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Optical Biosensors: Fundamentals in Optics B

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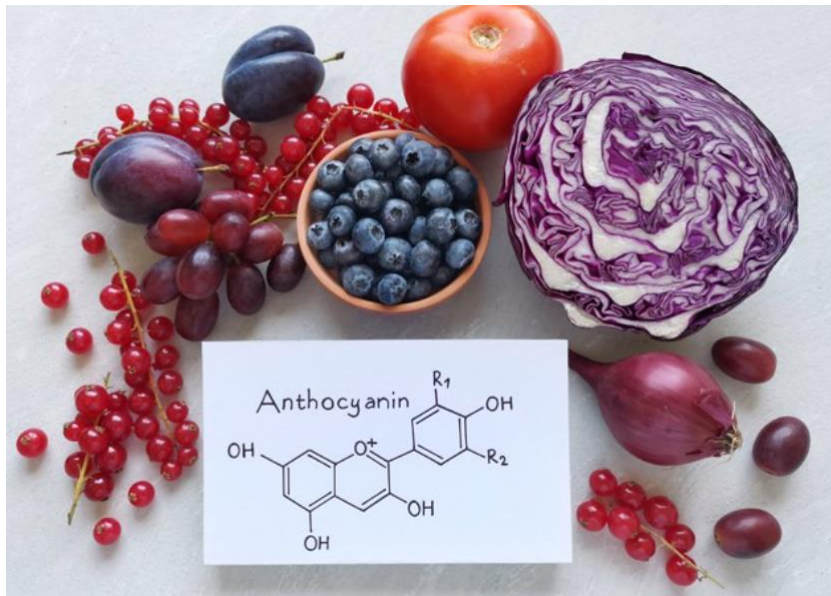
Web: <http://www.fzu.cz/> | <https://www.dpu-research-list.at/> | <http://www.jakubdostalek.cz>

Content

- **Localized and propagating surface plasmons, Mie scattering, plasmonic field confinement.**
- **Diffraction, coupling to guided waves.**
- **Hybridization of plasmon modes. Plasmonic ruler.**
- **Photonic crystals, structural colors.**
- **Metallic nanostructures and their use.**

On colors...

Physical-chemical: absorption at certain wavelength due to transitions between quantized energy levels of dyes.



Shutterstock.com

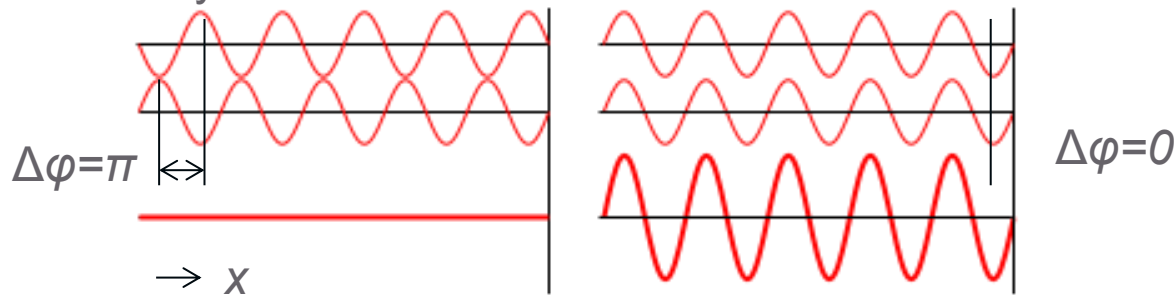
Structural: typically occurring due to refraction or interference on periodic structures or thin films.



<https://www.eudonev.com/portfolio/structural-color/>, www.geologyin.com

Interference

Optical phenomenon arising from (coherent) superimposing of amplitudes of two spatially overlapping waves. When changing a phase φ of one of the waves, intensity is varied.



Field amplitudes are subtracted – destructive interference

Field amplitudes are added – constructive interference



$\Delta\varphi = k_0 n d$ – a minute changes in refractive index shifts the phase and alters the intensity

$$u(x, t) \propto \sin(k_0 n x - \omega t)$$

Exploited in (arguably) most sensitive optical measurements: Frequency stabilized lasers for metrology, microscopy with phase contrast, narrow optical filters,...

Diffraction



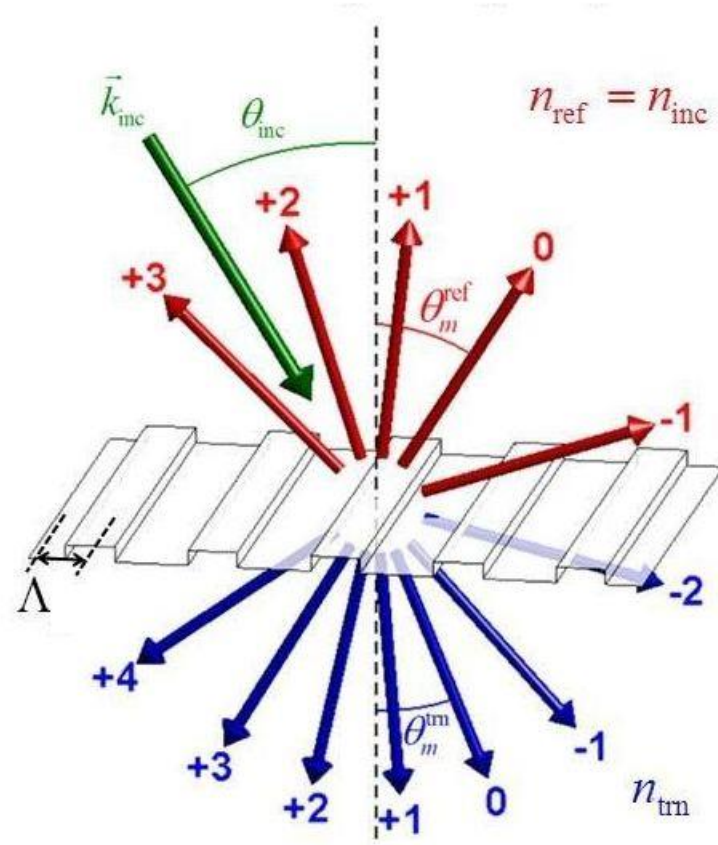
Periodic structures with a period $\Lambda \sim \lambda$ leads to coupling to series of propagating (and evanescent) diffraction orders.

