Optical spectroscopy and biosensors for investigation of biomolecules and their interactions

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Light-Matter Coupling Continued…

Optics / Photonics - Light Propagation / Confinement

Propagation of light and its interaction with matter can be treated at different levels (accuracy):

Size of an object Δx

Less accurate (and simpler to use…)

Ray optics	- refraction, reflection…	$\Delta x >> \lambda$
Wave optics	- wavelength λ, phase, interference…	$\Delta x <\sim \lambda$
Electromagnetic optics	- polarization, surface waves…	
Quantum optics	- quantized energies (photons)…	$\Delta x <\sim 1$ nm

More general (and complicated…)

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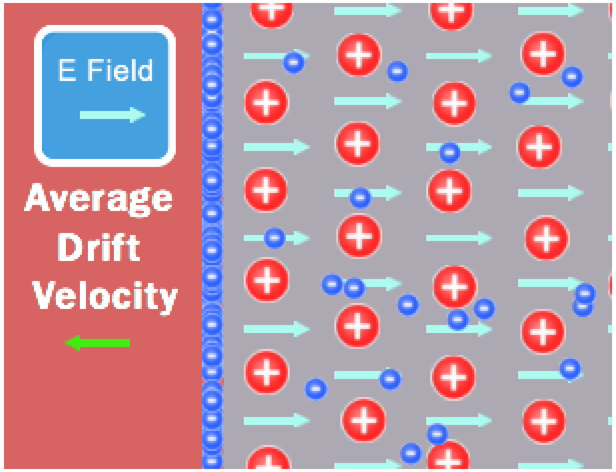
Metallic Materials

Refractive index of metals can be described by Drude model. It deals with electron density cloud that is fluid and a static positively charged lattice representing the metal crystal lattice.

$$n^2 = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$$



$$\omega_p^2 = \frac{Ne^2}{m_e \varepsilon_0}$$ Plasma frequency

For $\omega < \omega_p$ – n is complex and radiation is attenuated.
For $\omega > \omega_p$ – n is real and radiation is not attenuated(transparent).

ω_p for Au, Ag is of 9.6, 8.5 eV and for visible wavelengths behaves as metallic (highly reflective non-transparent).

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Dielectric Materials

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon_0 \vec{E}(1+\chi) = \varepsilon_0 \varepsilon \vec{E}$$

χ Susceptibility

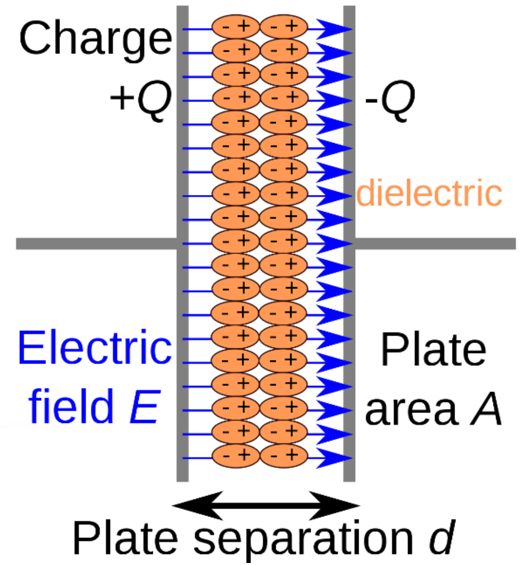
For more details, see Lorenz Lorenz or Clausius-Mossotti theories for taking the local and macroscopic field into account:

$$\frac{\chi}{(3+\chi)} = \frac{N\alpha}{3\varepsilon_0}$$

α Polarizability

$$n^2 = \varepsilon$$

Refractive index



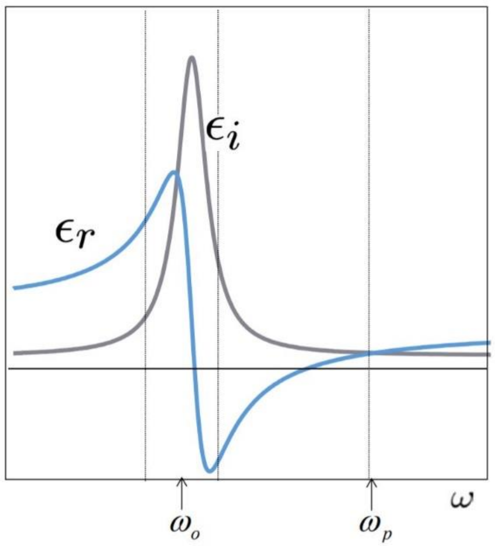
$$n^2 + 2 = \frac{3}{1 - \frac{4}{3}\pi \frac{N_A}{M_w}\rho\alpha}$$

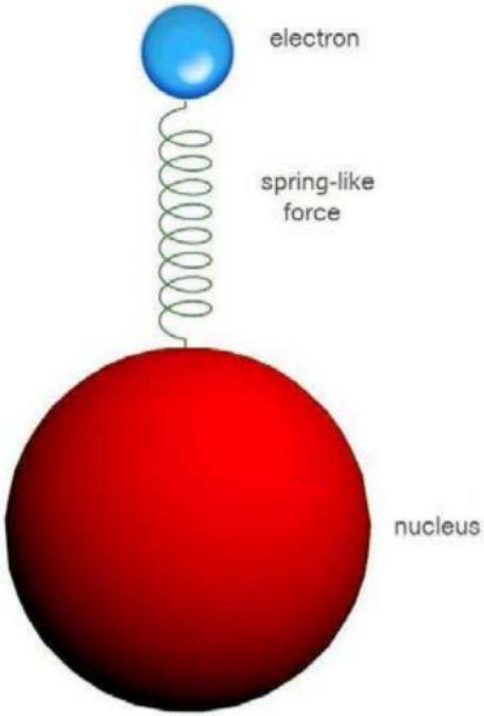
n – Refractive Index
N_A – Avogadro's constant
M_w – Molar weight
ρ – Density
α – Molecular polarizability

Yang; C., Jenekhe, S. *Chem. Mater.* 1995, *7*, 1276

Dielectric Materials

- ω is the angular frequency of the time-varying electric field driving the oscillator
- ω_o is the resonance (angular) frequency of the oscillator
- ω_p is the plasma frequency of the material





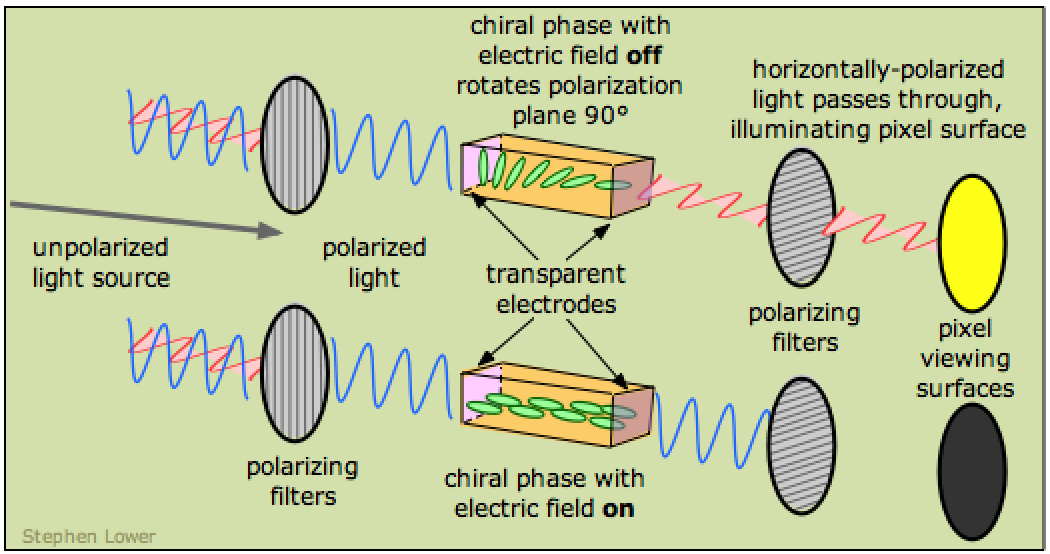
$$\epsilon_r(\omega) - 1 = \frac{\omega_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2}$$

$$\epsilon_i(\omega) = \frac{\omega_p^2\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2}$$

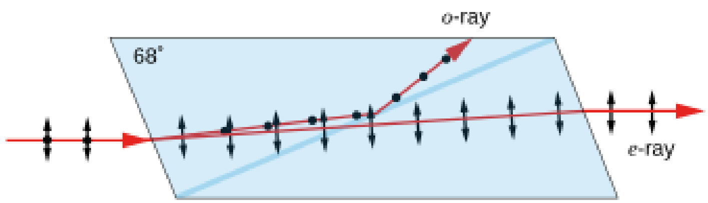
https://ocw.mit.edu/courses/electrical-engineering-and-computer-science/6-007-electromagnetic-energy-from-motors-to-lasers-spring-2011/readings/MIT6_007S11_lorentz.pdf

Birefringence – Orientation of EM Field Vectors

In birefringent materials the orientation of the electric field intensity vector matters (refractive index varies depending on its orientation).



