



NTNU

Norwegian University of
Science and Technology

TMT4320 Nanomaterials **October 10th, 2016**

- Biosensors

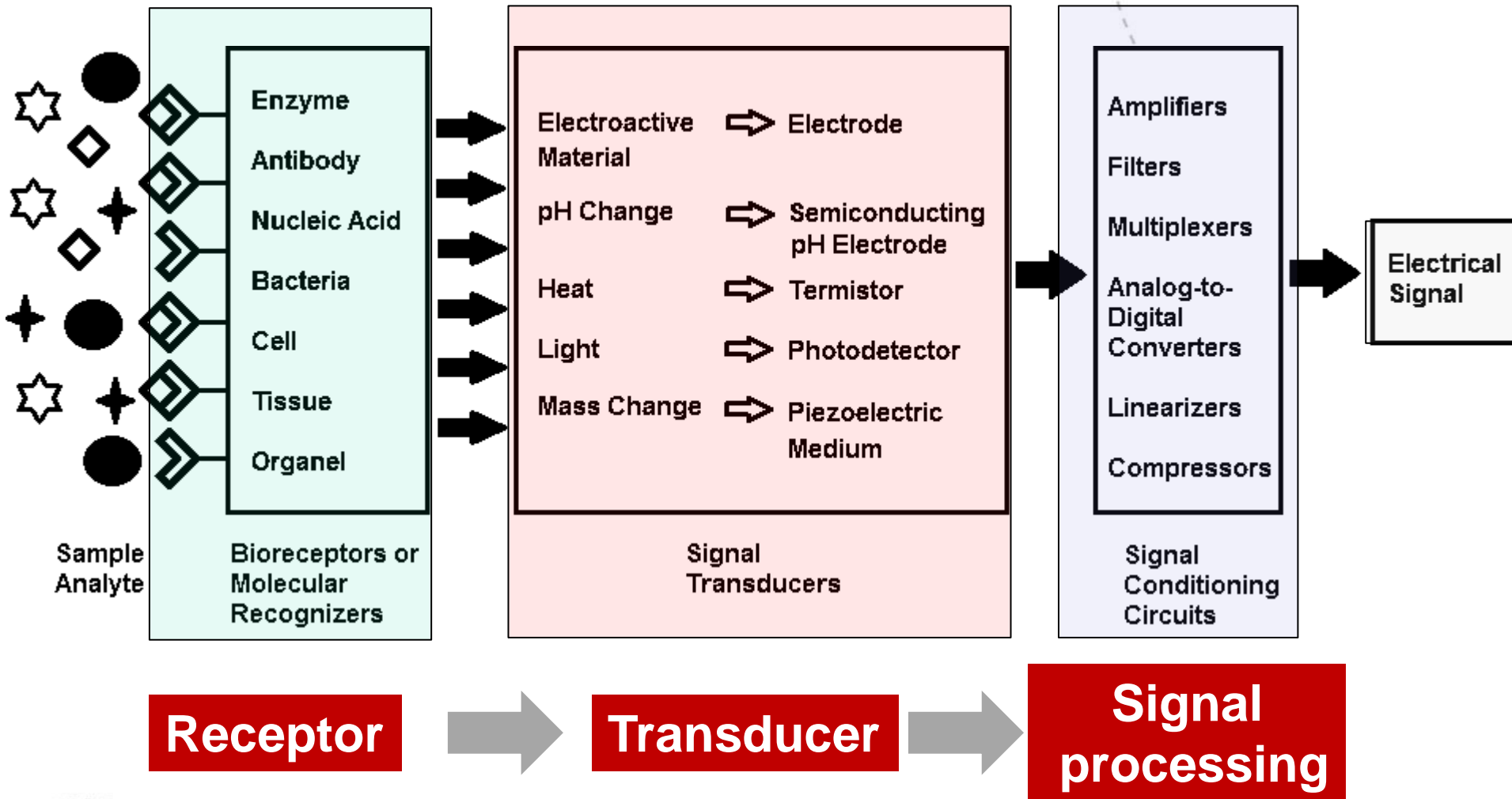
Outline

- Introduction to Biosensors
- UV-Visible spectroscopy and biosensing
- Surface Plasmon (SP) and Localized Surface Plasmon (LSP) for biosensing
- Comparing SR and LSP based nano-biosensors

What are biosensors?

Biosensors are analytical devices which convert a biological response into an electrical signal

How do biosensors work?

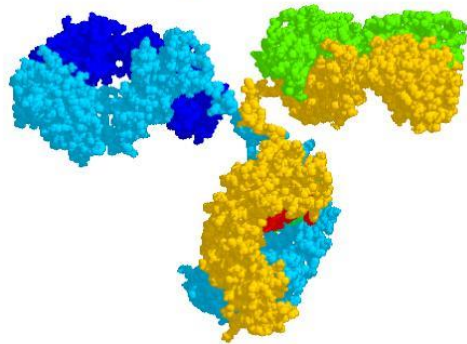


Receptors for biosensors

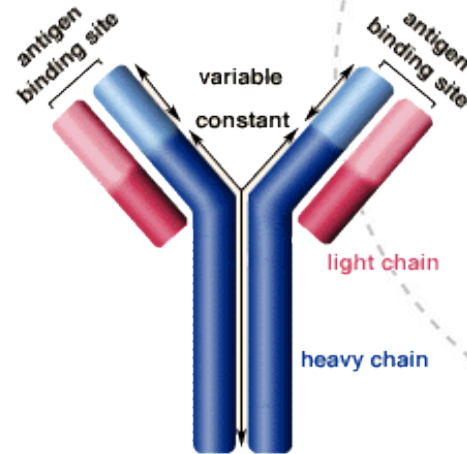
- ❖ Biological materials: e.g. Tissue, microorganisms, cells, enzymes, antibodies, nucleic acids, ...
- ❖ Biologically derived materials: e.g. recombinant antibodies, engineered proteins, aptamers,...
- ❖ Biomimecs: e.g. synthetic receptors, biomimetic catalyst, combinatorial ligands,...

Biomimecs are synthetic materials inspired in nature

Antibody Structure



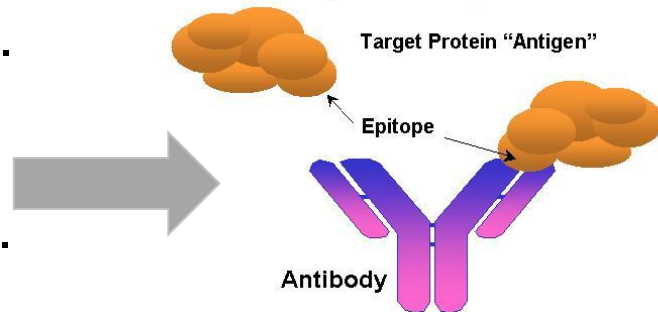
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Antibodies are special proteins made by immune system cells of mammals.

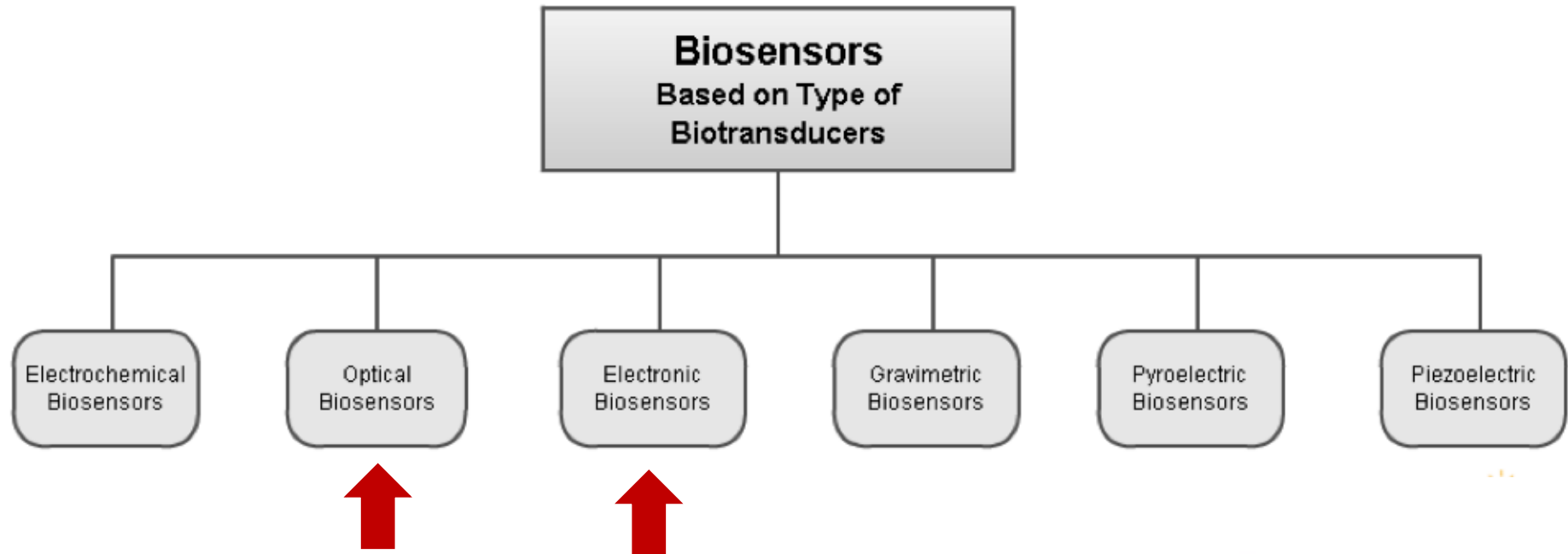
Illustration of antibody-antigen interactions. Strength of binding is determined by 3-dimensional 'fit' and chemical interactions between antibody and antigen.

Antibody-Antigen Binding



Transducers for biosensors

Classification of biosensors is based on the type of the transducers



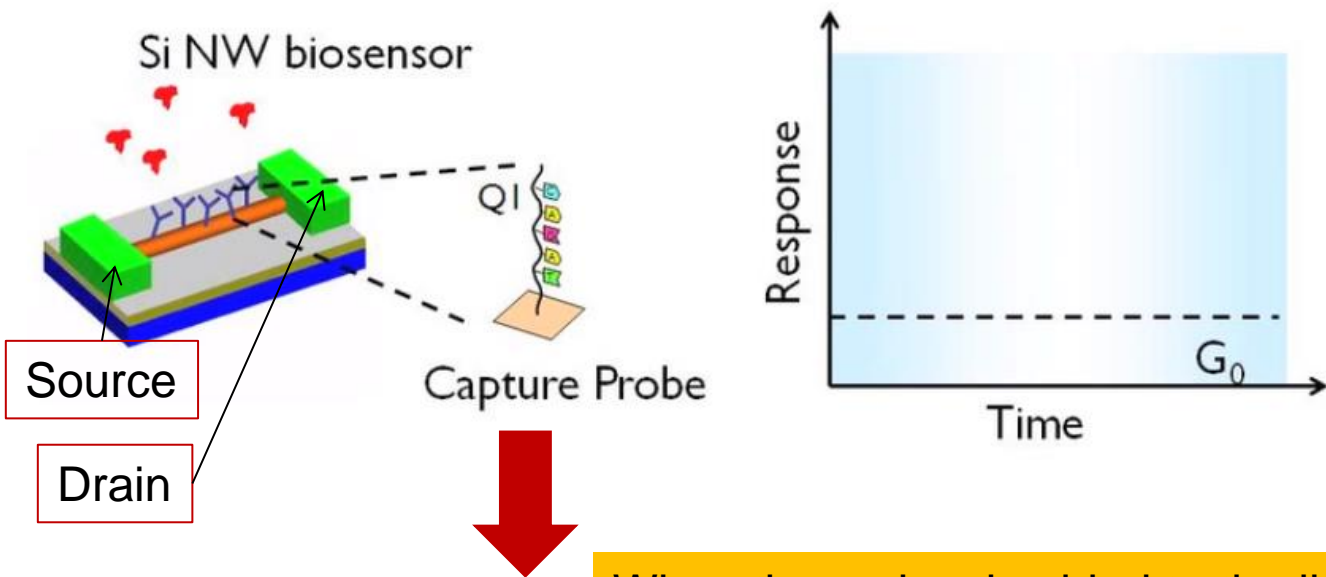
Classification of biosensors (1)

- **Electrochemical biosensors:** *Based on enzymatic catalysis of a reaction that produces or consumes electrons*
- **Gravimetric biosensors:** Based on piezoelectric quartz crystals. The mass response is inversely proportional to the crystal thickness
- **Piezoelectric biosensors:** Measure the change in frequency (related to the change in mass) which occurs when the analyte binds to the bioreceptor.
- **Pyroelectric biosensors:** Based on the changes of temperature that give rise to a voltage across the material.