Reflection Region

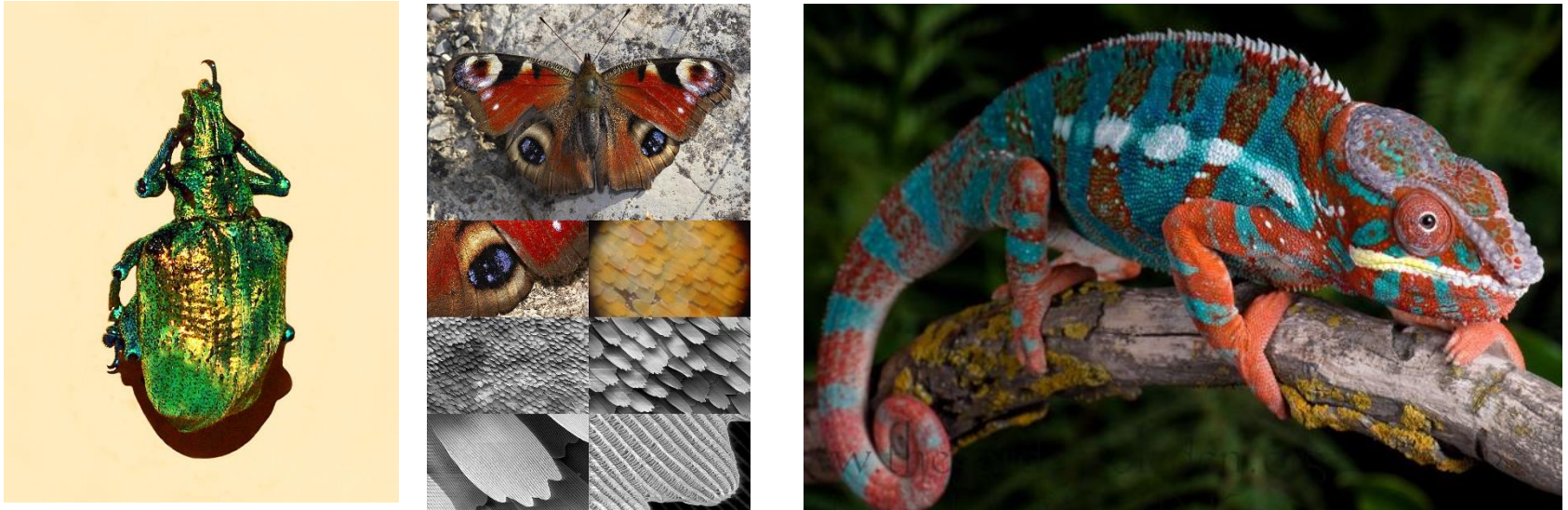
$$\underbrace{n_{\text{ref}} \sin \theta_m = n_{\text{inc}} \sin \theta_{\text{inc}} - m \frac{\lambda_0}{\Lambda}}_{\text{Reflection Region}}$$

Transmission Region

$$\underbrace{n_{\text{tm}} \sin \theta_m = n_{\text{inc}} \sin \theta_{\text{inc}} - m \frac{\lambda_0}{\Lambda}}_{\text{Transmission Region}}$$



Nature-Made Structural Colors

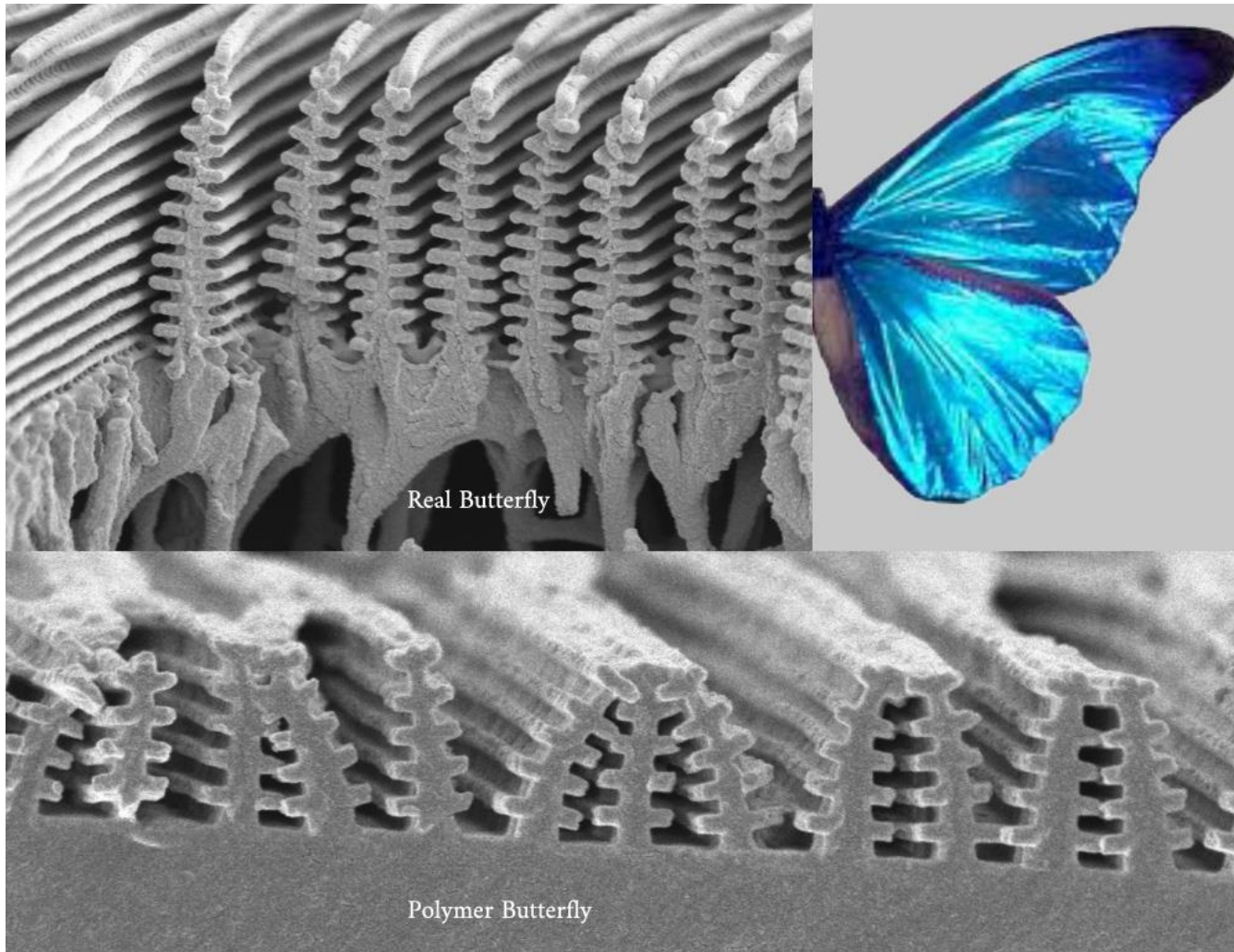


<https://en.wikipedia.org/>

A chameleon has **two superimposed layers** within its skin, and the **upper layer** consists of **nanocrystals** of different sizes. A chameleon **changes its color** by **changing the size and shape** of these **nanocrystals**.