Liquid crystals utilize orienting of elongated molecules (that exhibit different polarizability along and perpendicular to the axis).



Nicol polarizers based on difference in the TIR angles for different polarization.

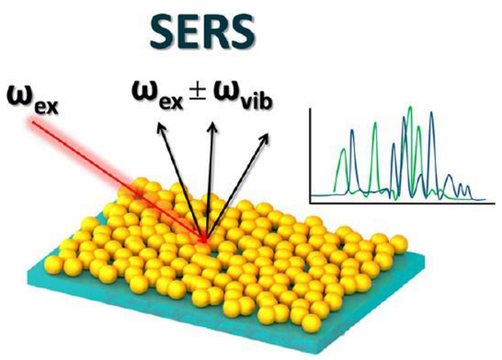
High EM Field Intensity

The description of refractive index independently on the electromagnetic field is valid for weak optical fields. For high field intensities *E* the polarizability can be treated in form of Taylor series:

$$P_i = \varepsilon_0 \left[\sum_j \chi_{ij}^{(1)} E_j + \frac{1}{2} \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k + \frac{1}{6} \sum_{j,k,l} \chi_{ijkl}^{(3)} E_j E_k E_l + \dots \right]$$

The higher order susceptibilities $\chi^{(2),(3)\dots}$ lead to non-linear optical effects such as:

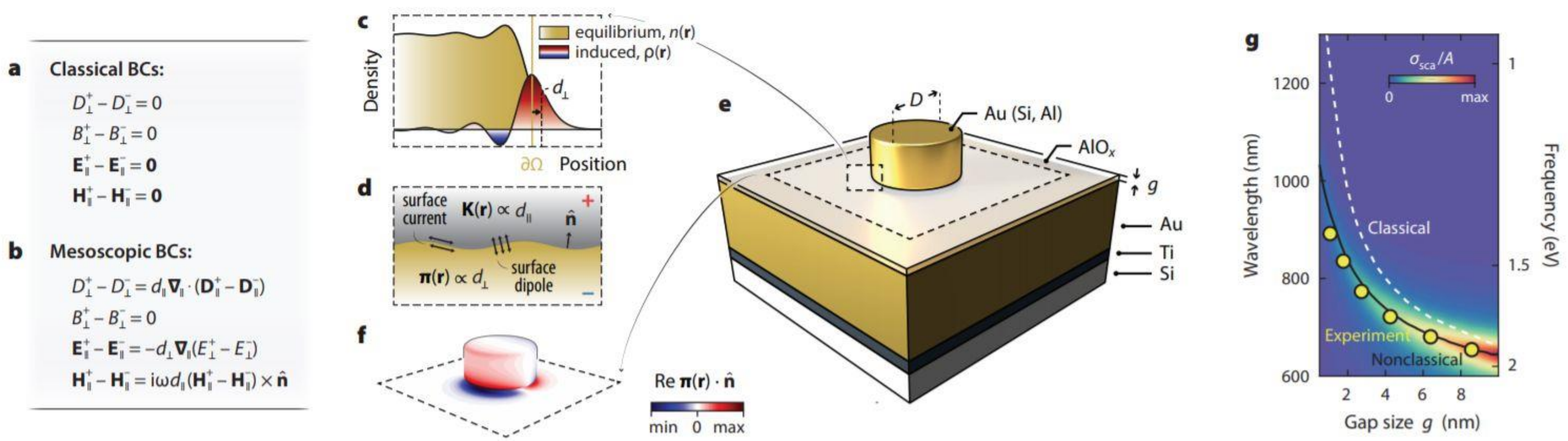
- Second harmonic generation $\chi^{(2)}$
- Raman scattering $\chi^{(3)}$
- ….



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

Spatial Confinement - Nonlocal Effects

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}) = \left(\frac{\omega}{c}\right)^2 \int d\mathbf{r}' \varepsilon(\mathbf{r},\mathbf{r}')\mathbf{E}(\mathbf{r}')$$



https://doi.org/10.1038/s41586-019-1803-1

Particularly for metallic nanostructures with very narrow gaps (~1 nm), refractive index at certain location is dependent on the response in its close vicinity – non-local effects.

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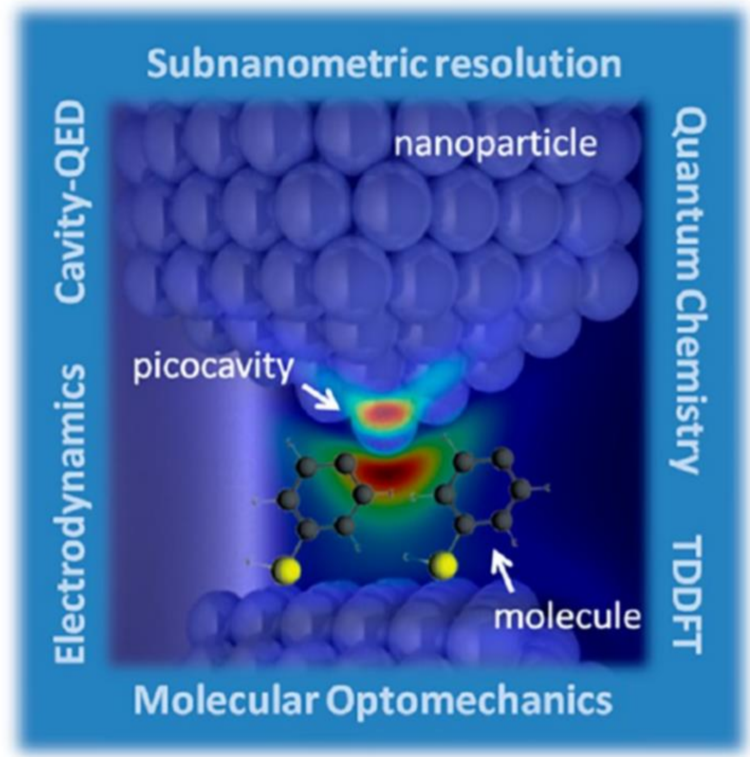
Spatial Confinement and High Field Intensities

For very small cavities and high field intensity, the classical picture in not applicable and quantum mechanics needs to be employed.

- Strong coupling regime (dephasing time of the plasmon field is comparable with the dephasing of the probed molecular system)
- Modifying of electronic structure of molecules in small optical cavities…

$$\hat{H}_{\text{int}} = -\hbar g_o (\hat{a}^{\dagger}\hat{a}) \cdot (b^{\dagger} + b)$$

Interaction Hamiltonian, where $\hat{a}^{\dagger}$,$\hat{a}$ ($b^{\dagger}$,b) are the plasmon (phonon) creation, annihilation operators, and g_o is the vacuum optomechanical coupling.



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

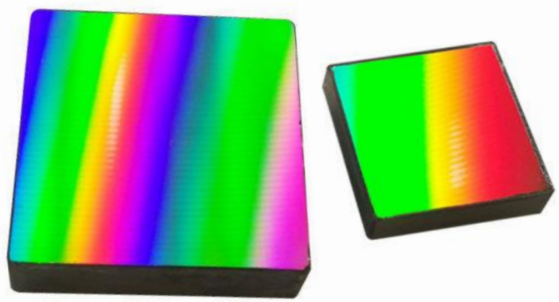
Optical Properties of Nanostructured Materials

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.
- Lithography, self-assembly and synthesis for the preparation of nanostructures.

Photonic Crystals (Dielectric)

Diffraction



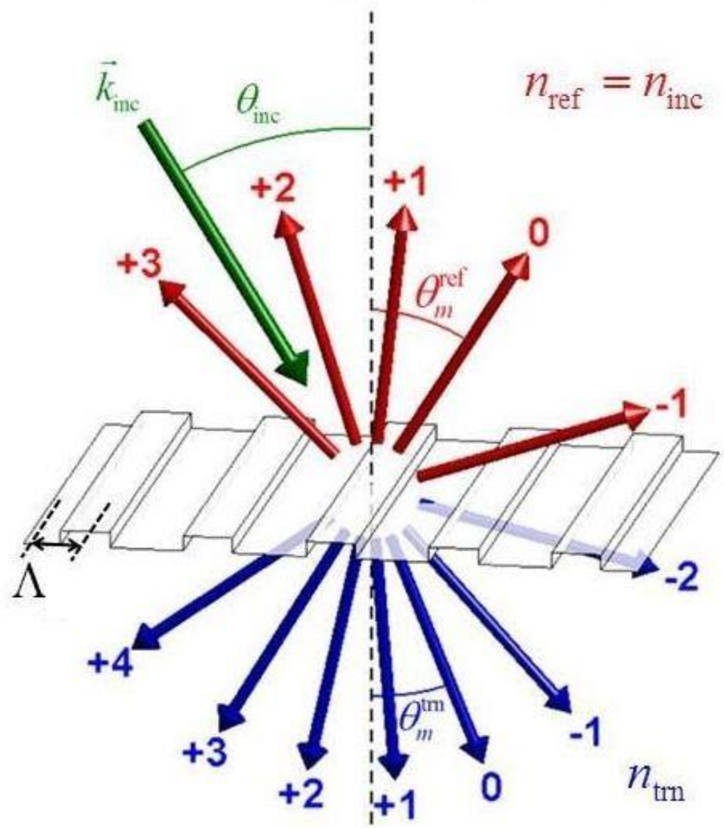
Periodic structures with a period $\Lambda \sim \lambda$ leads to coupling to series of propagating (and evanescent) diffraction orders.

