$

Step 6.

$$\lambda_s = \frac{\lambda_a}{n_s} = \frac{475}{1.4} = 339 \text{ nm}$$

Step 7.

$$2t = \left(m + \frac{1}{2}\right)\lambda_s$$

with $m = 0$(minimum thickness)

$$t = \frac{1}{2}\left(0 + \frac{1}{2}\right)339 = \frac{339}{4} = 84.8 \text{ nm}$$

□

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