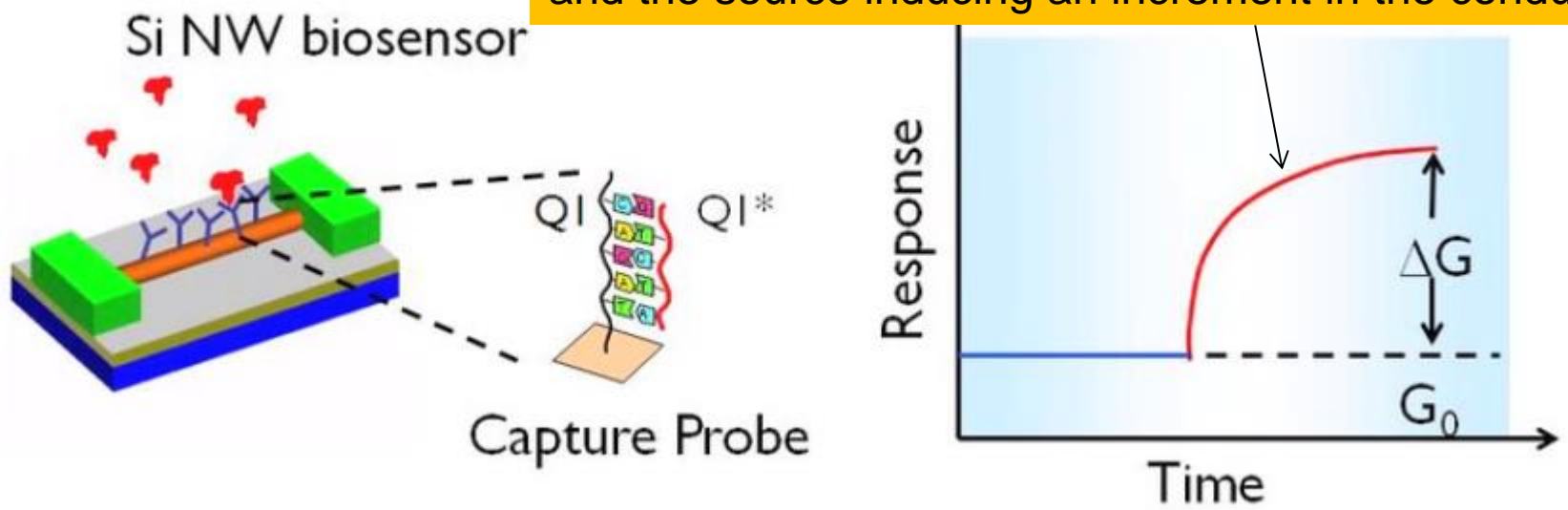
Classification of biosensors (2)

- **Optical biosensors:** Based on the change in the phase, amplitude, polarization, or frequency of the input light in response to the physical or chemical change produced by the biorecognition process
- **Electronic biosensors:** Based on a broad range of nanoscale transistors (e.g. incorporating carbon nanotubes or nanowires as channel between source and drain)

Electronic biosensor (example)



When the molecules bind to the ligand, the charges change between the drain and the source inducing an increment in the conductivity



When nanomaterials are involved in biosensing

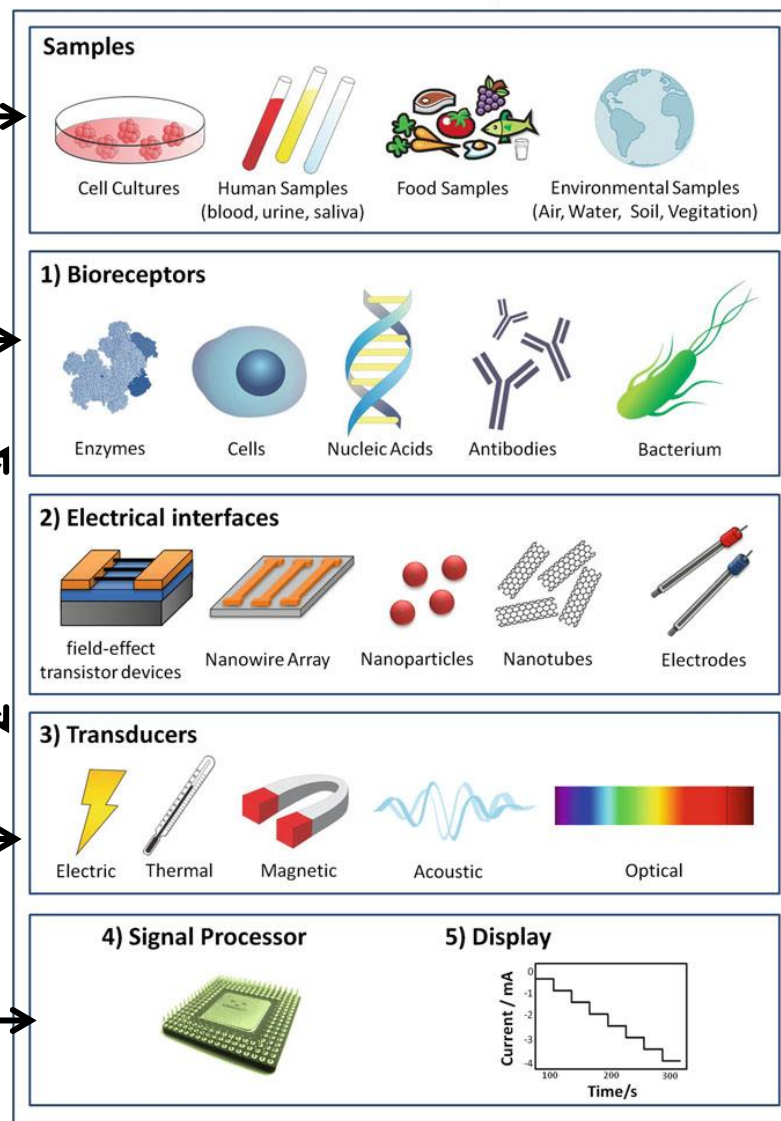
Sample to analyse

Bioreceptors

Nanomaterials can be part of the bioreceptor or the transducer

Transducers

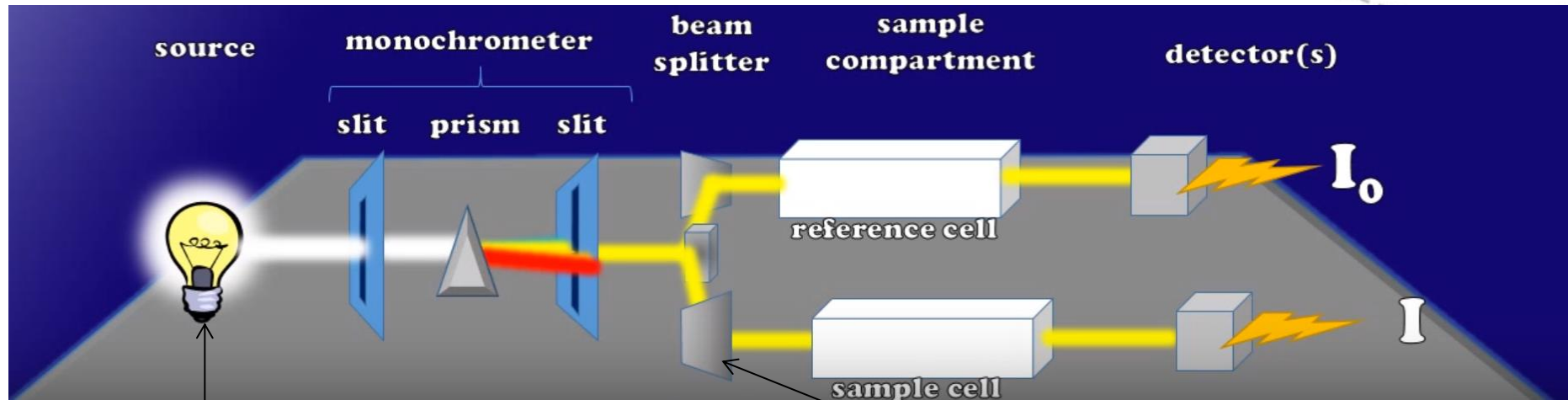
Signal processing



UV-Visible spectrophotometry

What is spectrophotometry?

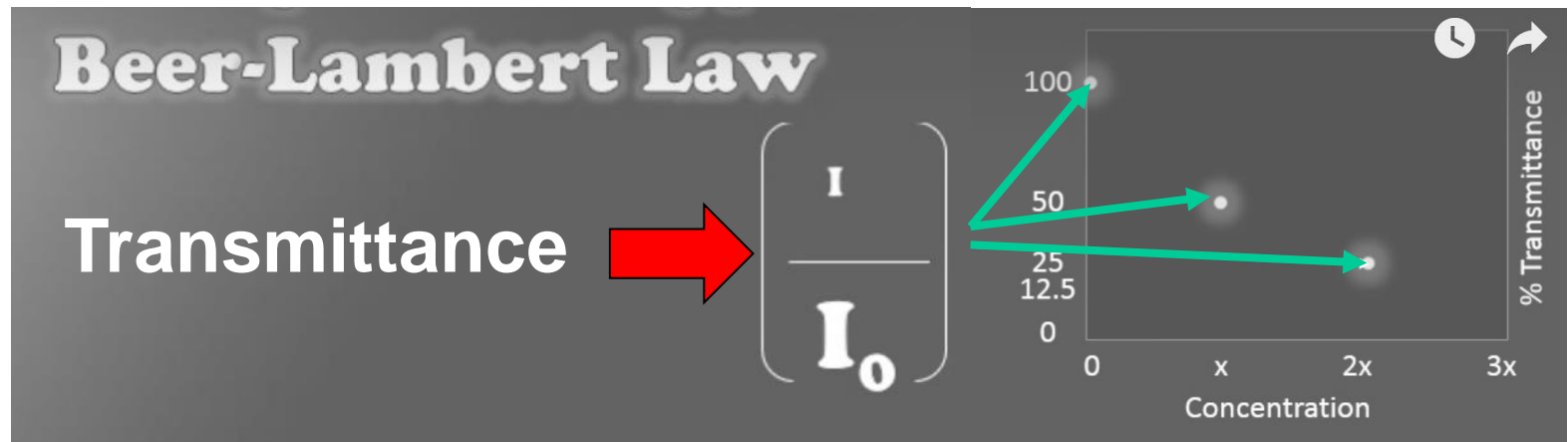
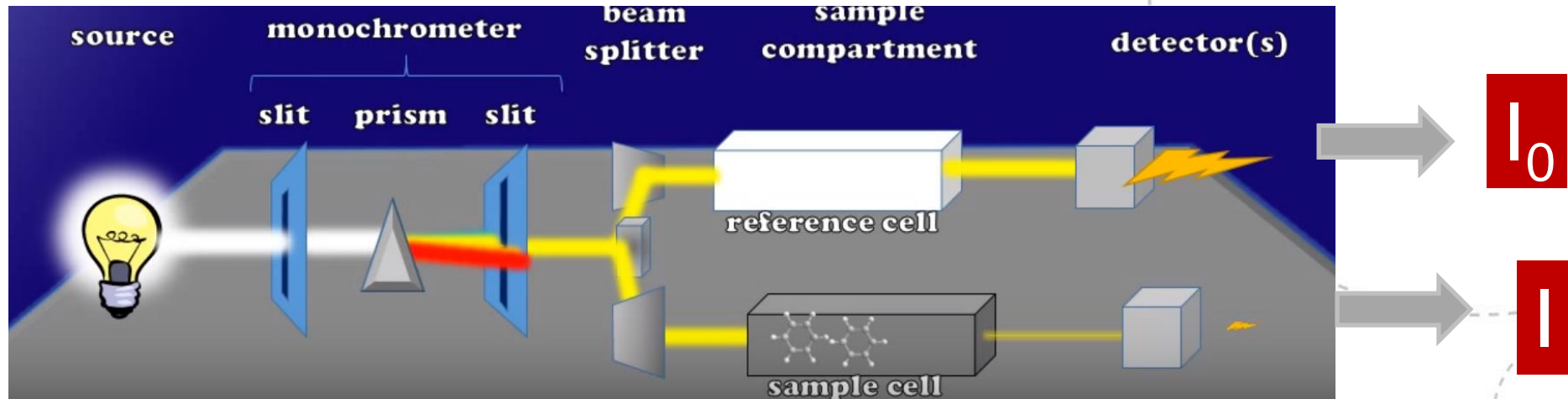
- ❖ A spectrophotometer is an instrument that measure the Changes in the light passing through a material (suspension)



Deuterium lamp
Xenon lamp
Normal lamp

The beam is divided into
2 equal parallel beams

What happens when light passes through a sample ?