Reflection Region

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

Transmission Region

$$n_{\text{trn}} \sin \theta_m = n_{\text{inc}} \sin \theta_{\text{inc}} - m \frac{\lambda_0}{\Lambda}$$



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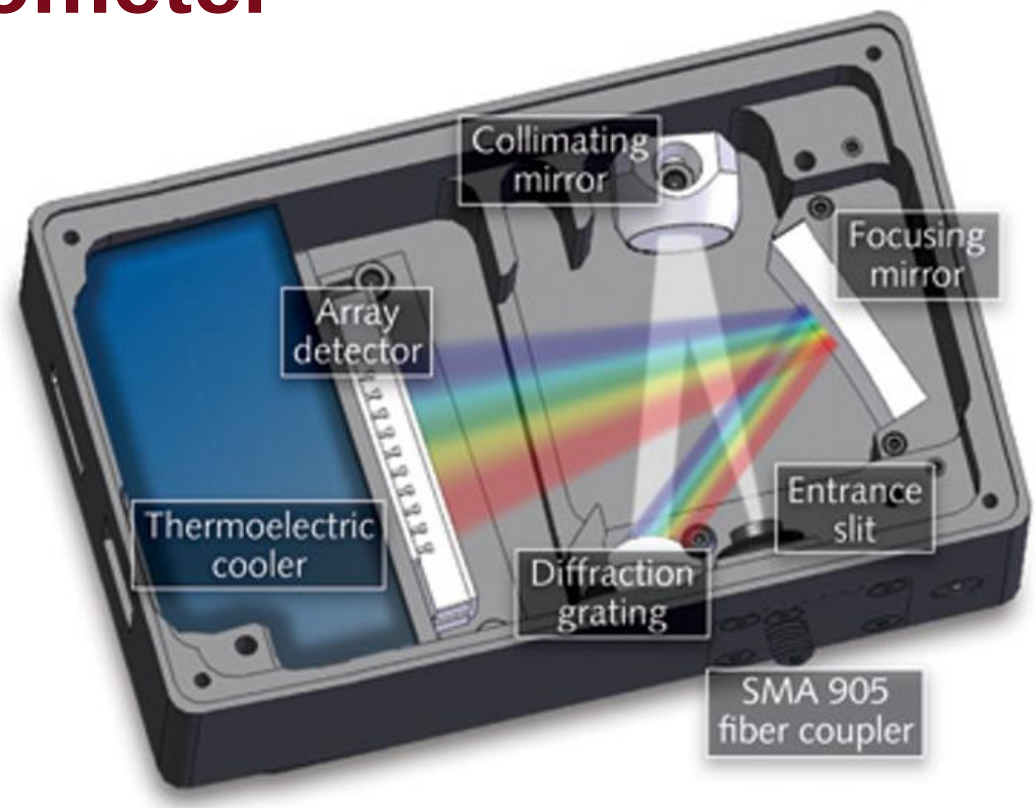
Spectrometer



Diffraction on periodic gratings is used to disperse light at different wavelengths in the majority of spectrometers (showed Czerny-Turner optical design).

1D Photonic Crystals

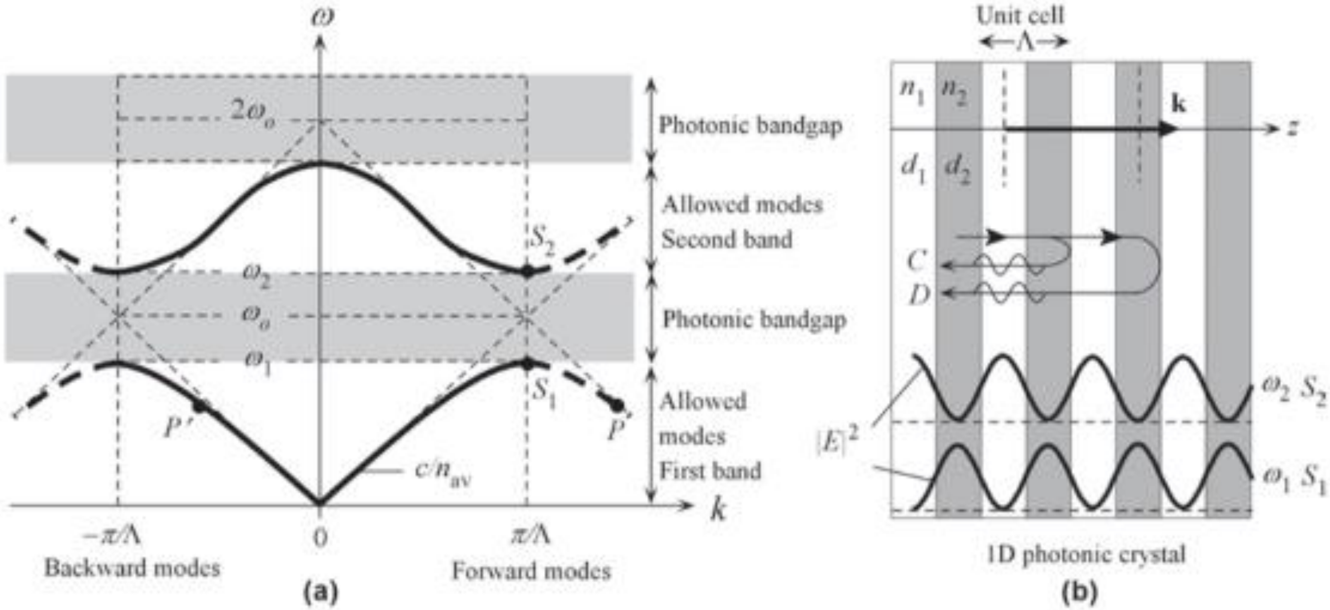


Figure 1.51
(a) Dispersion relation, ω vs. k, for waves in a 1D PC along the z-axis. There are allowed modes and forbidden modes. Forbidden modes occur in a band of frequencies called a photonic bandgap. (b) The 1D photonic crystal corresponding to (a), and the corresponding points S_1 and S_2 with their stationary wave profiles at ω_1 and ω_2.

Alternating dielectric layers with different refractive index n1 and n2 arranged in a period manner allow to ban propagation of light forming a photonic bandgap (analogically to electrons in semiconductors exhibiting a electronic bandgap).

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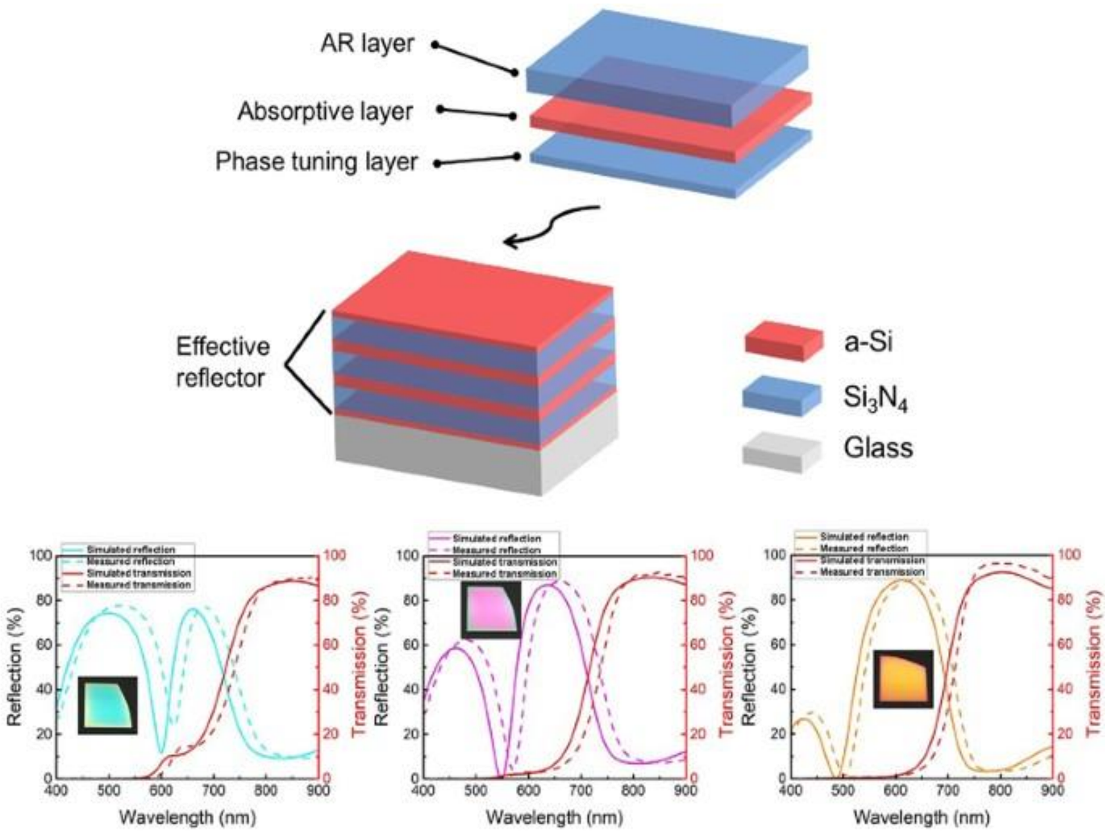
1D Photonic Crystal – Employment in Filers