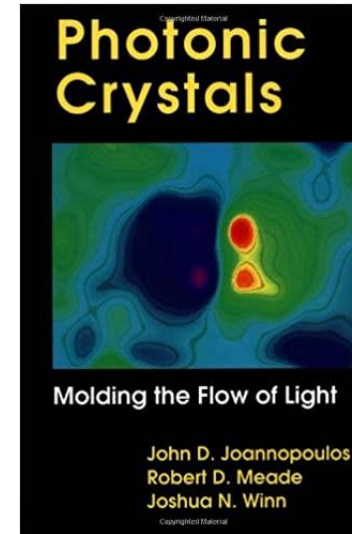
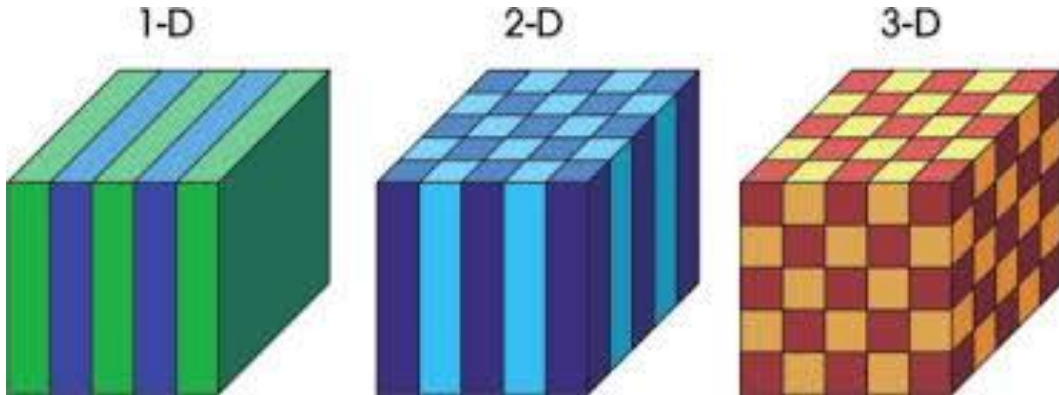
- When a chameleon is in a **relaxed state**, the nanocrystals in the **skin are closer** to each other and they **reflect shorter wavelengths**, like **blue and green**.
- When a chameleon is **excited**, the distance between nanocrystals **increases** and it reflects **longer wavelengths**, such as **red, orange and yellow**.

Butterfly

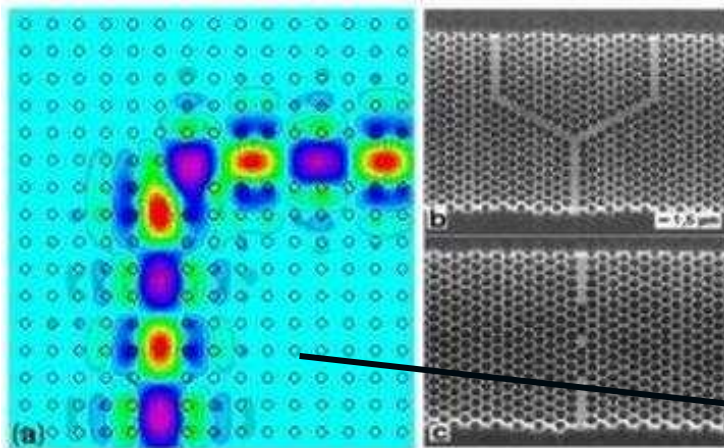


<https://www.eudonev.com/portfolio/structural-color/>

Man-Made Photonics Crystals



The concept of photonics crystals was introduced in 1990ties, flourished in various optical research and technologies.



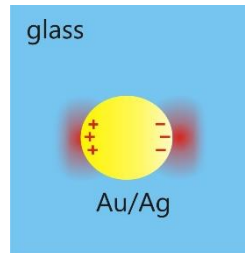
Confinement of light by surrounding with material exhibiting the photonic bandgap

On colors associated to metallic nanostructures

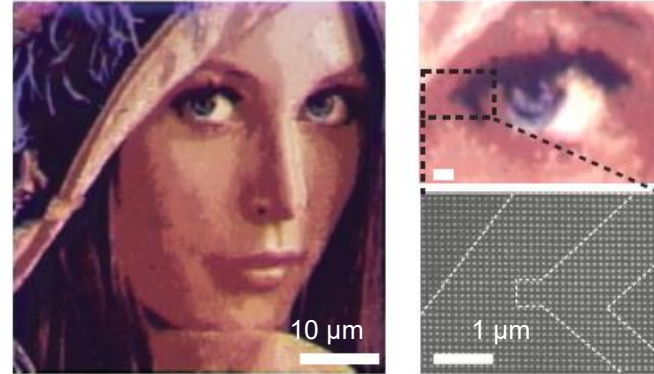


Lycurus cup, 4th century AD
British museum

Au/Ag nanospheres:

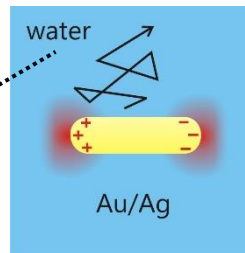


Al nanodisks:



Kumar et al., Nature Nanotechnology (2012) DOI:
10.1038/NNANO.2012.128

Au nanorods:



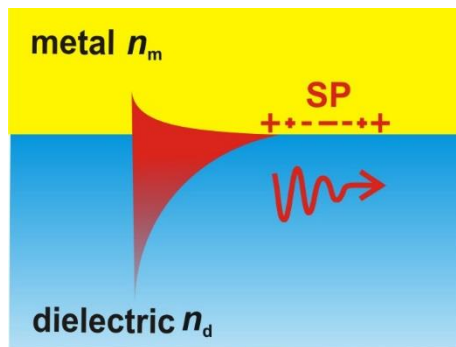
Nanopartz Inc.

Surface Plasmon Resonance:
can generate structural colors through collective oscillations of free electrons in metals, tunability by the geometry of metallic nanostructures.

Propagating Surface Plasmons

Surface plasmons (SPs) or also called surface plasmon polaritons (SPPs) are waves originating from coupled oscillations of electron plasma density and associated electromagnetic field on a metal – dielectric interface.

They travel along single interface which serves a waveguide.



Propagation constant β can be analytically expressed as:

$$\beta = \frac{2\pi}{\lambda} \sqrt{\frac{n_m^2 n_d^2}{n_m^2 + n_d^2}}$$

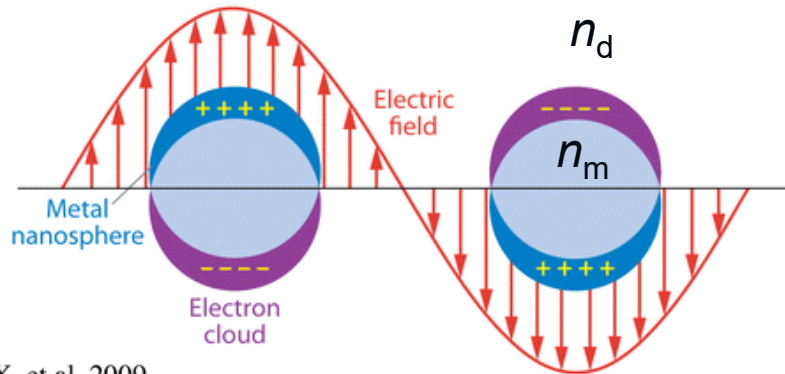
- ➡ SPs allows for tight confinement of electromagnetic field at the interface.
- ➡ For visible near infrared wavelength typically gold and silver is used where the $\text{Re}\{n_m^2\} < 0$.
- ➡ Majority of the field is probing the dielectric n_d .