Definitions

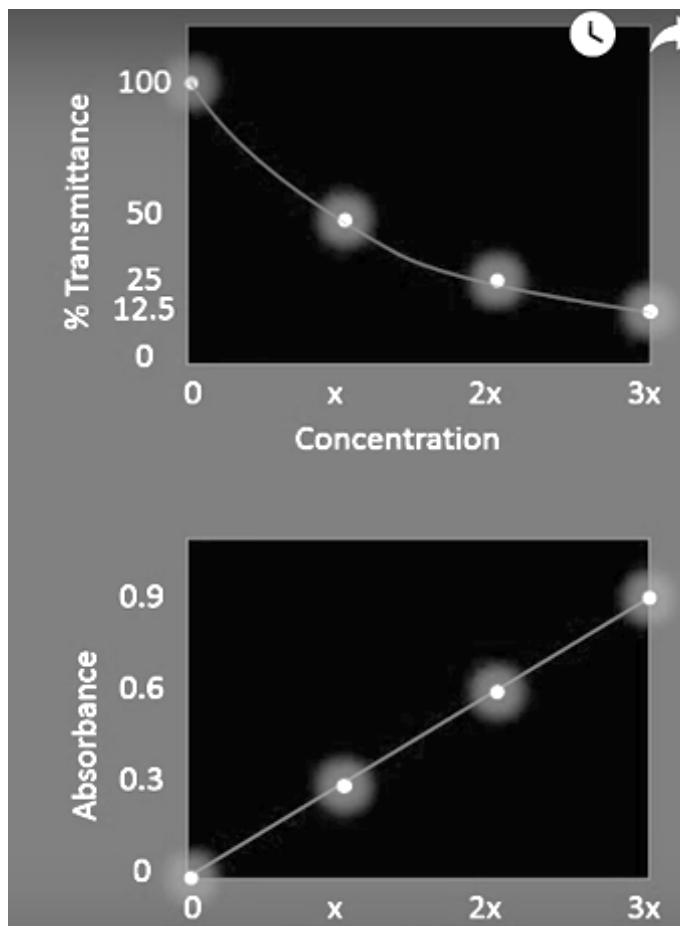
Lambert's Law

- When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the intensity of the incident light.

Beer's Law

- When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the intensity of the incident light as well as concentration of the solution.

From transmittance to absorbance



Beer-Lambert Law

$$T = 10^{-\epsilon(\text{conc})(\text{length})}$$



$$\text{Abs} = -\log T$$



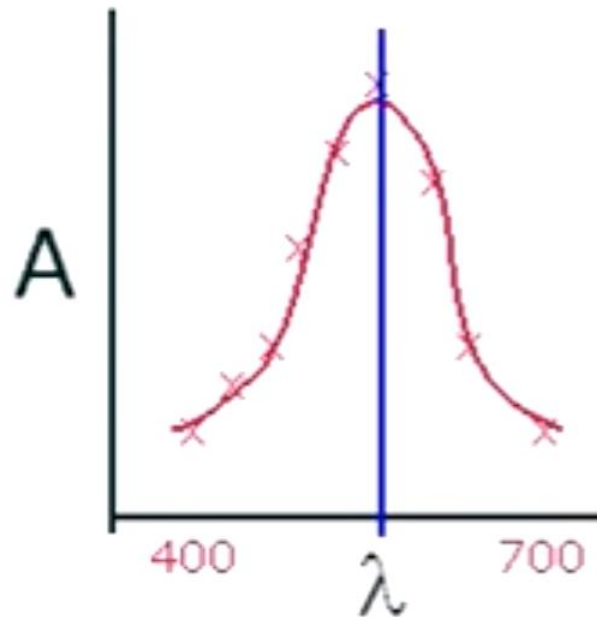
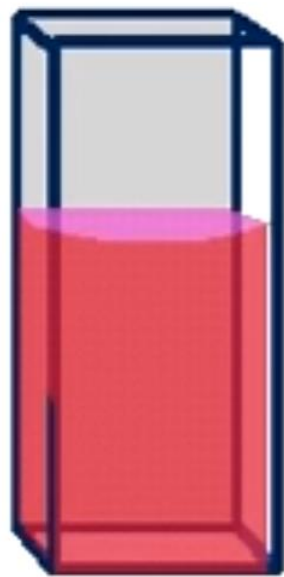
$$\text{Abs} = \epsilon(\text{conc})(\text{length})$$

Conc: concentration of the suspension

Length: is the path length of the beam of light through the material sample

ϵ : is the molar attenuation coefficient of the absorbing species *in the* sample

How to select the optimum wavelength?



Optimum
wavelength (λ)
for
maximum
absorption

To obtain accurate results from an assay the process should be performed at this wave length

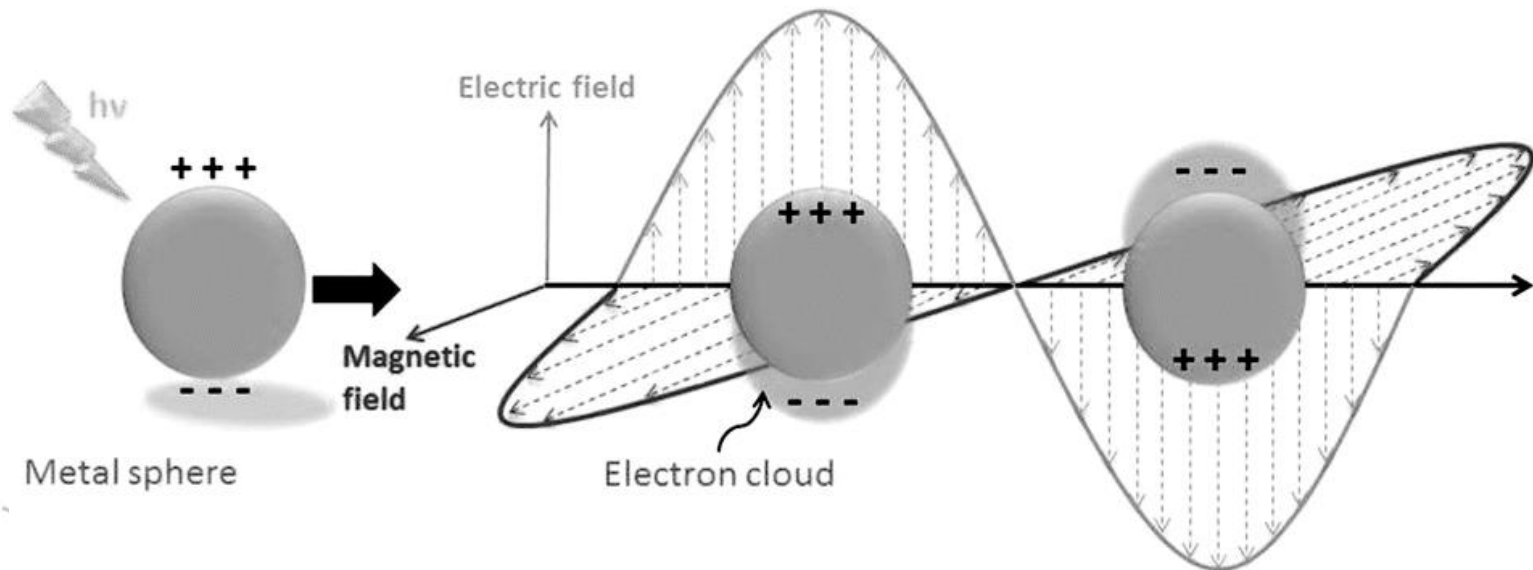
What are Surface Plasmons and Localized Surface Plasmons?

Surface Plasmon Resonance (SPR)
Localized Surface Plasmon Resonance (LSPR)

Plasmonics are the study of the interaction between electromagnetic field and free electrons in a metal.

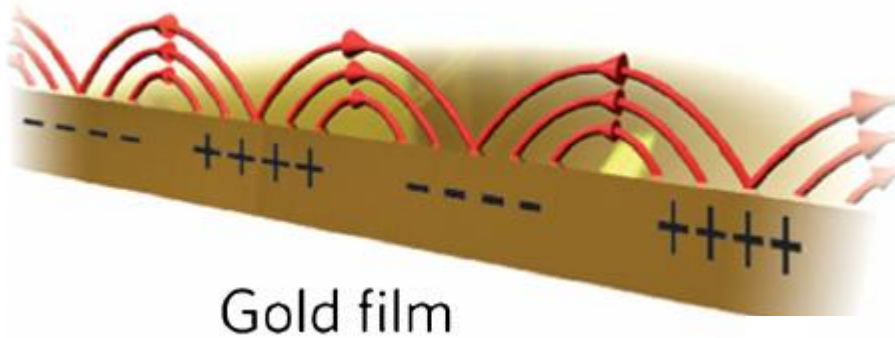
Free electrons in the metal can be excited by the electric field to have collective oscillations.

The absorption of light can be enhanced in the metal by proper designing metal patterns for Surface Plasmon excitation.