The 1D photonic crystal – like structures can be engineered to serve as efficient mirrors, band pass and stop band filters.

https://doi.org/10.1007/s12274-018-2249-8

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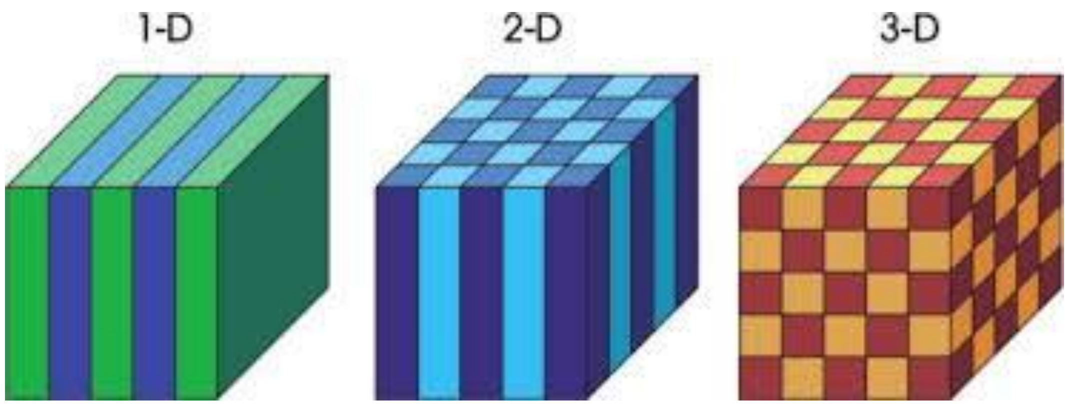
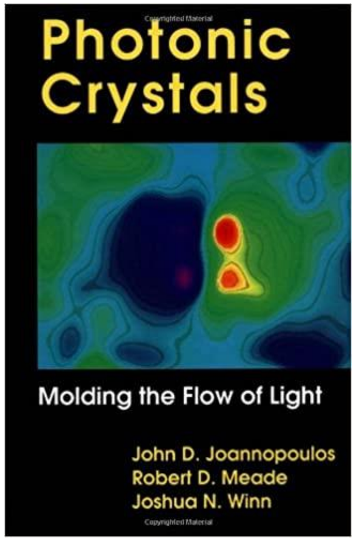
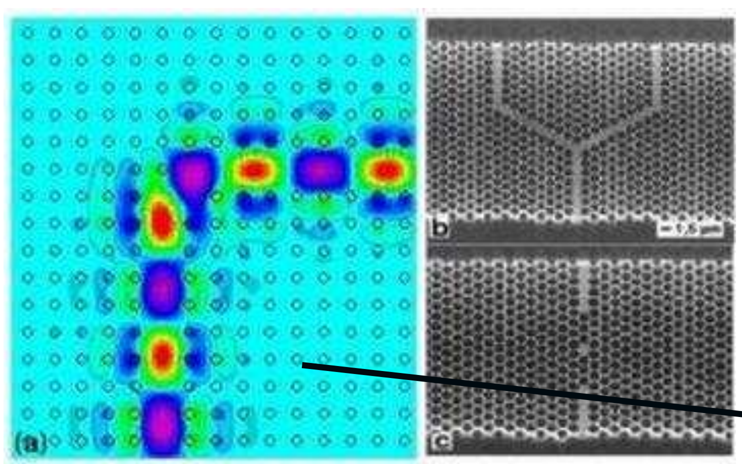
Photonics Crystals





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

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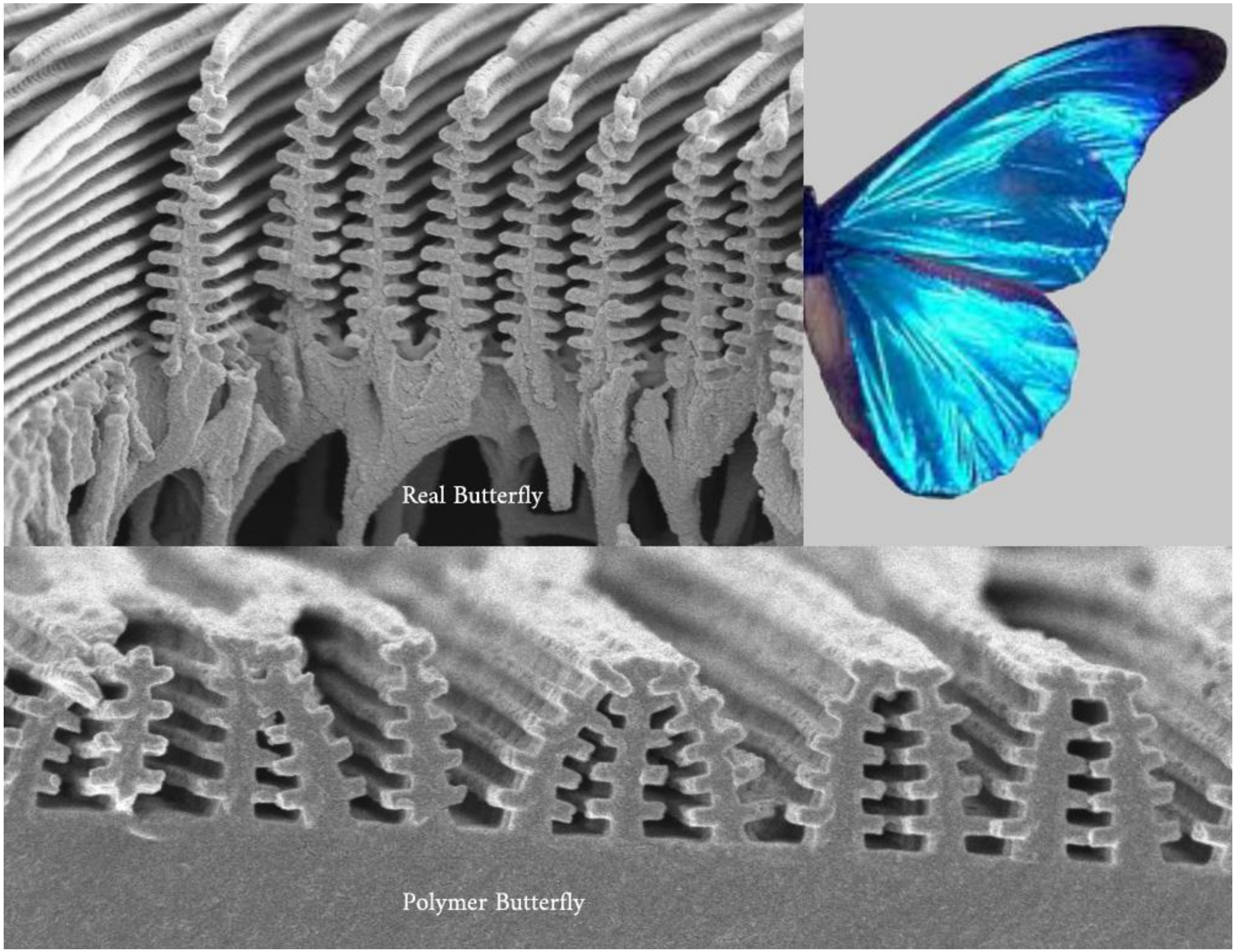
Structural Colors



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

Inspiration by Nature

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.**

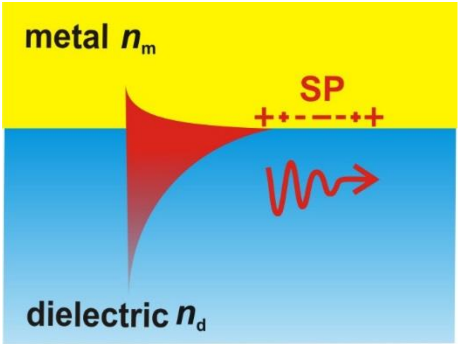
•When a chameleon is **excited,** the distance between nanocrystals **increases** and it reflects **longer wavelengths, such as red, orange and yellow.**

Plasmonic Nanostructures (Metallic)

Metallic Waveguides – Surface Plasmons (PSP)

Propagating surface plasmons (PSPs) 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.