Localized Surface Plasmons

Localized surface plasmons (LSPs) are associated with electron plasma density oscillations on metallic nanoparticles. Provides unique optical / plasmonic characteristics.

Resonant effect, e.g. for spherical metallic nanoparticle with $d \ll \lambda$ the resonance wavelength λ_{LSPR} obeys:

$$\text{Re}\{n_m^2(\lambda)\} + 2n_d^2(\lambda) = 0$$



Localized surface plasmon resonance is associated with strong:

- ➔ Absorption
- ➔ Scattering
- ➔ Field confinement and enhancement

Lu X, et al. 2009.
Annu. Rev. Phys. Chem. 60:167–92

Mie Scattering

The Mie solution to Maxwell's equations (also known as the Lorenz–Mie solution, the Lorenz–Mie–Debye solution or Mie scattering) describes the scattering of an electromagnetic plane wave by a homogeneous sphere. The solution takes the form of an infinite series of spherical multipole partial waves. It is named after Gustav Mie.

Rayleigh approximation (scattering)
 $d \ll \lambda$

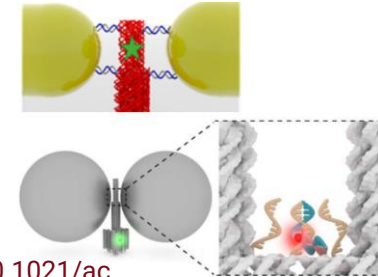
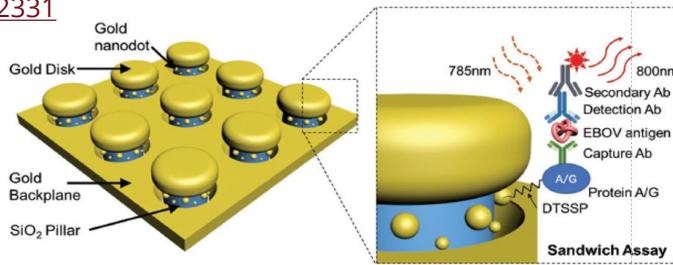
$$I_{scattered} \sim \left(\frac{2\pi}{\lambda} \right)^4 \left(\frac{n_m^2 - n_d^2}{n_m^2 + 2n_d^2} \right)^2 \left(\frac{D}{2} \right)^6$$

Valid for small spherical nanoparticles, other shapes and geometries needs to be typically treated numerically: finite difference time domain (FDTD), discrete dipole approximation (DDA)...

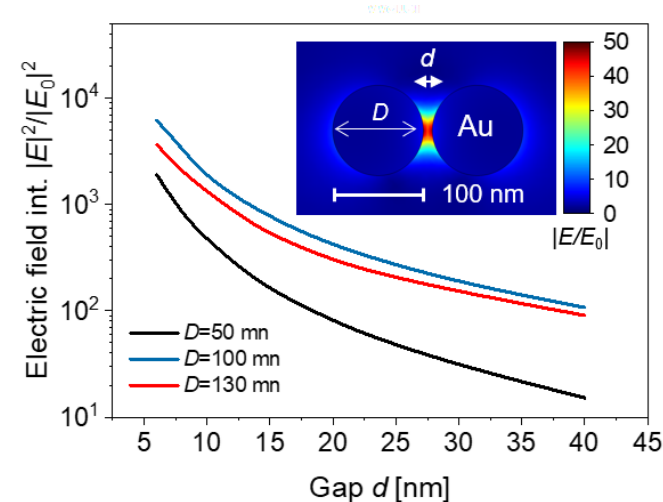
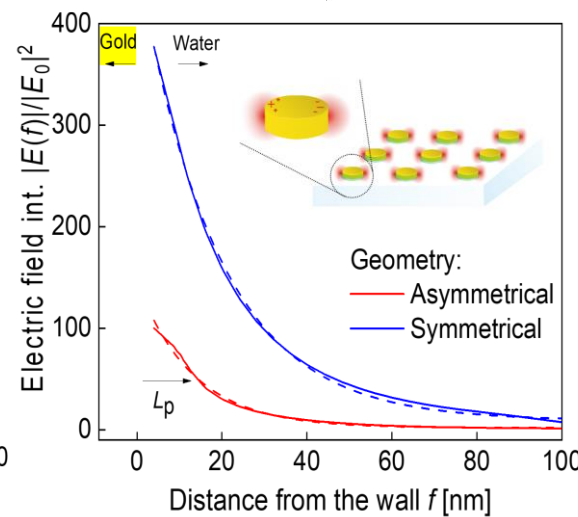
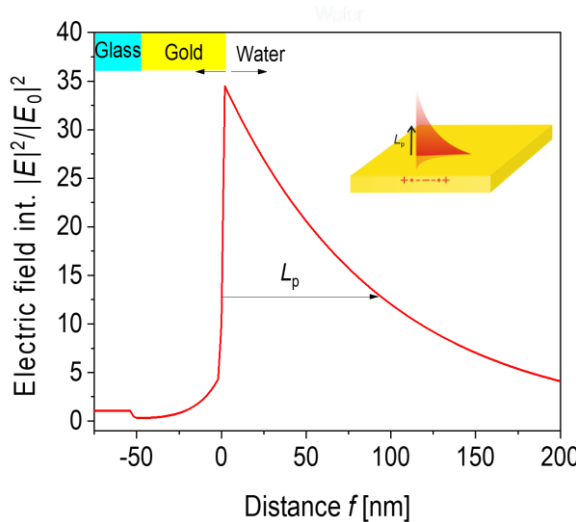