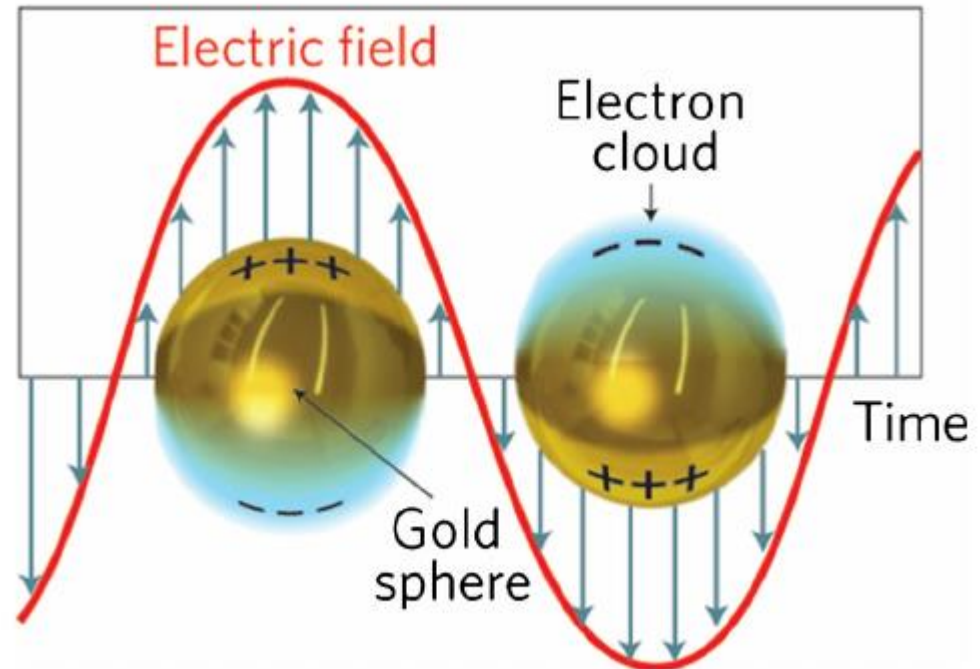
The two main ingredients of plasmon resonance

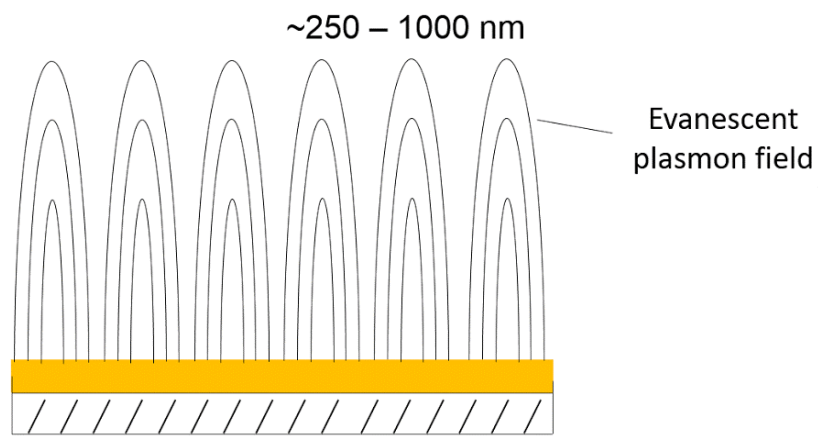
Under an electric field:



SPR: Propagation of surface plasmon polaritons along the dielectric – metal interface

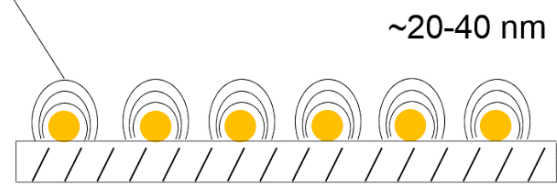
LSPR: Localized surface plasmons on the surface of a metal nanoparticles





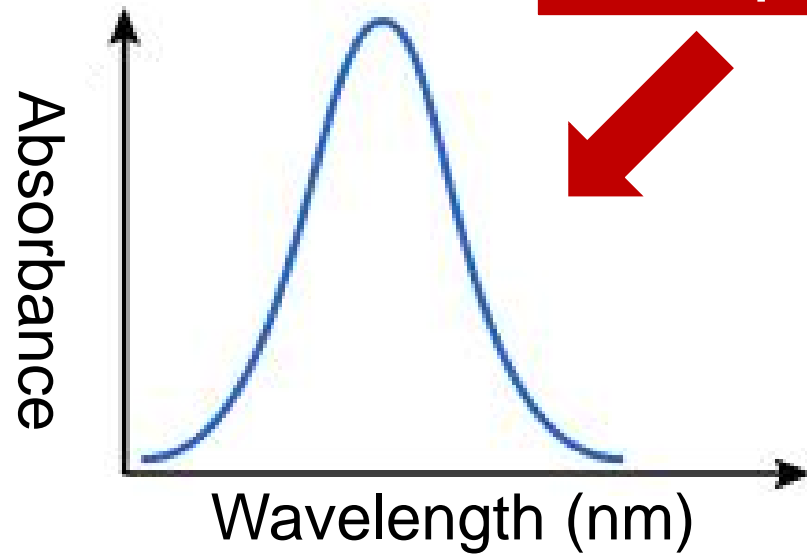
SPR
Subject to Bulk Effect

SPR are generated from thin films



LSPR
Negligible Bulk Effect

LSPR can be generated from
1- Supported nanoparticles
2- Nanoparticles in suspension



UV-Vis Spectrum

How SPR and LSPR are used for biosensing

Surface Plasmon Resonance (SPR)

Localized Surface Plasmon Resonance (LSPR)

Effect of the environment (dielectric) on LSPR

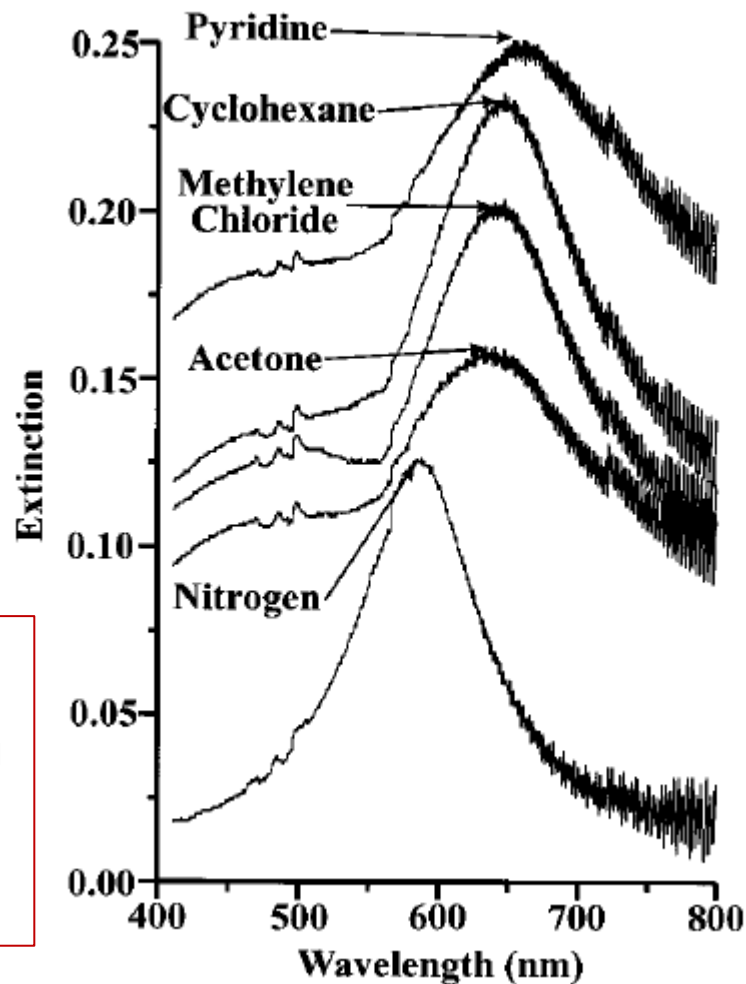
❖ Silver (Ag) nanoparticles suspended in different solutions



❖ Shift of LSPR peak to higher wavelength

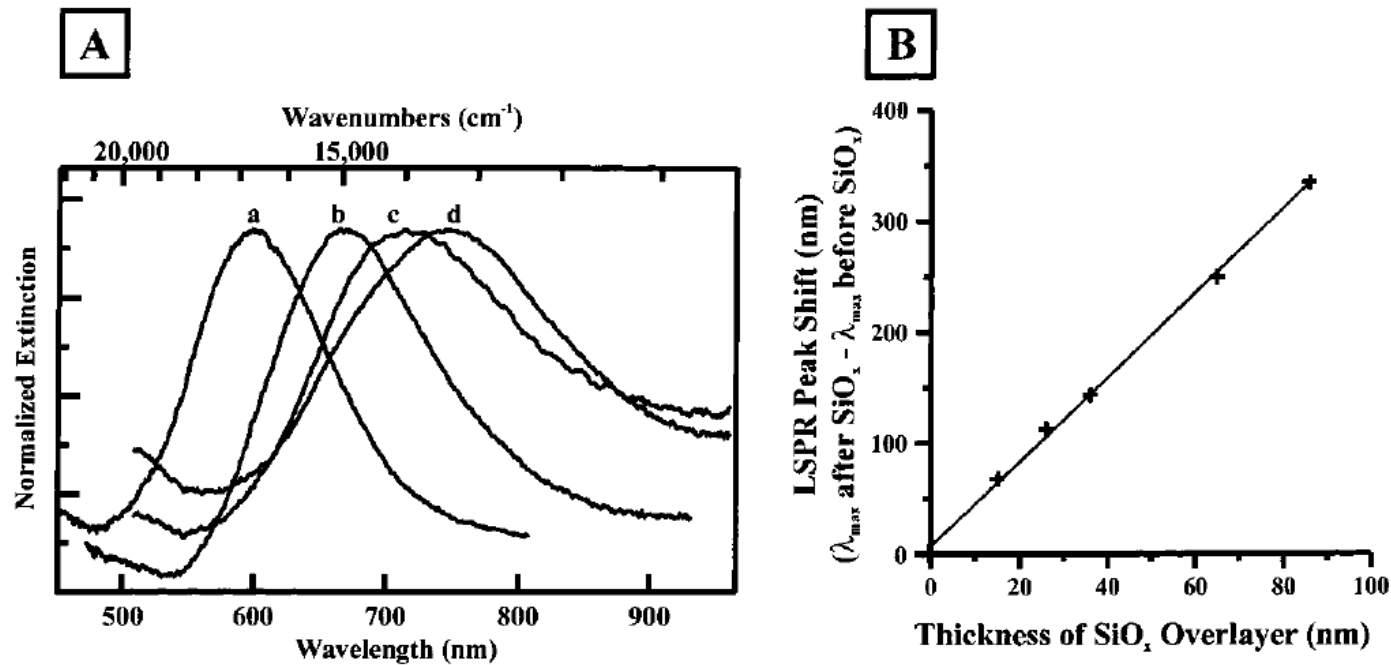


❖ LSPR peak position depends strongly on the surrounding medium (refractive index of the medium)



Effect of the environment (dielectric) on LSPR

Chem. B, Vol. 105, No. 24, 2001



Ag Nanoparticles were coated with a SiO_x thin film:

- a (No SiO_x) $\lambda = 597$ nm
- b (15 nm), $\lambda = 669$ nm
- c (26 nm), $\lambda = 714$ nm
- d (36 nm), $\lambda = 745$ nm

LSPR and SPR peak positions are highly sensitive to the surrounding environment

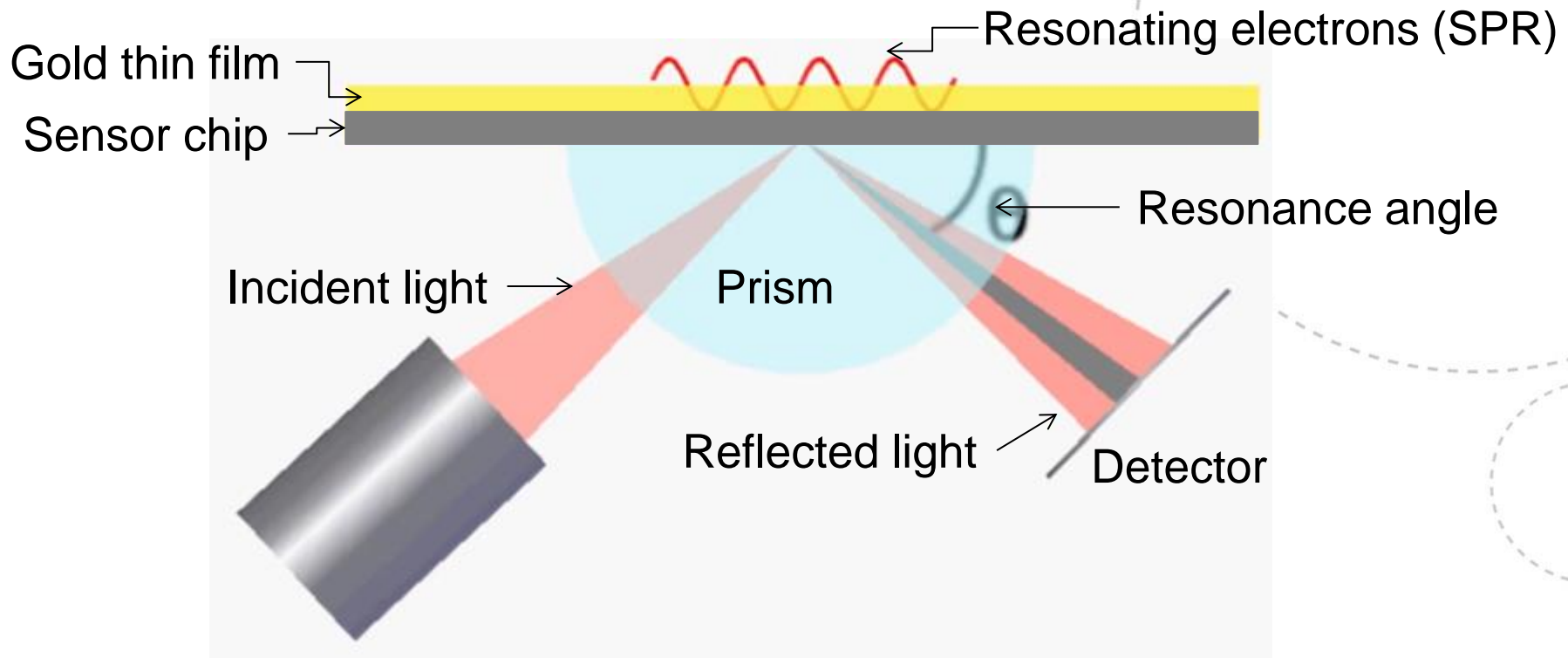


LSPR SPR peak positions are highly sensitive to the changes in the refractive index in the interface between the metal and the surrounding medium