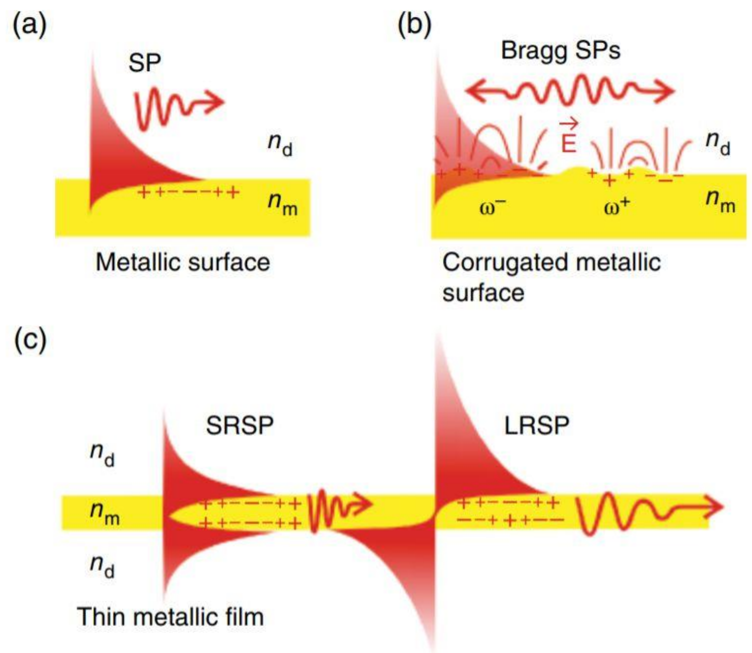


Propagation constant β can be analytically expressed as:

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

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

Metallic Waveguides – Propagating Surface Plasmons (PSP)

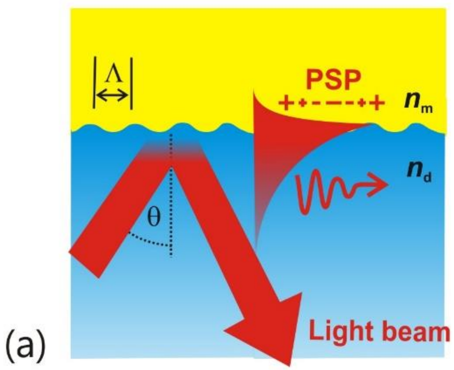


Surface plasmons at multiple interface can couple giving rise to modes:

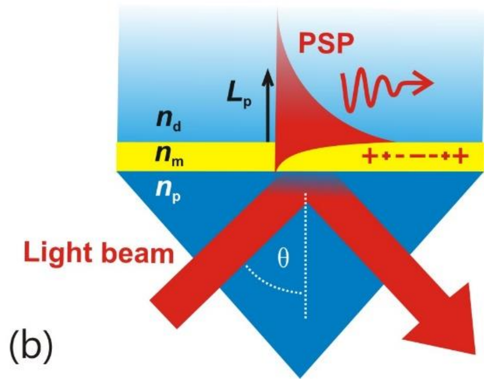
(a) PSPs traveling along a flat metallic surface (‘1D plasmonic crystal’)
(b) Bragg-scattered PSPs on periodically corrugated metallic surface
(c) Long- and short-range PSPs on a thin metallic film.

Propagating Surface Plasmons (PSP)

Also called surface plasmon polaritons (SPPs) are waves originating from coupled <u>oscillations of electron plasma density</u> and associated electromagnetic field on a metal – dielectric interface.



Grating coupling



Prism coupling

- Phase matching condition:

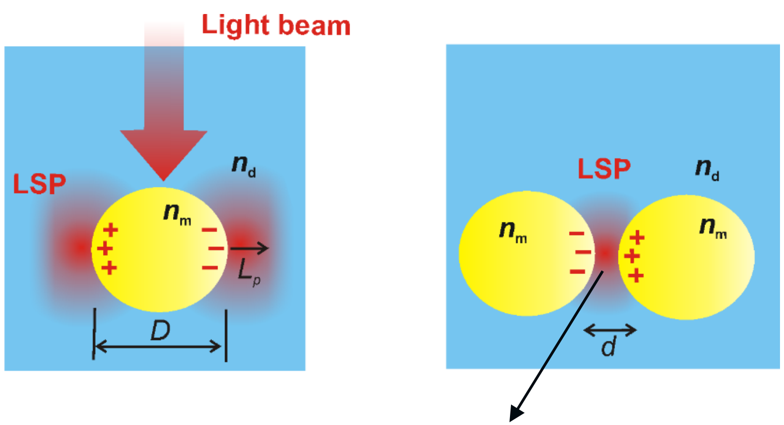
$$\beta = \frac{2\pi}{\lambda}\sqrt{\frac{n_m^2 n_d^2}{n_m^2 + n_d^2}}$$

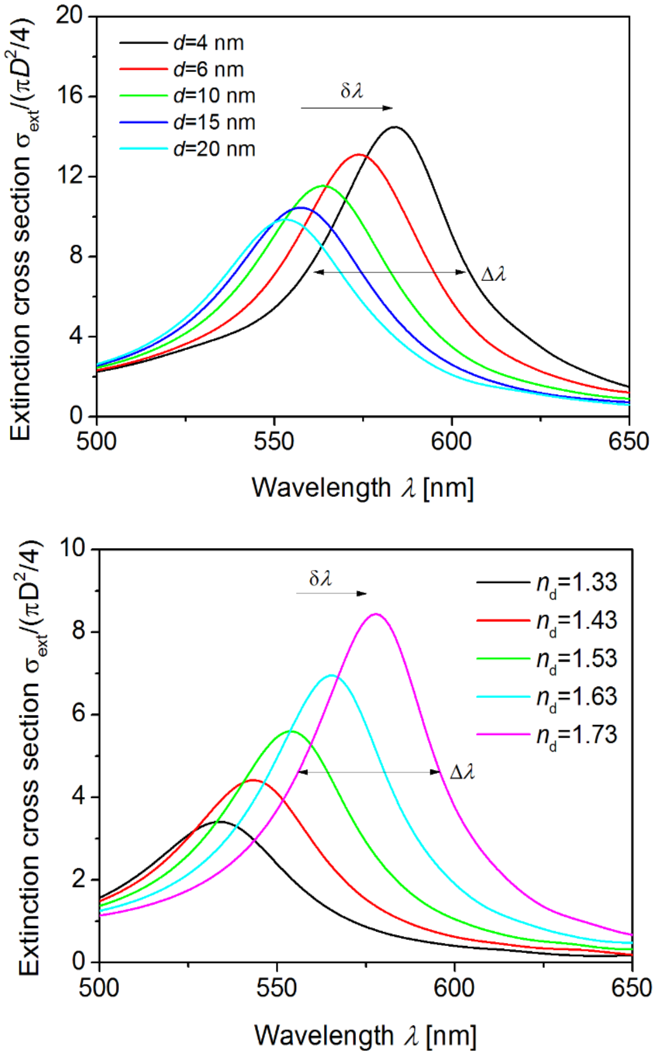
a) $$\mathrm{Re}\{\beta\} = \frac{2\pi}{\lambda} n_d \sin(\theta) \pm p\frac{2\pi}{\Lambda}$$

b) $$\mathrm{Re}\{\beta\} = \frac{2\pi}{\lambda} n_p \sin(\theta)$$

- SPs allows for **confinement** of electromagnetic field at the interface (L_p > 100 nm).
- Accompanied with **increased field strength |*E*|**, **local density of optical states (LDOS)**, and generation of **heat**.