Surface Plasmons – field enhancement

<https://doi.org/10.1002/adma.201902331>

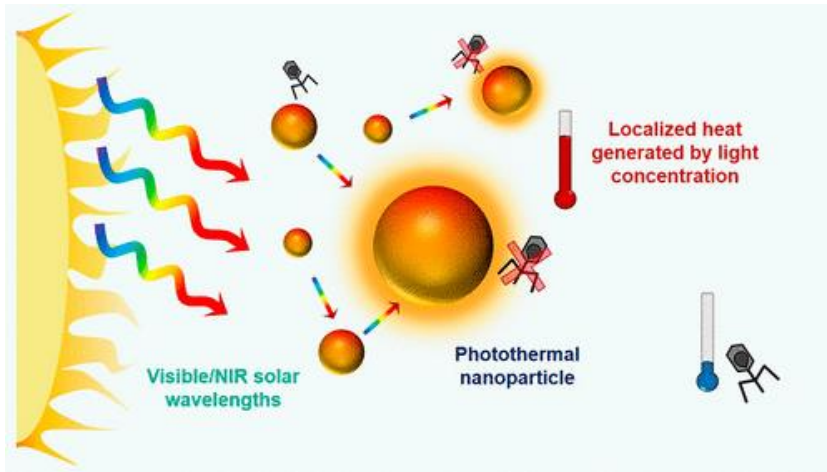


<https://doi.org/10.1021/acs.accounts.1c00307>

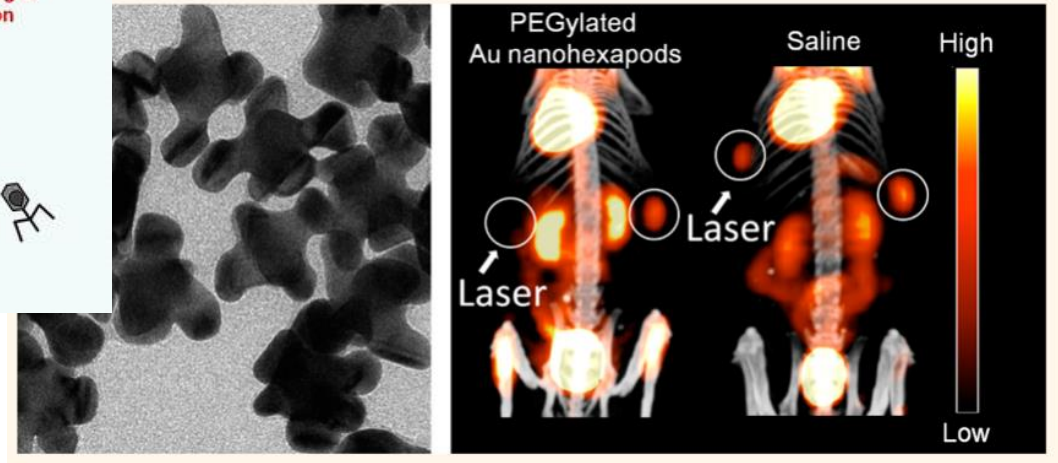


- ➔ **Propagating surface plasmons (PSPs)** offer weaker field intensity enhancement in delocalized homogeneous plasmonic hotspot.
- ➔ **Localized surface plasmons** provides tighter confined and more intense field profile in narrow plasmonic hotspots.

Local heating by Surface Plasmons



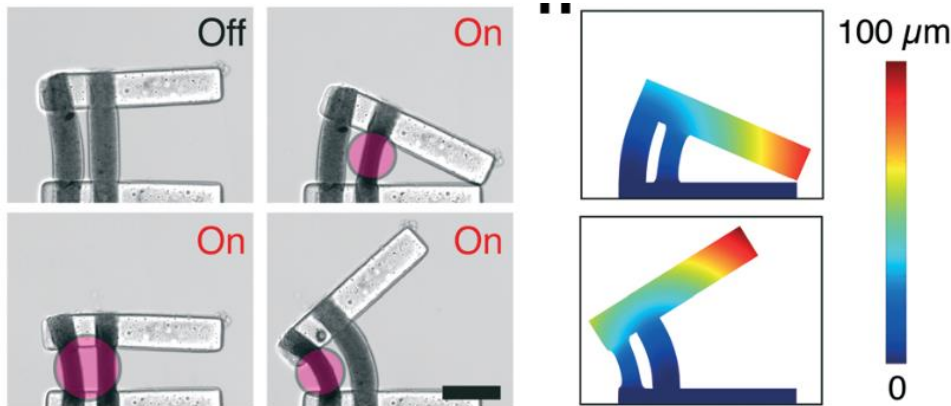
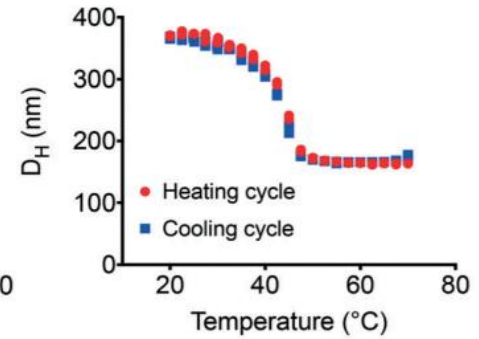
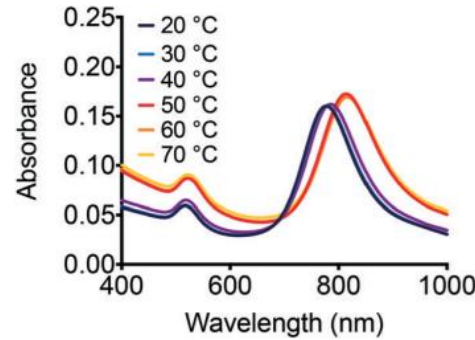
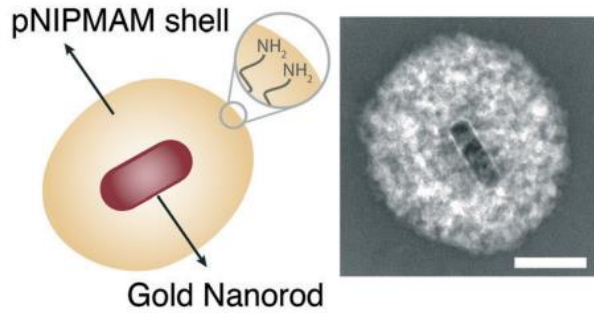
10.1021/nn304332s



<https://doi.org/10.1021/acs.est.7b04442>

- ➔ Local heating by LSPS has been utilized for generation of steam nano/microbubbles, disinfection, photo-acoustic imaging and photo-thermal treatment.

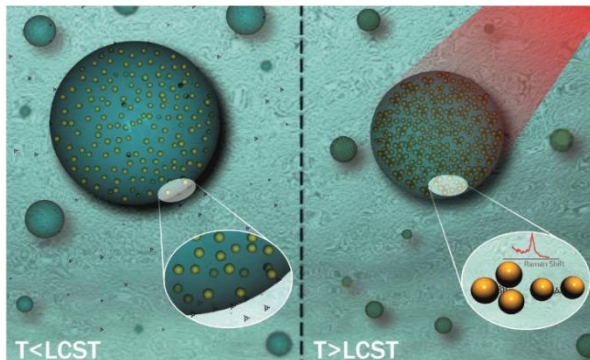
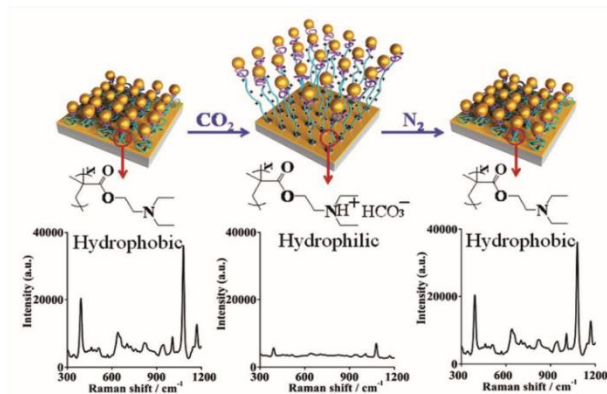
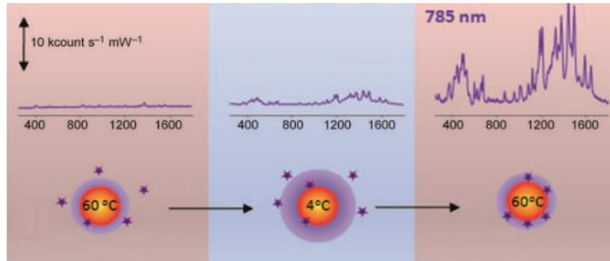
Soft robotics



- ➔ A combination of plasmonic nanostructures with thermo-responsive hydrogels.
- ➔ Designing of optically driven 'muscles' for miniature machines.