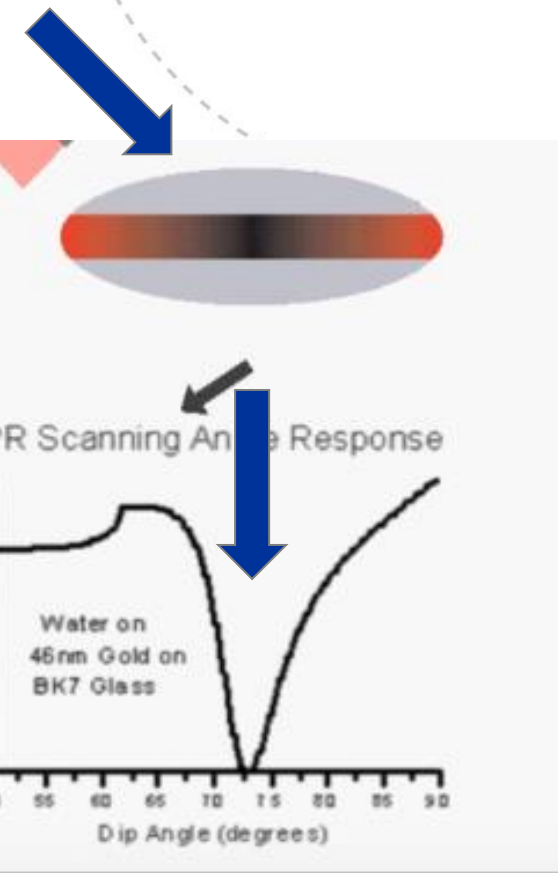
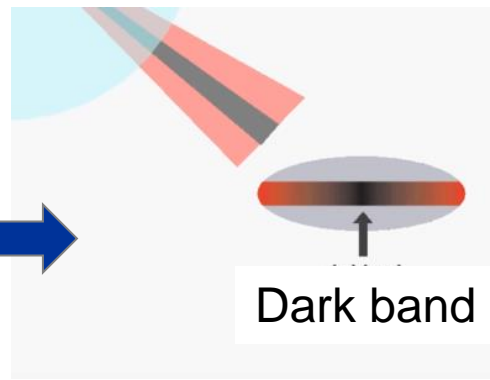
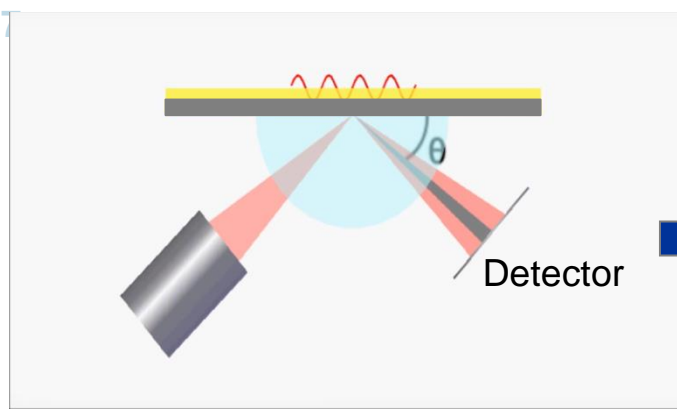


Used for highly sensitive Nanobiosensing

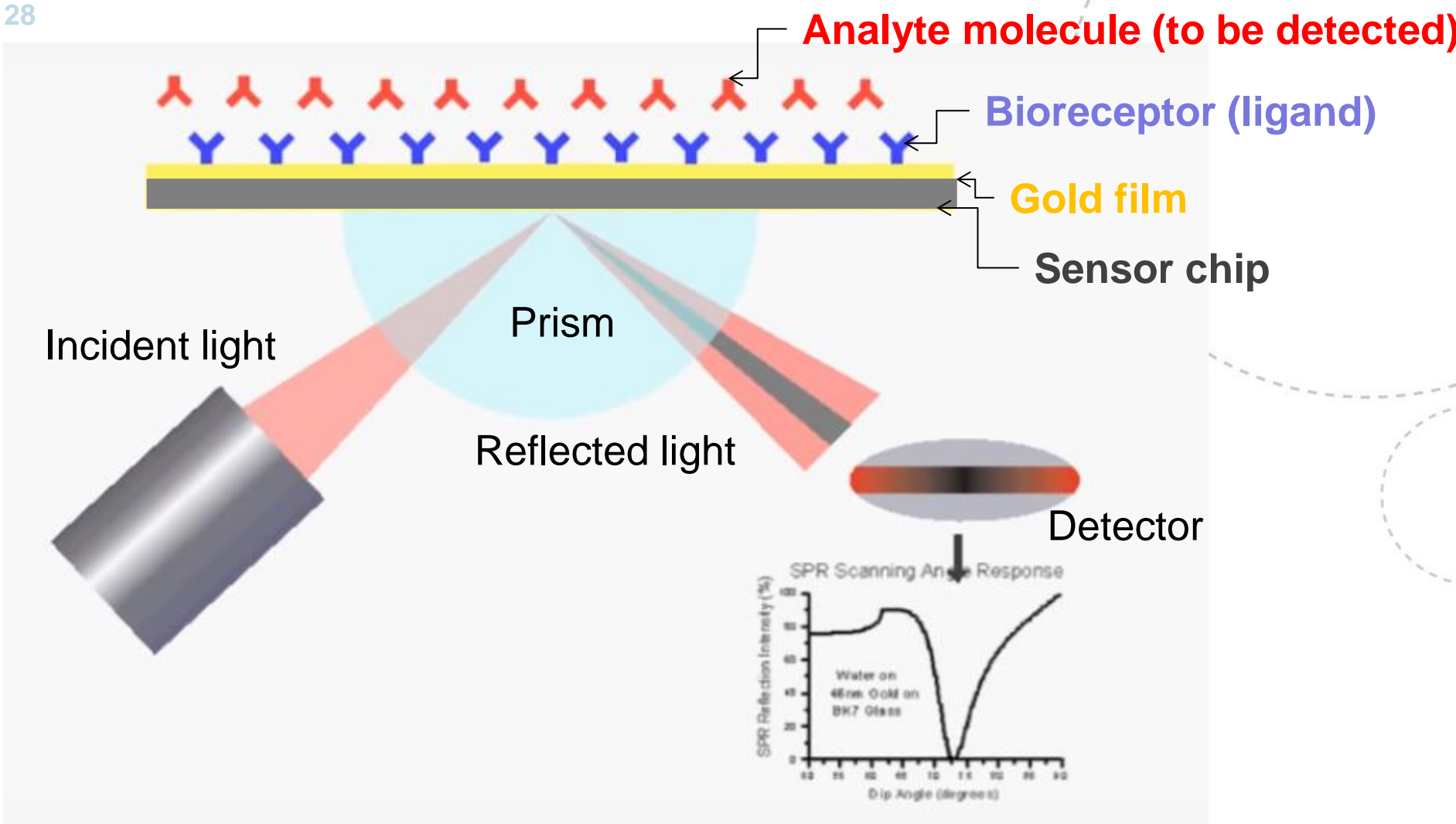
SPR based biosensors



- Light is absorbed causing the e^- s resonance
- This resonating e^- s are known as surface plasmon
- This resonance results in a decrease in the intensity of the reflected beam

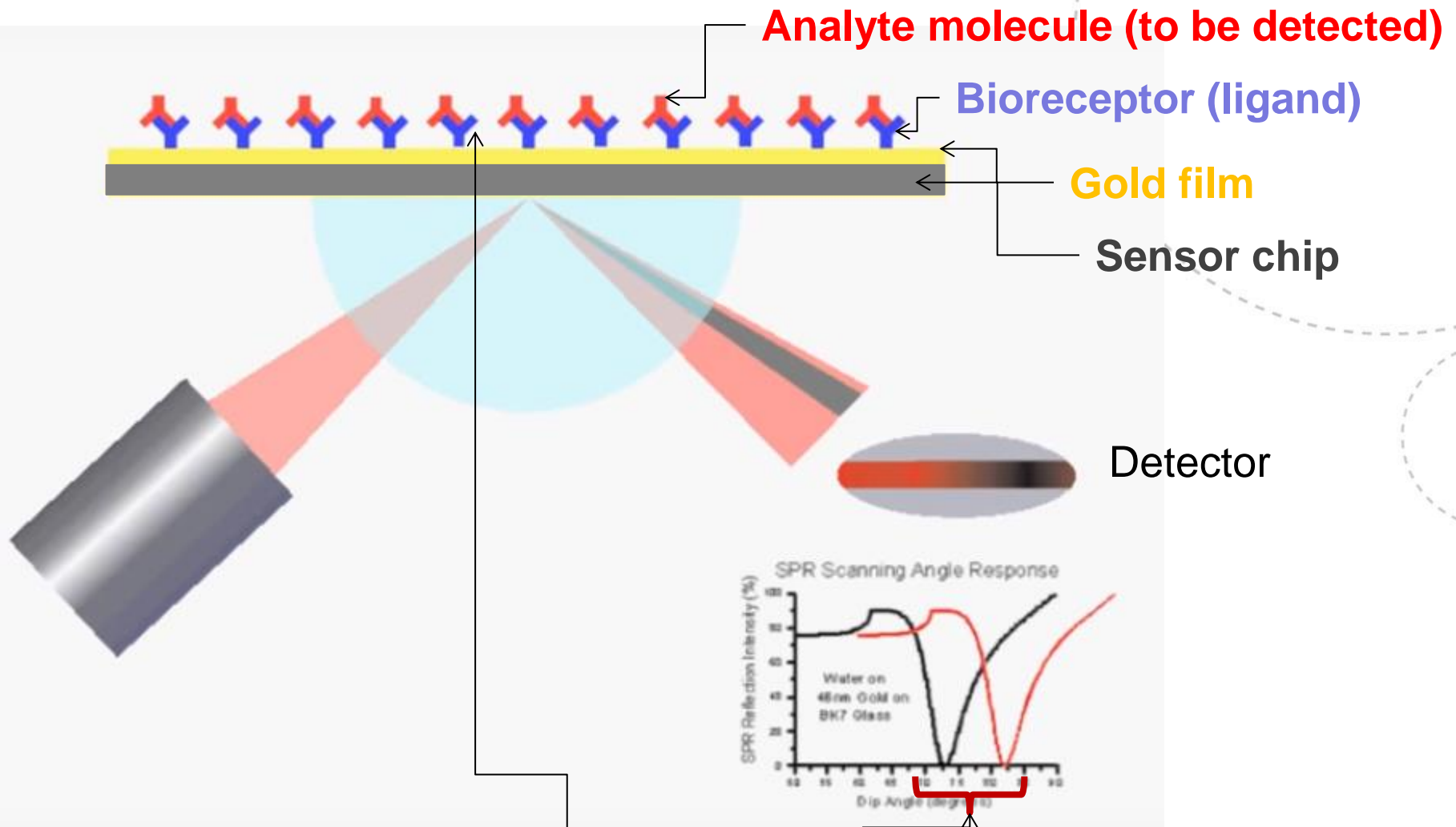


- The decrease in the intensity of the reflected light appears as a dark band on the detector
- And can be seen as a dip in SPR curve.