Localized Surface Plasmons (LSPs)

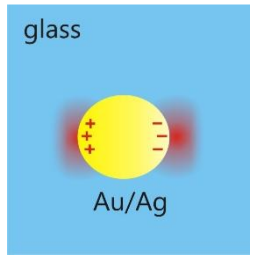




- **Resonant effect, e.g. for spherical metallic nanoparticle with *D<<λ* the resonance wavelength λ_{LSPR}.**
- **Confined electromagnetic field intensity, $L_p \sim D$.**

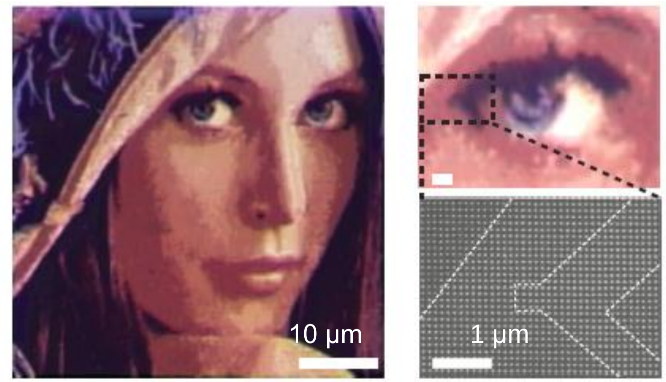
Localized Surface Plasmons

Au/Ag nanospheres:



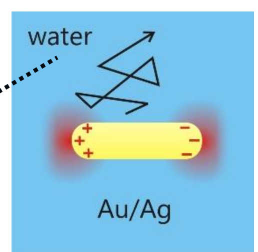
Lygurcus cup, 4th century AD
British museum

Al nanodisks:



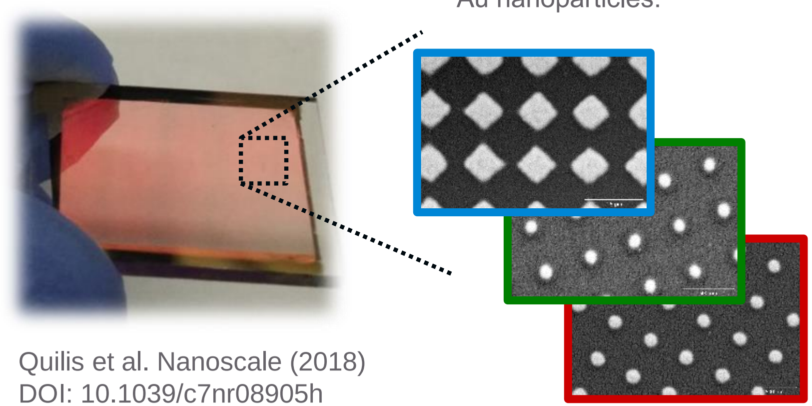
Kumar et al., Nature Nanotechnology (2012) DOI: 10.1038/NNANO.2012.128

Au nanorods:



Nanopartz Inc.

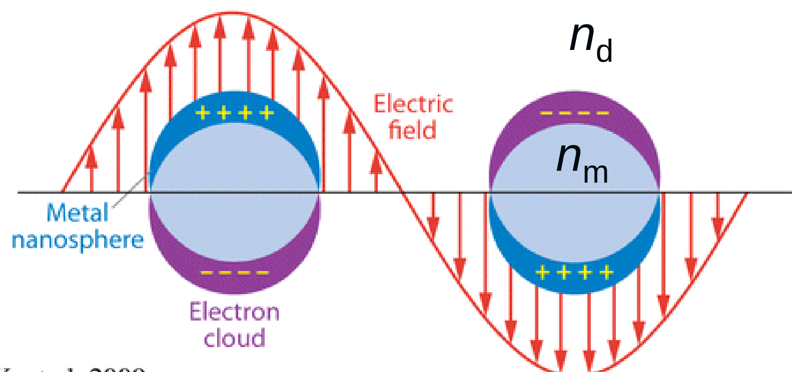
Au nanoparticles:



Quilis et al. Nanoscale (2018)
DOI: 10.1039/c7nr08905h

Localized Surface Plasmons (LSPs)

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



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

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

$$\mathrm{Re}\left\{n_m^2(\lambda)+2n_d(\lambda)\right\}=0$$

Localized surface plasmon resonance is associated with strong:

- **Absorption**
- **Scattering**
- **Field confinement and enhancement**

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<<λ

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

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

How to Make the Optical Micro / Nanostructrues?

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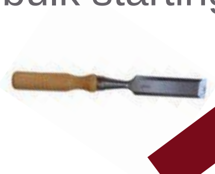
Preparation of Optical Nano/Micro - Structures

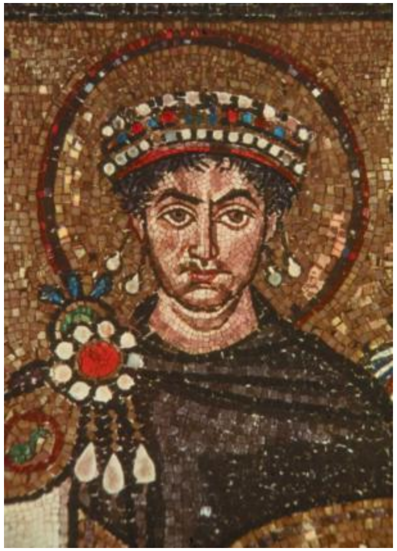
"Top down" and "bottom up" approaches can be used for preparation of micro/nano structures.

A subtractive process from bulk starting materials



David (Michelangelo), Florence

An additive process that starts with precursor atoms or molecules

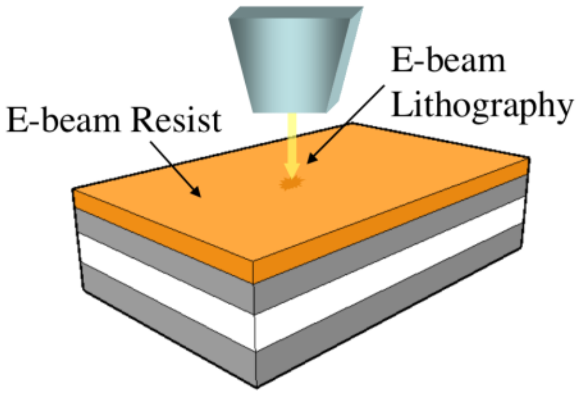


Mosaic of Justinian and Retinue at Apse Entry, San Vitale, Ravenna, 6th century

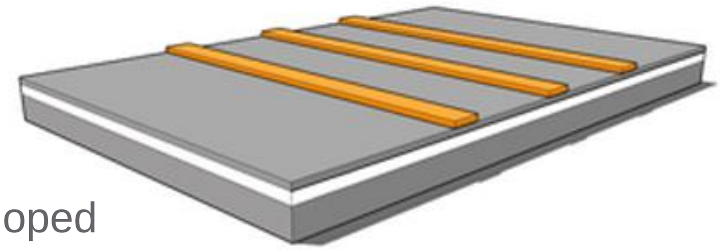
Electron Beam Lithography (EBL)

A method to pattern resist layers (e.g. PMMA) spun onto a substrate. Features of few tens of nanometers or below are possible to prepare. Limitation is the (slow) patterning time and difficult structuring of large areas (>100 × 100 μm).

1) Electrons from a scanning electron microscope are accelerated and passes through the resist and into the silicon. Secondary electrons are produced.
2) These electrons travel through the resist where they break the bonds of the polymer chain.
3) When the sample is developed, the now short chained polymers are dissolved, leaving the written pattern behind.



Scanning over the resist surface



Resist is developed leaving the patterned resist mask

http://people.ece.cornell.edu/lipson/nature/fabrication.htm

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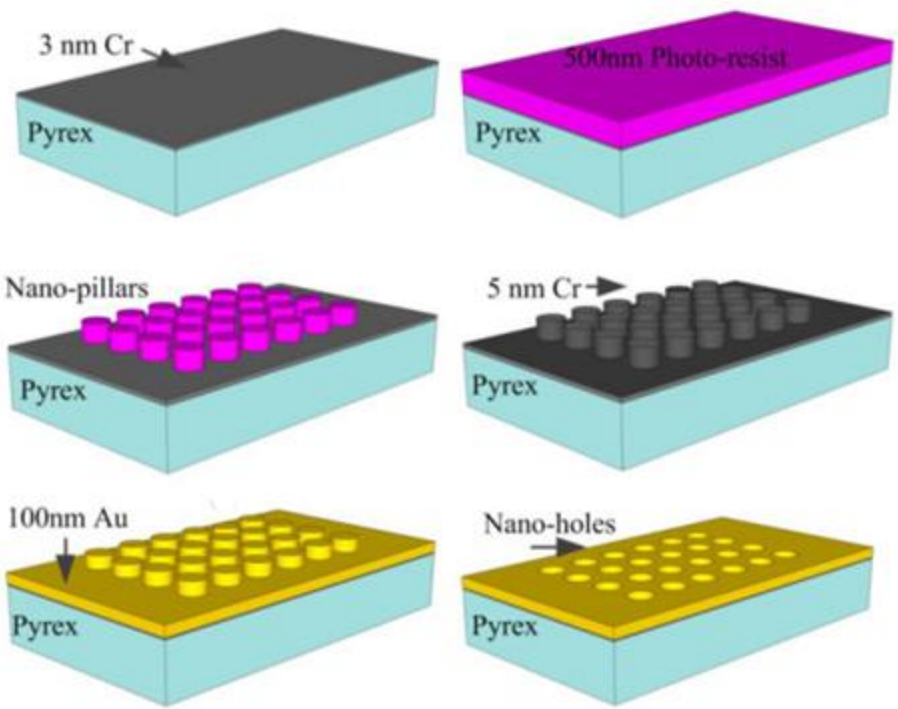
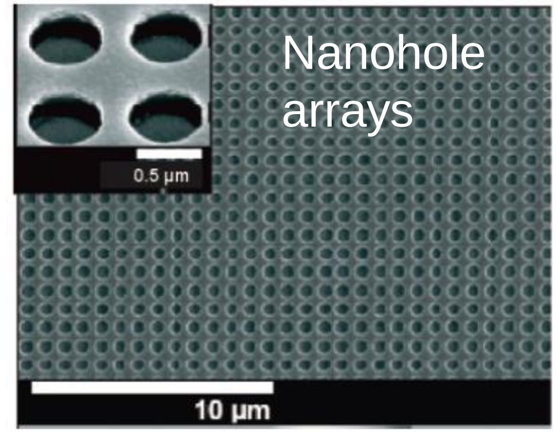
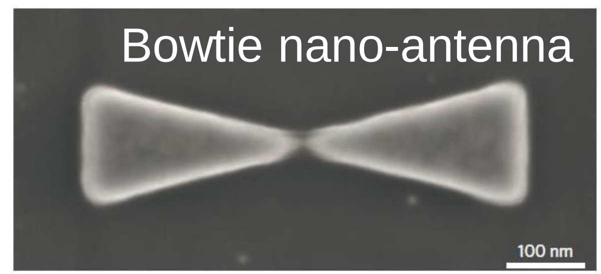
EBL – Examples