Ozkale, Lab Chip, 2019,19, 778-788

Surface-enhanced Raman spectroscopy



Embedding of metallic nanoparticles to architectures with responsive hydrogel moieties:

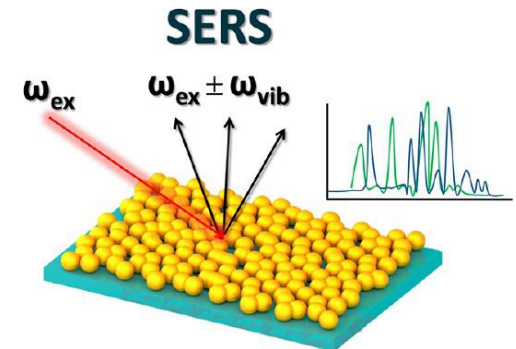
- ➔ On demand tuning of resonant wavelength and forming tight hotspots when closing gaps
- ➔ Collecting of analyzed species in the gaps where the sensitivity is highest

H. Chen, Y. Wang, X. Li, B. Liang, S. Dong, T. You and P. Yin, *RSC Adv.*, 2018, **8**, 22177–22181

<https://doi.org/10.1021/acsnano.9b04224>

R. A. Álvarez-Puebla, R. Contreras-Cáceres, I. Pastoriza-Santos, J. Pérez-Juste and L. M. Liz-Marzán, *Angew. Chemie - Int. Ed.*, 2009, **48**, 138–143.

A. C. Manikas, A. Aliberti, F. Causa, E. Battista and P. A. Netti, *J. Mater. Chem. B*, 2015, **3**, 53–58.



Amplification of Raman Scattering

➔ Electromagnetic field mechanism:

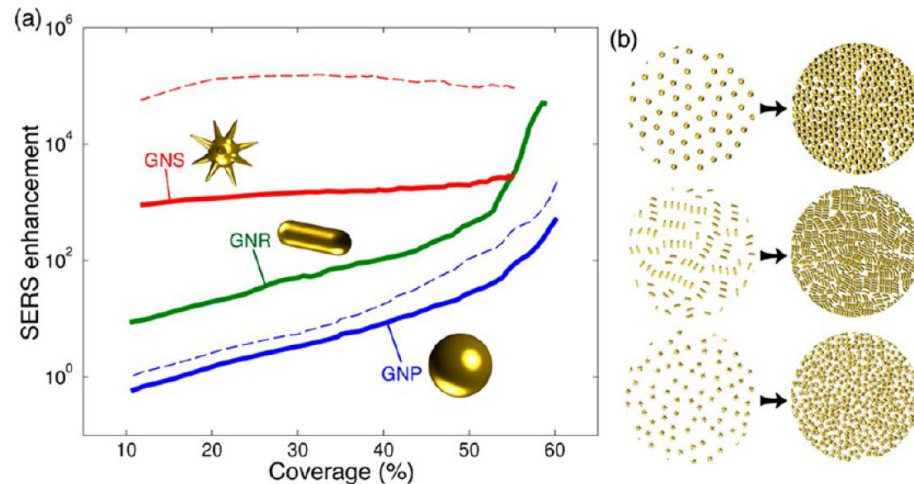
Universal, associated to the field intensity strength, reaching up to $EF=10^9$

$$EF \sim \frac{|E(\omega_P)|^2 |E(\omega_S)|^2}{|E_0|^4}$$

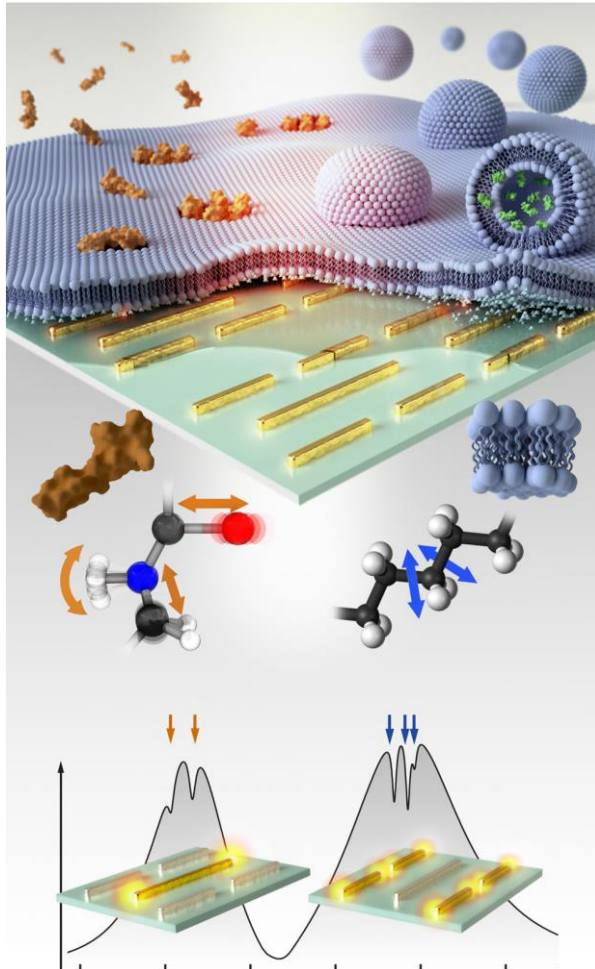
➔ Chemical mechanism:

Ascribed to transfer of electrons between analyte and the metal, yields $EF=10^2-10^3$.

Solis, S. M.; Taboada, J. M.; Obelleiro, F.; Liz-Marzán, L. M.; García de Abajo, F. J. Optimization of Nanoparticle-Based SERS Substrates through Large-Scale Realistic Simulations. ACS Photonics, 2017, 4, 329–337.