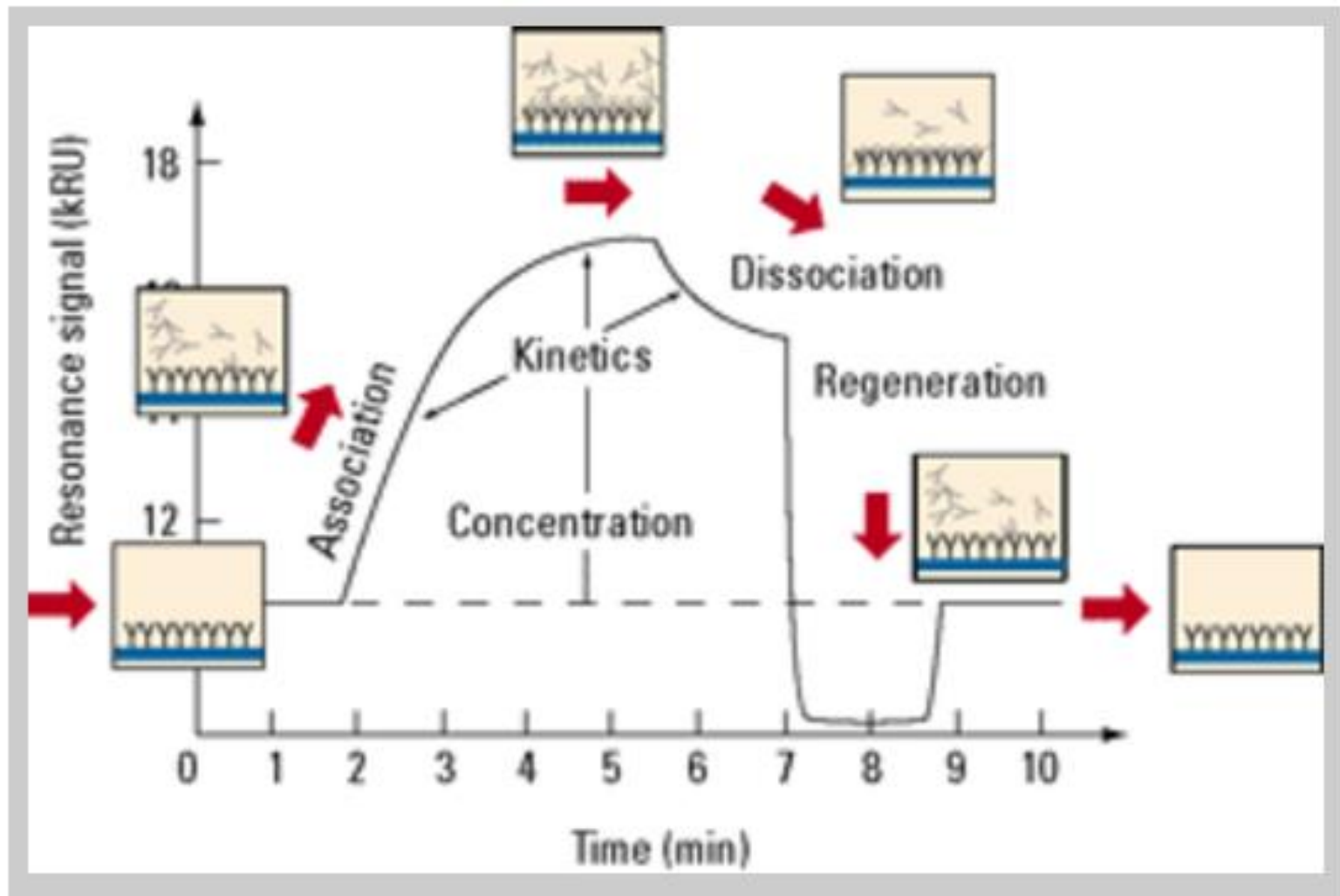
Surface plasmons are sensitive to the surrounding environment

Direct method of detection



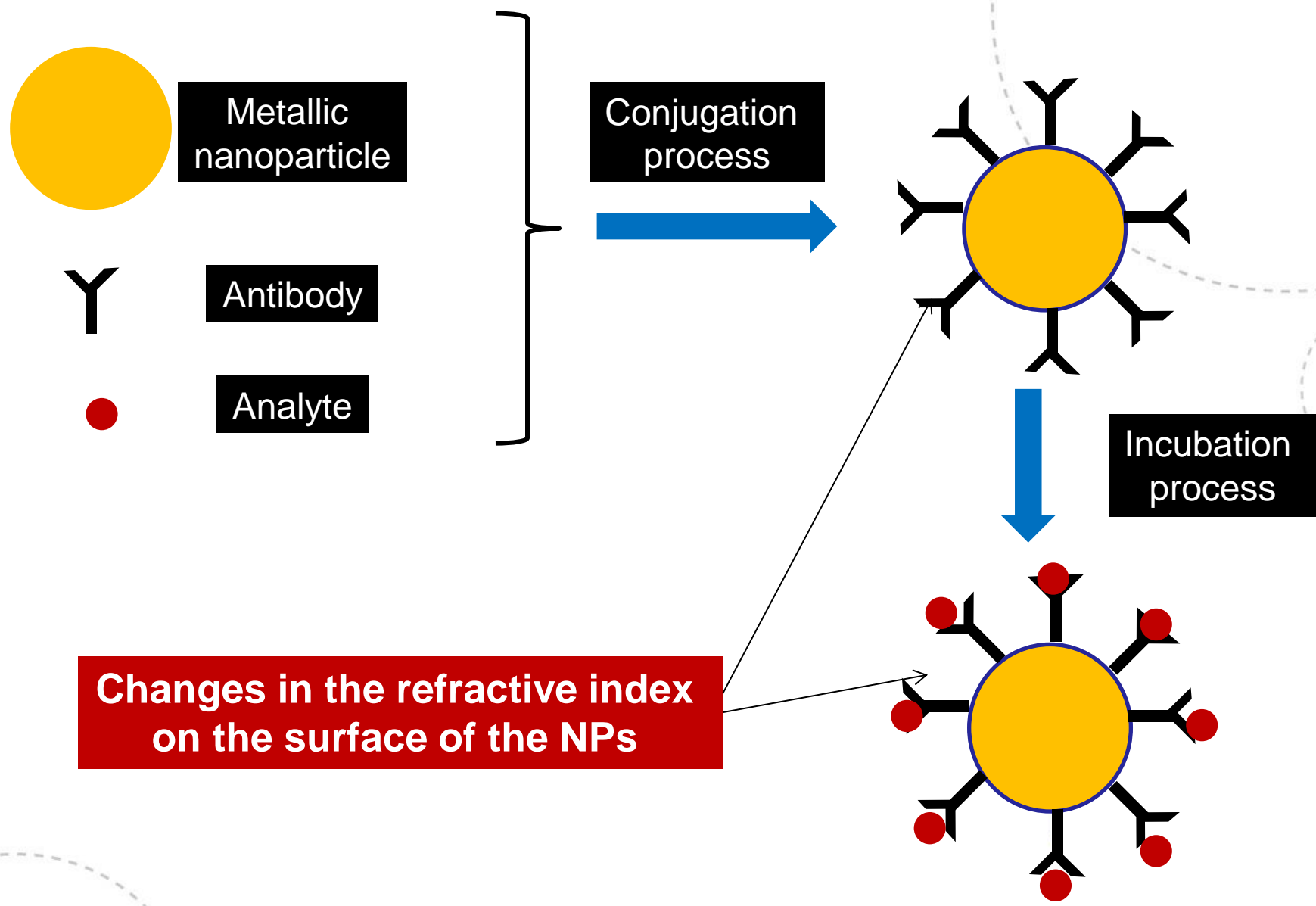
A change in the refractive index is detected when the analyte is captured inducing the SPR peak shift

Indirect method of detection



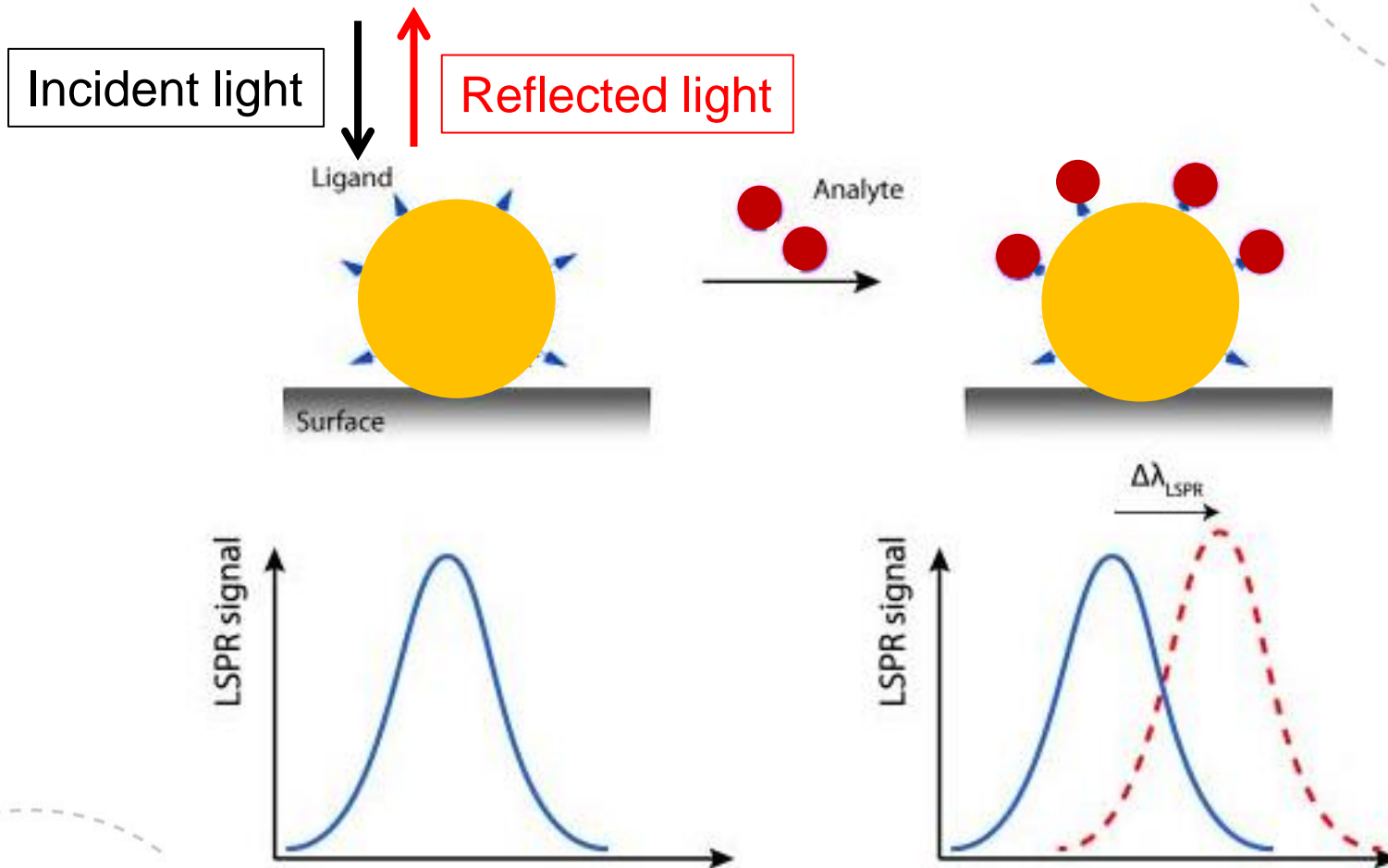
The main difference is based on signal processing