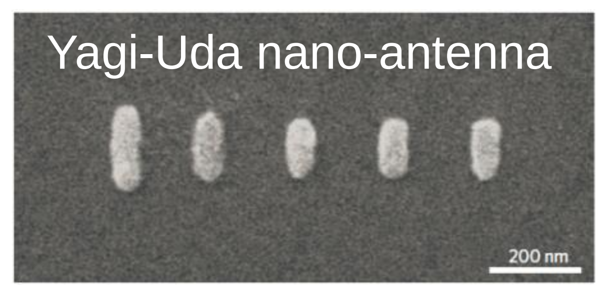
Lift-off of sacrificial resist layer is combined with EBL to prepare target micro/nano-structures.



Optics Express, Vol. 19, Issue 27, pp. 26186-26197 (2011)

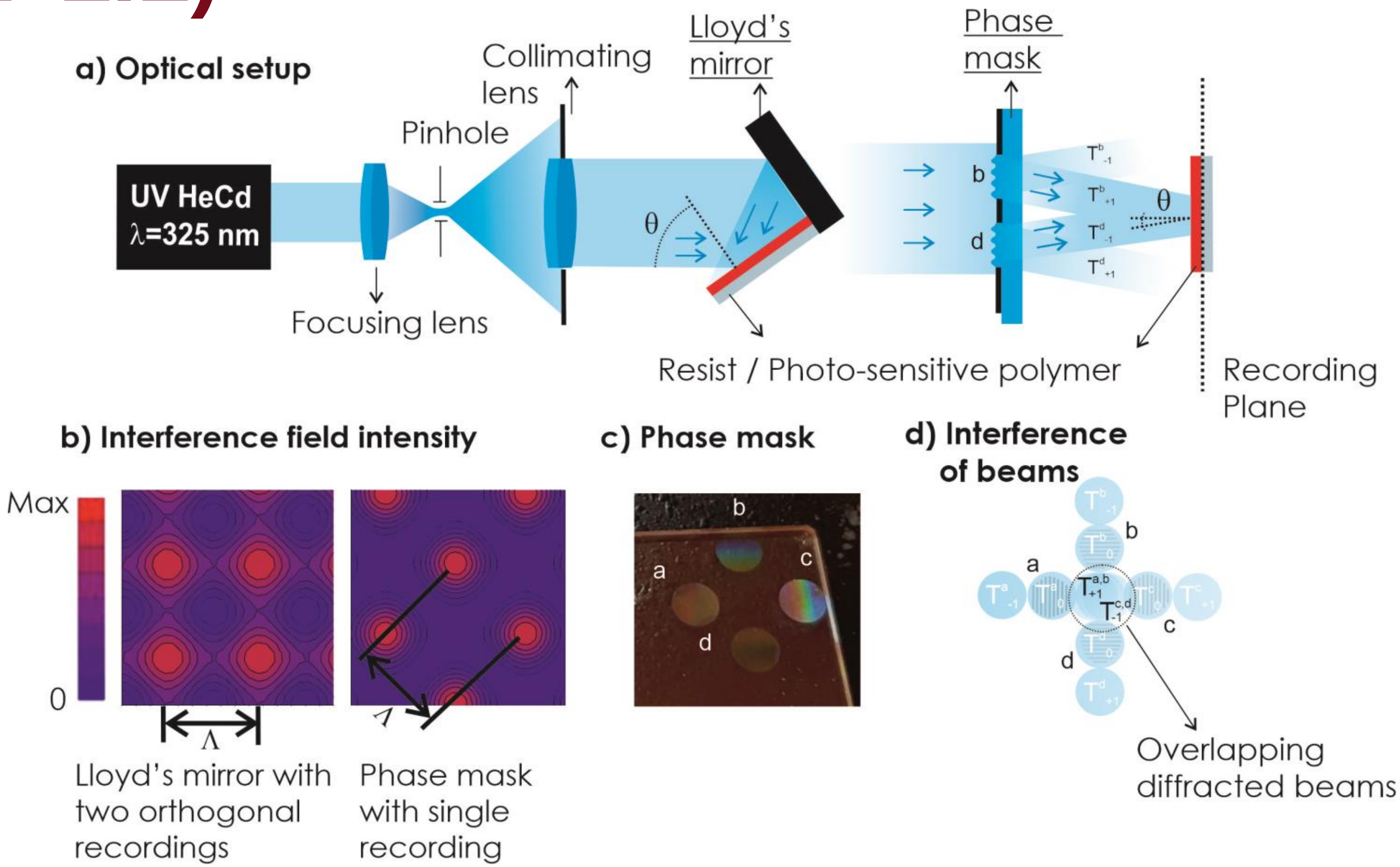






Novotny, van Hults, Nature Photonics, doi: 10.1038/nphoton.2010.237

UV Laser Interference Lithography (UV-LIL)



Nestor G. Quilis et al., Tunable laser interference lithography preparation of plasmonic nanoparticle arrays tailored for SERS, Nanoscale, 2018, 10, 10268-10276.

Nestor G. Quilis et al., UV-Laser Interference Lithography for Local Functionalization of Plasmonic Nanostructures with Responsive Hydrogel, 2019, in preparation.