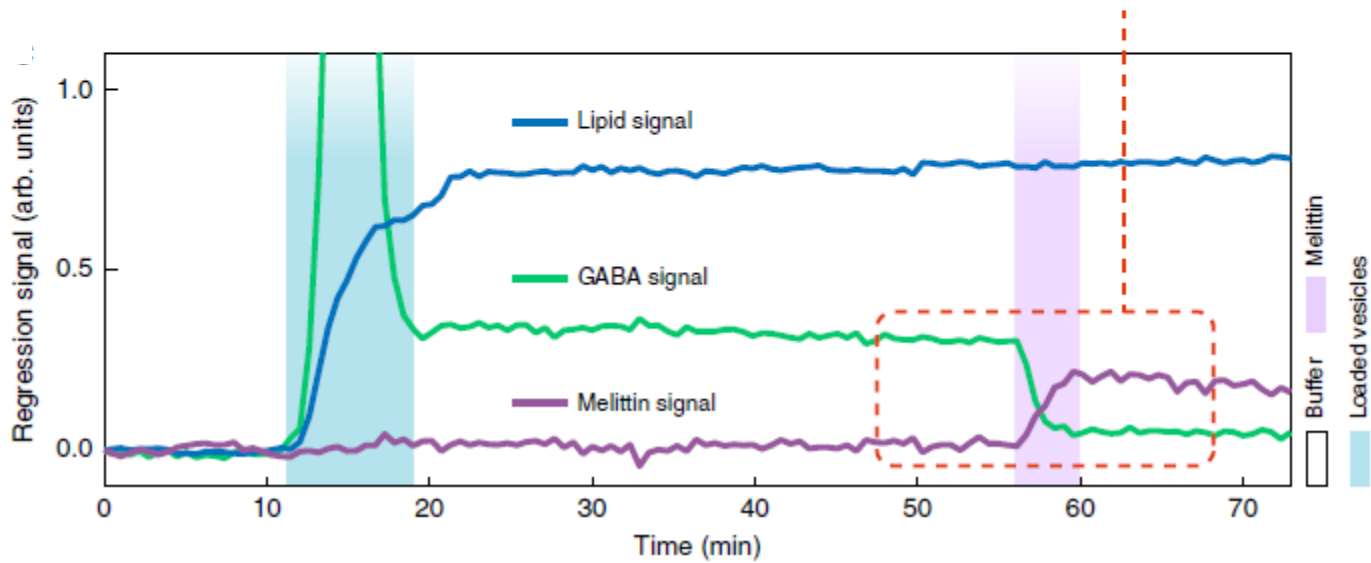
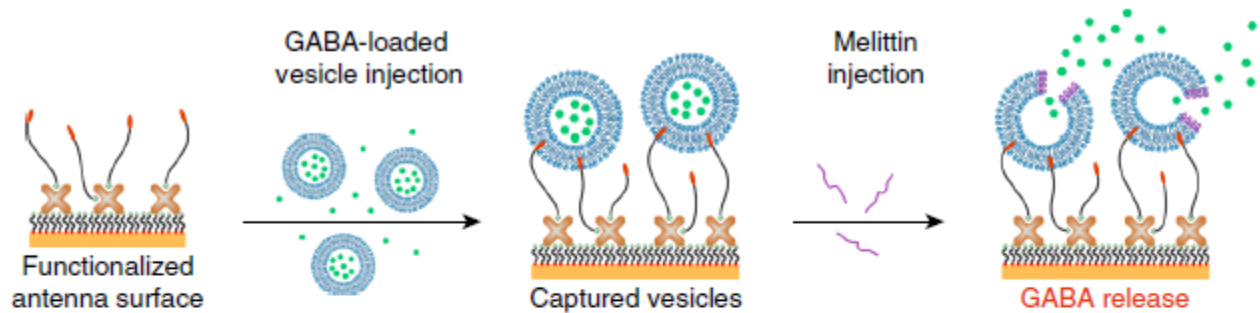
SEIRA on Engineered Antennas



- ➔ Arrays of plasmonic antennas tuned to excite localized surface plasmons at specific spectral bands.
- ➔ Antenna resonance positions are engineered to simultaneously overlap with the vibrational signatures of both the amide I, II, and the CH_2 , CH_3 absorption bands, allowing for the simultaneous enhancement and detection of lipid- and protein-induced absorption changes.

<https://www.nature.com/articles/s41467-018-04594-x>

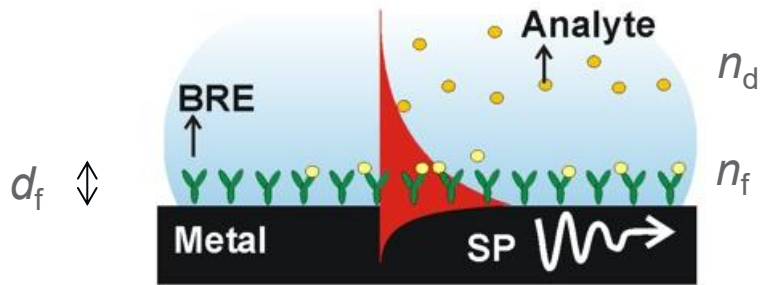
SEIRA on plasmonic antennas



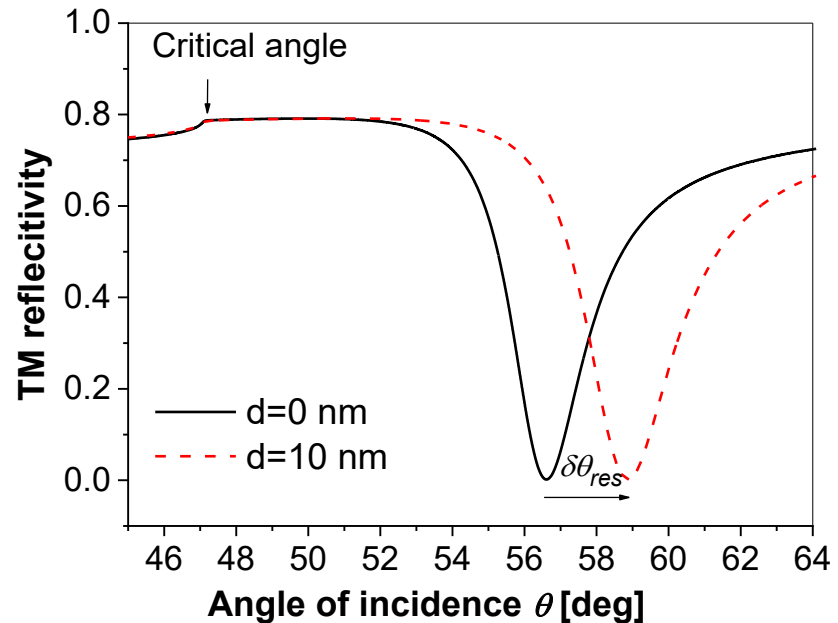
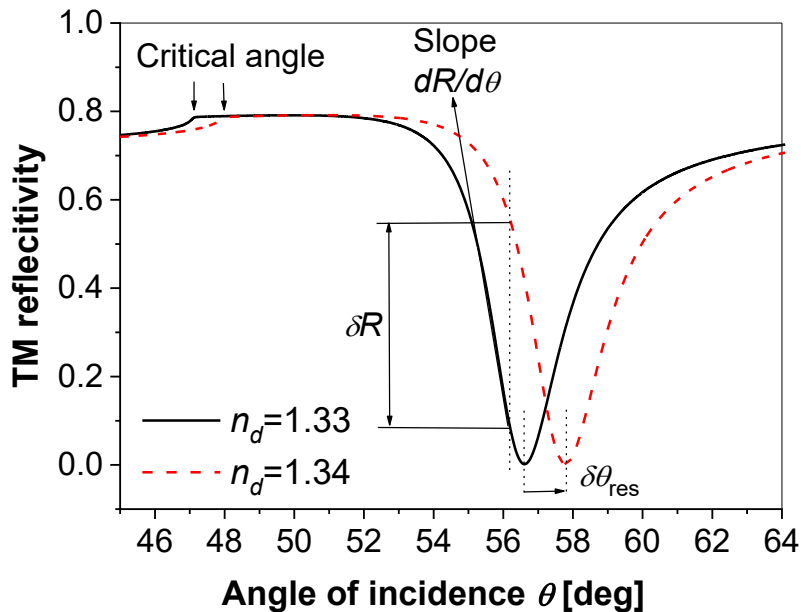
<https://www.nature.com/articles/s41467-018-04594-x>

➡ Monitoring of cargo release from tethered lipid vesicles.