LSPR based biosensors (Functionalization of NPs)

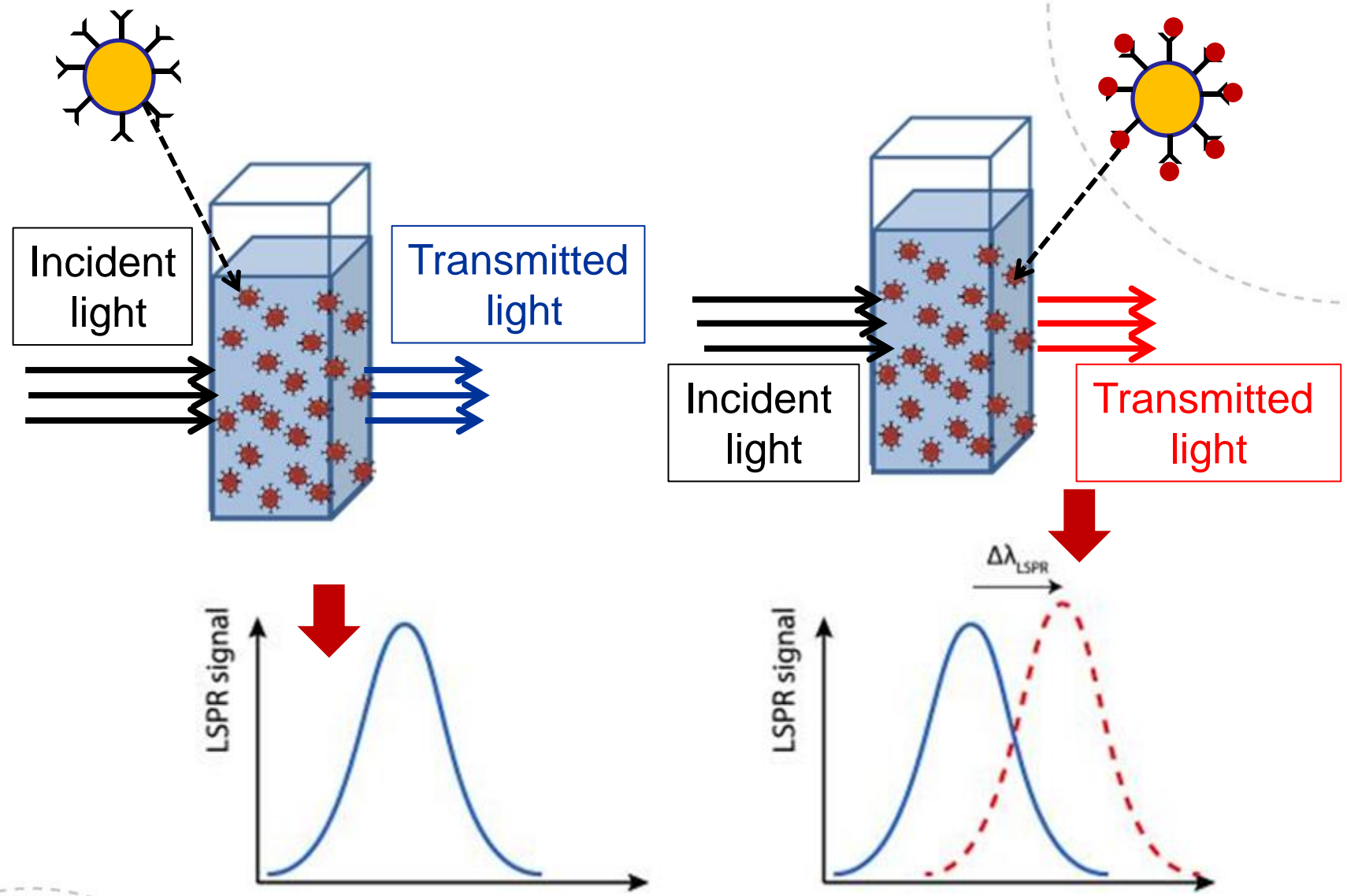


LSPR based biosensors (supported nanoparticles)

LSPR peak position depends on the refractive index in the interface between the metal and the medium



LSPR based biosensors (nanoparticles in suspension)

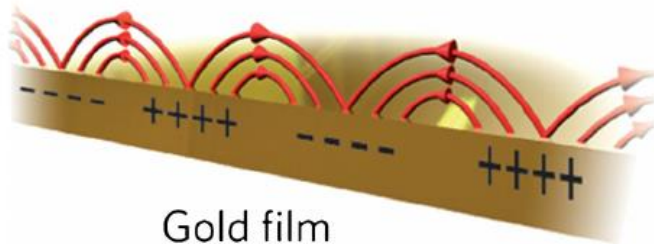


Comparing SPR and LSPR

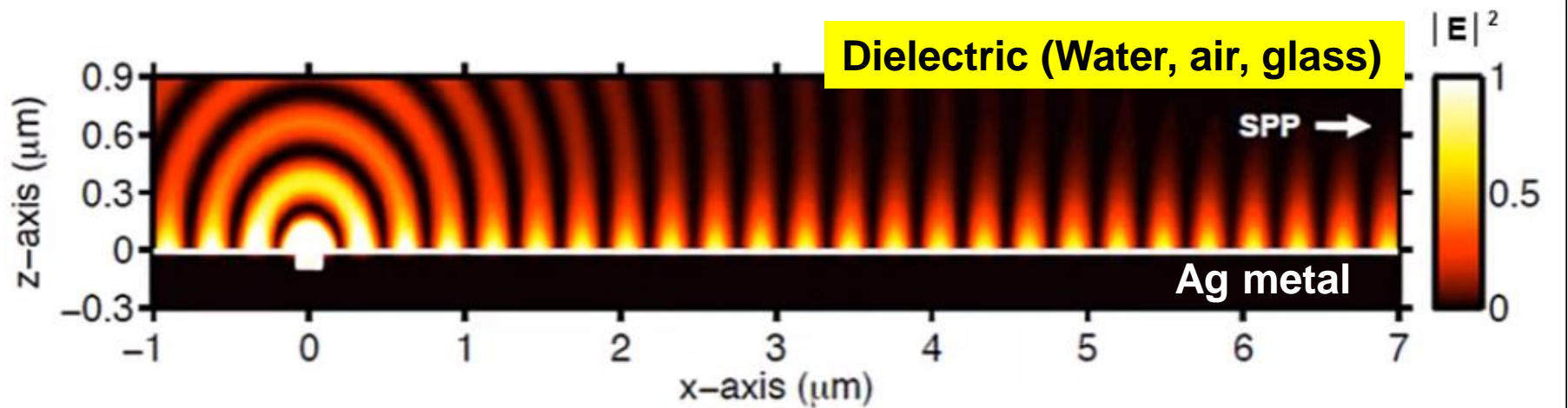
Advantages and disadvantages

FDTD Computational modelling

(Finite-Difference Time-Domain)



SPR: Propagation of surface plasmon polaritons along the dielectric – metal interface

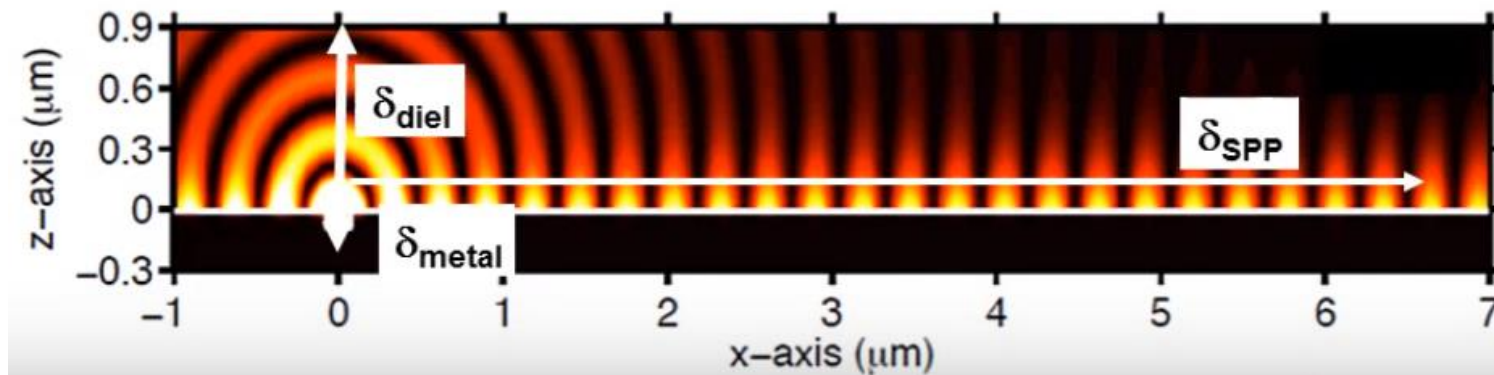


Lindquist et al. Rep. Prog. Phys. 75 (2012) 036501

Order of magnitude of the Plasmon lengths in SPR

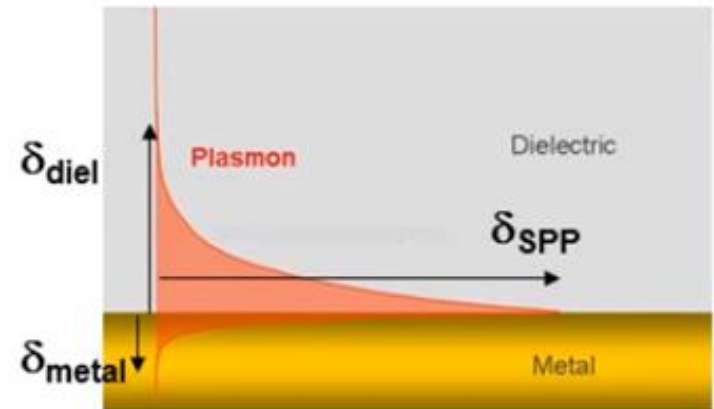


- δ_{diel} : **Evanescent field in the dielectric**
- δ_{metal} : **Evanescent field in the metal**
- δ_{SPP} : **Surface plasmon propagation**



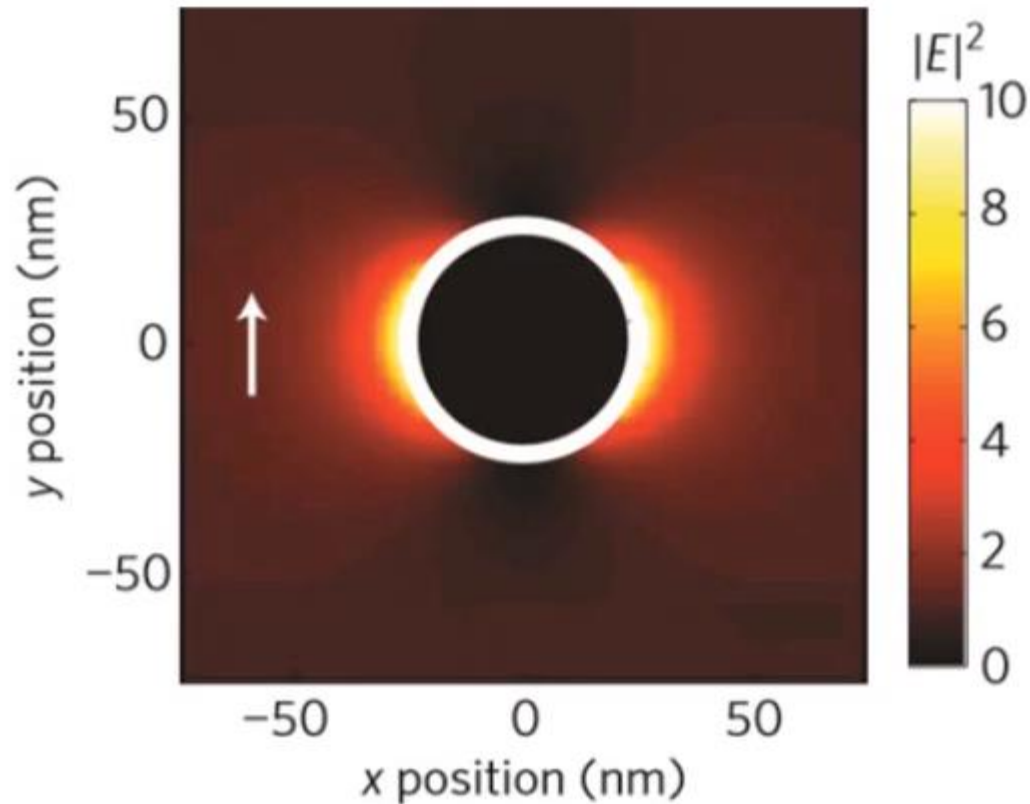
Order of magnitude of the Plasmon lengths in SPR

- λ : wavelength of light (~ 500 nm)
- δ_{metal} ~ 5 nm
- δ_{diel} ~ 250 - 1000 nm
- δ_{SPP} ~ 2 - 20 μm at $\lambda \approx 500$ nm,
up to 1 mm at $\lambda \approx 1550$ nm



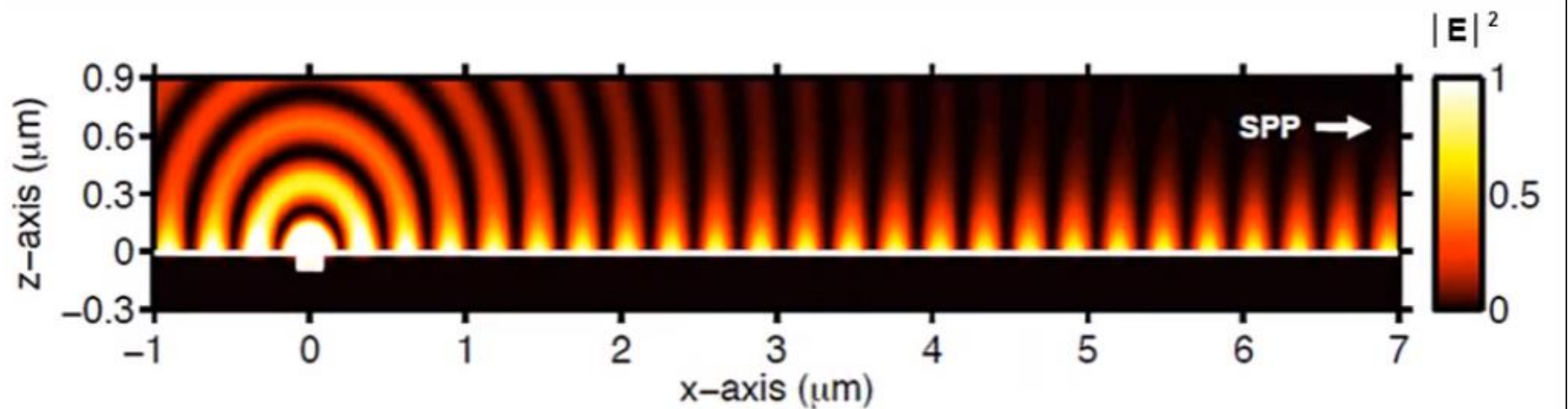
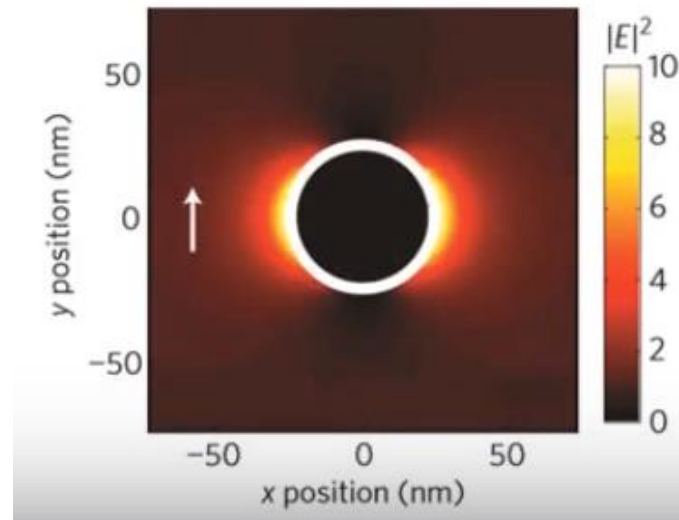
FDTD Computational modelling

(Finite-Difference Time-Domain)



**20 nm Ag spherical particle &
electromagnetic field intensity**

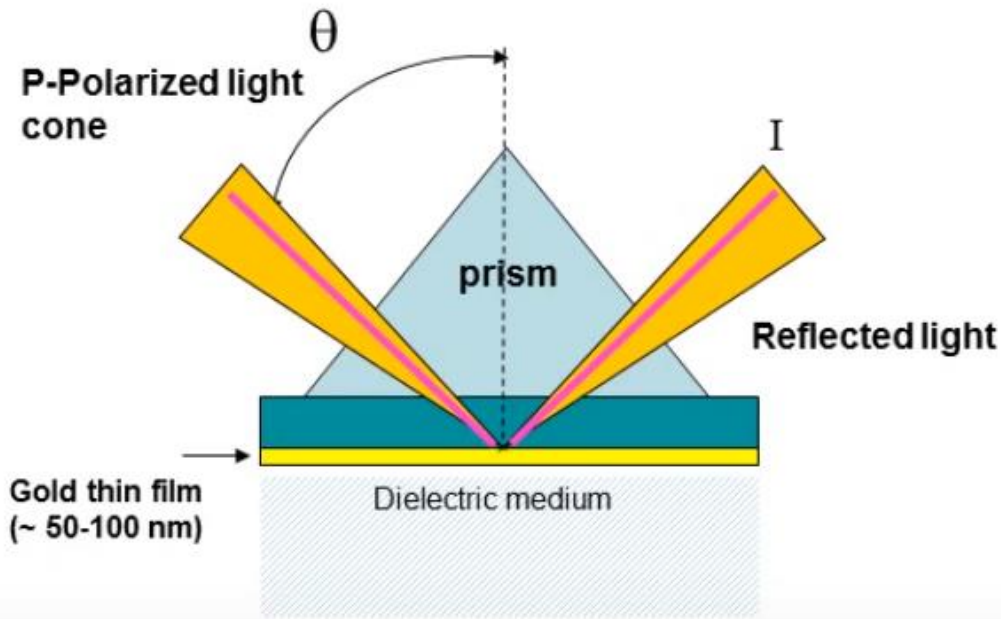
FDTD Computational modelling (*Finite-Difference Time-Domain*)



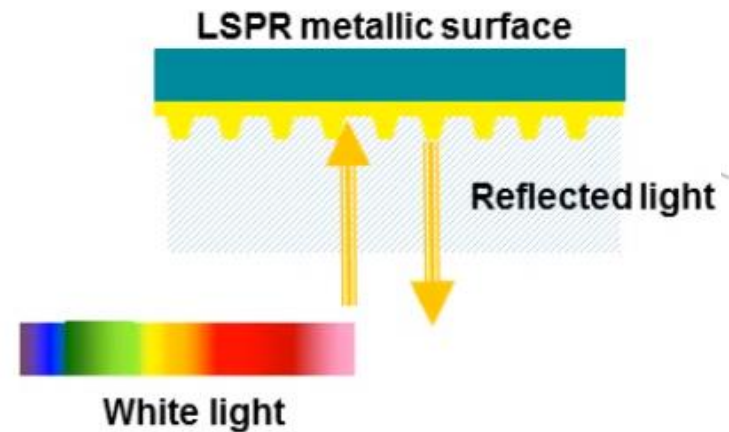
Lindquist et al. Rep. Prog. Phys. 75 (2012) 036501

LSPR is Instrumentally Simple vs. SPR

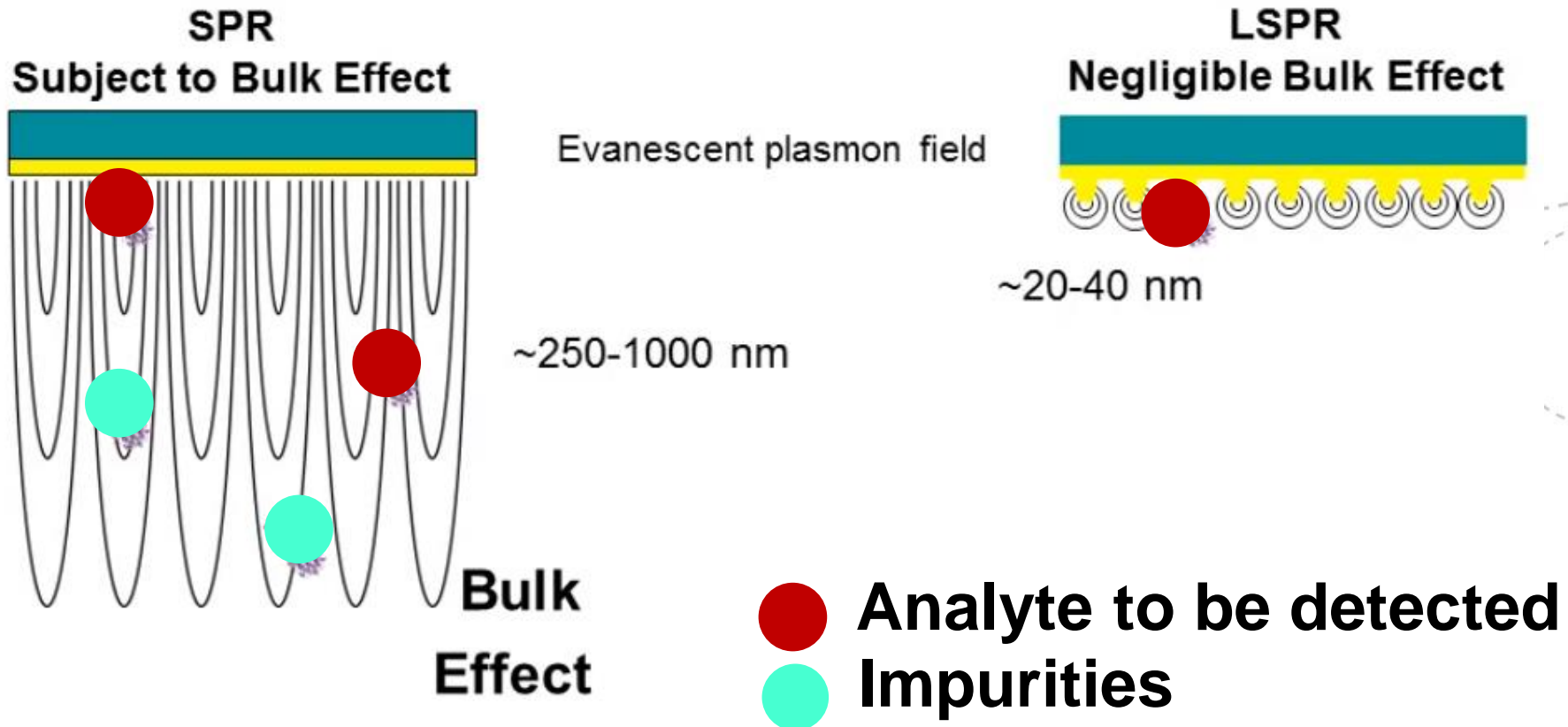
SPR: Instrumentally Complex



LSPR: Instrumentally Simple



LSPR has Marginal Bulk Effects vs. SPR



LSPR has unique advantages for diagnosis application

- ❖ LSPR and SPR are surface plasmon enabled sensing techniques
- ❖ LSPR advantages over SPR
 - Marginal bulk effects (higher precision in detection)
 - Instrumental simplicity. No adaptative optics or thermal controls needed
 - Easy to adapt to different types of assay enhancements
- ❖ Other LSPR advantages
 - Design flexibility, scalability and low cost
 - Minuaturization and mobility
 - Robust for high sensitivity diagnostic applications

Next Lecture

Nanomaterials and environment (Water treatments)