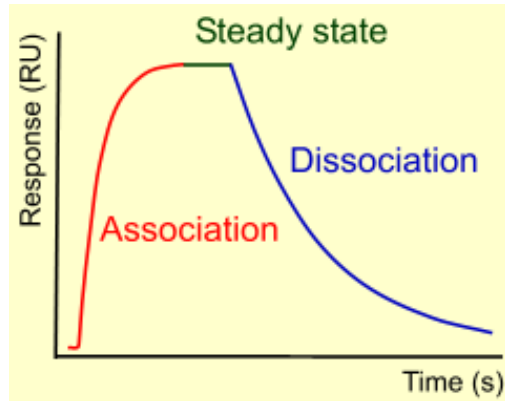
Surface Plasmon Resonance Biosensors



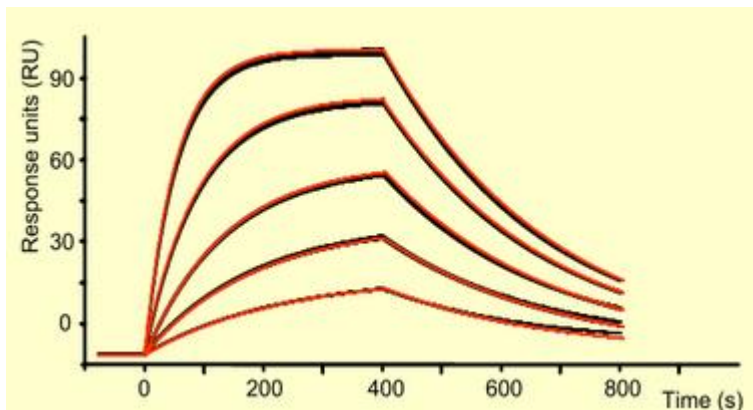
➔ SPR changes with both changes in the bulk n_d and surface refractive index changes.



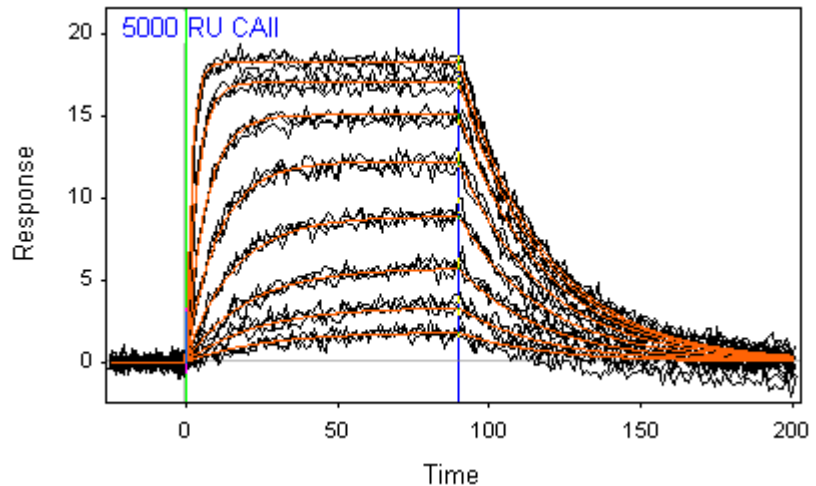
Global Analysis



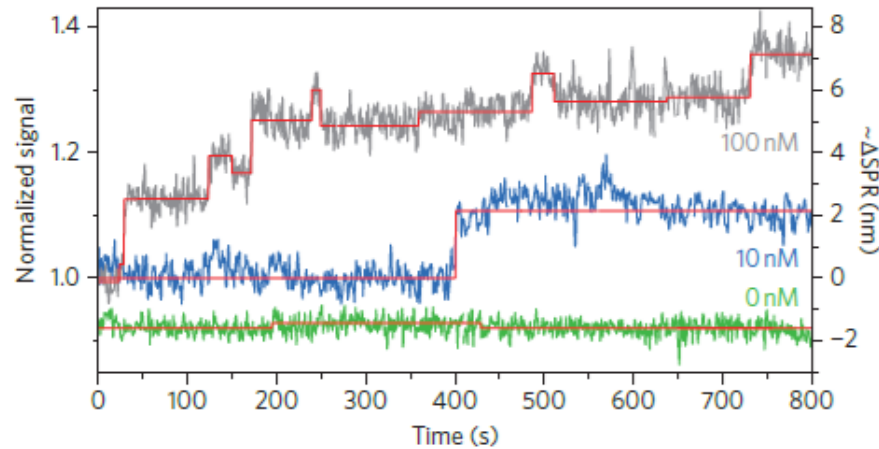
Fitting  kinetics



- ➔ Association and dissociation binding rates (k_a and k_d , respectively) or more complex parameters can be determined by fitting with a model.
- ➔ Applications for biomolecular interaction analysis serving, e.g. in therapeutic drug discovery.

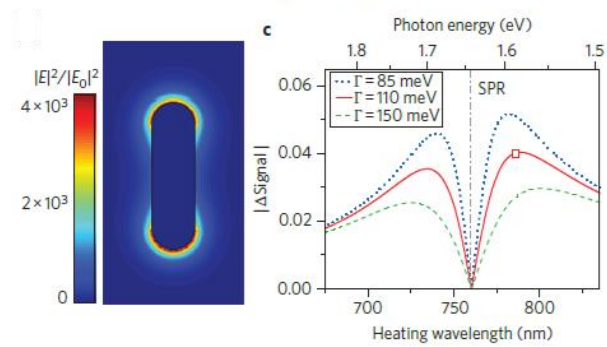
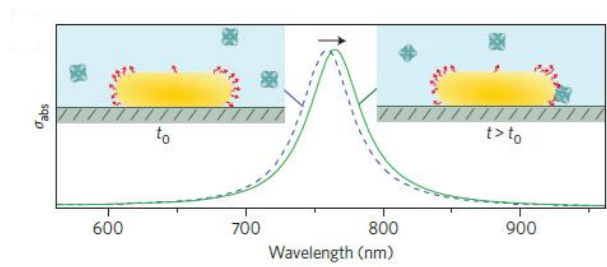


LSPR Observation of Single Molecule Binding Kinetics



➔ Tracking LSPR wavelength allows for monitoring of individual on and off binding events.

➔ First direct label-free detection of individual protein molecules demonstrate in 2012.



Zijlstra, P.; Paulo, P. M. R.; Orrit, M. Optical Detection of Single Non-Absorbing Molecules Using the Surface Plasmon Resonance of a Gold Nanorod. *Nat. Nanotechnol.* 2012, 7 (6), 379–382.