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Operational Programme Research,
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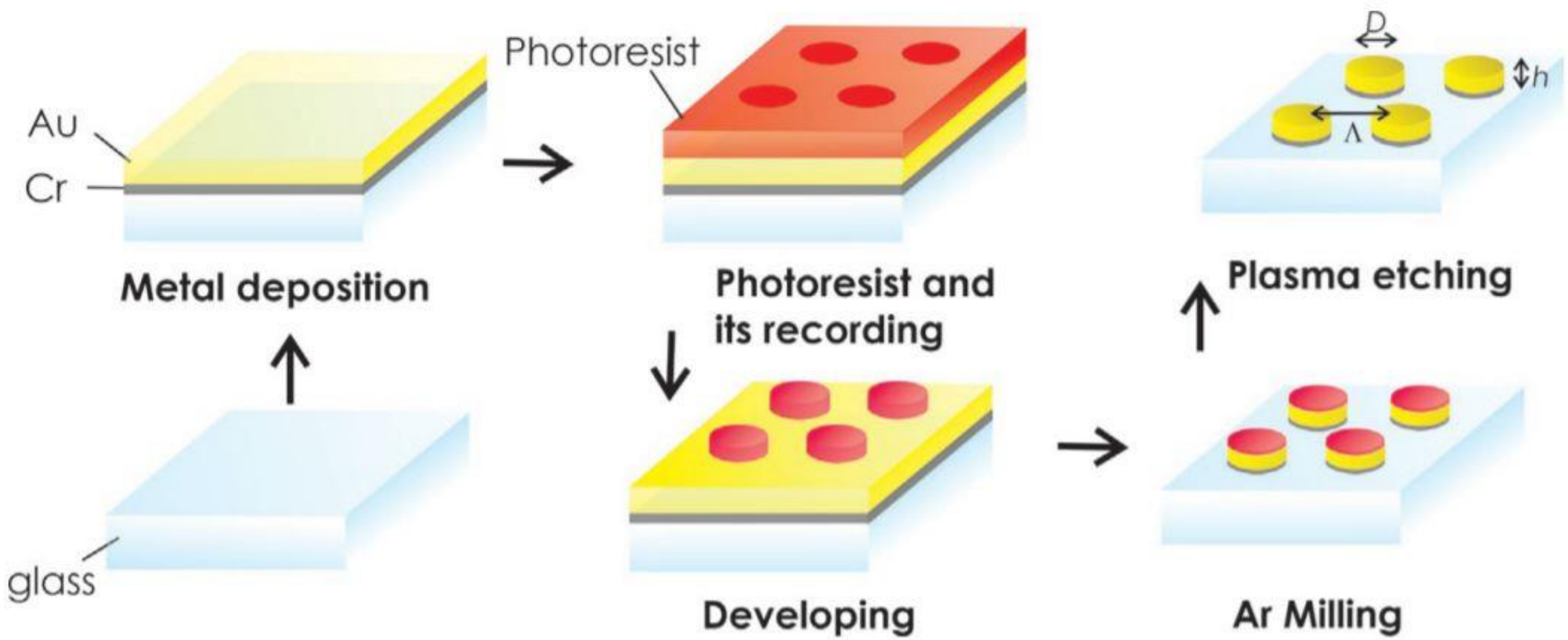
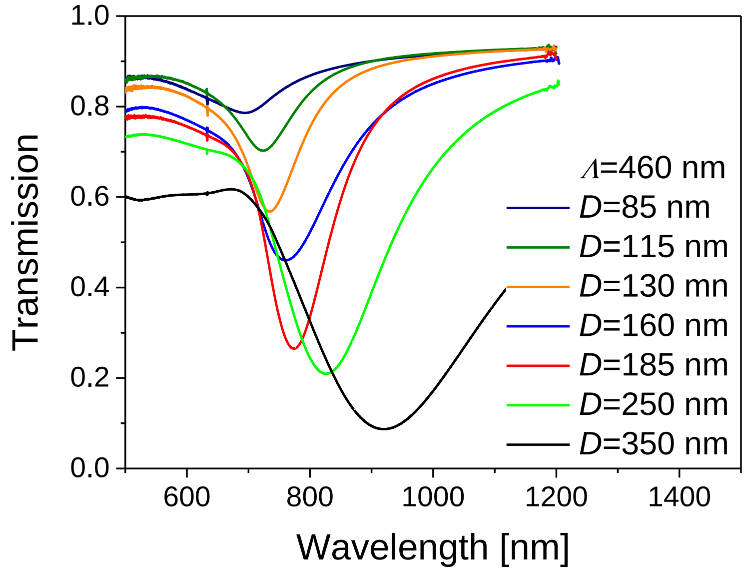
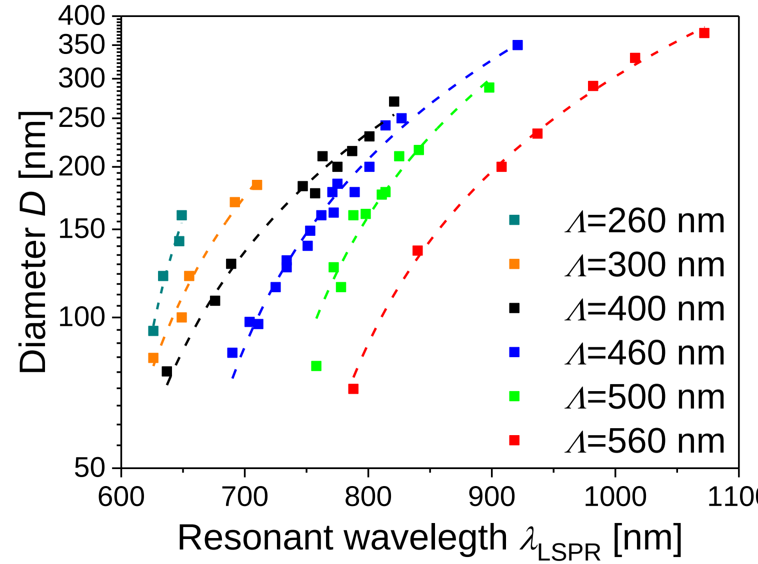
Metallic Nanoparticle Arrays Preparation

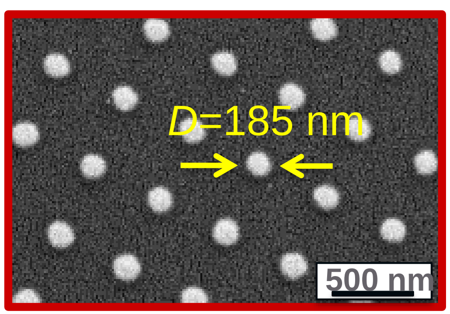


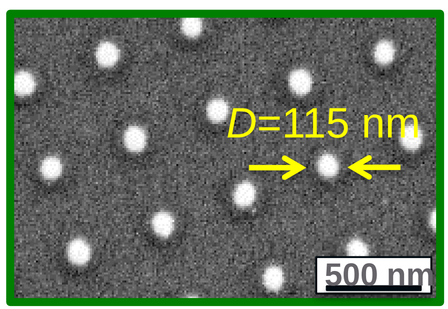
A. Bozdogan, S. Hageneder, J. Dostalek, Plasmonic biosensors relying on biomolecular conformational changes: Case of odorant binding proteins, Methods in Enzymology, Elsevier (2020), ISSN 0076-6879.

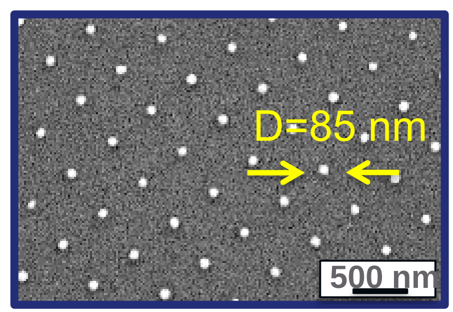
Tuning of Plasmonic Nanoparticle Arrays

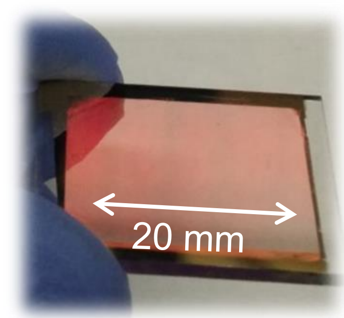








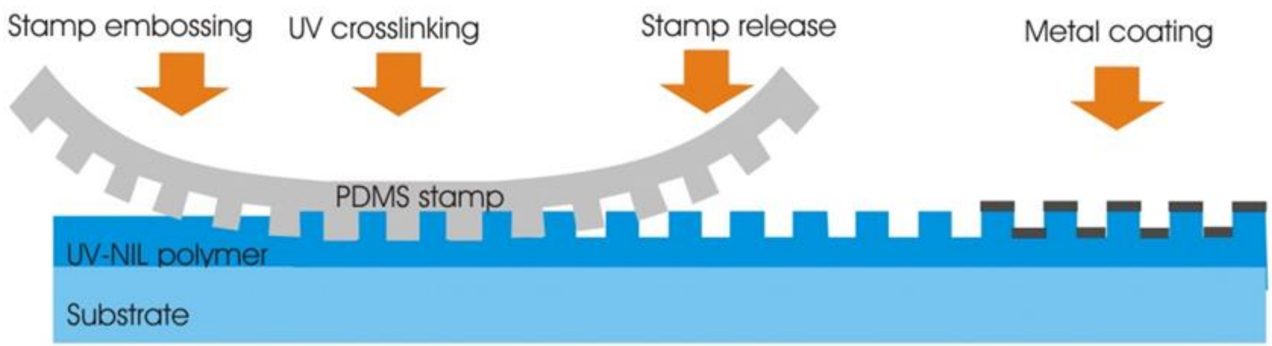




Nestor G. Quilis, Mederic Lequeux, Pryiamvada Venugopalan, Imran Khan, Souhir Boujday, Wolfgang Knoll, Marc Lamy de la Chapelle, Jakub Dostalek, Tunable laser interference lithography preparation of plasmonic nanoparticle arrays tailored for SERS, Nanoscale, 2018, 10, 10268-10276

Nano-Imprint Lithography (NIL)

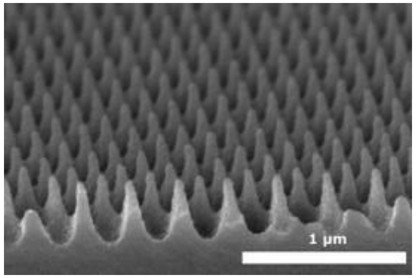
Method aimed at structuring with low cost, high throughput, and high resolution. Patterns are made by a mechanical deformation of an imprint resist. The imprint resist is typically a polymer that is cured by heat or UV light during the imprinting.



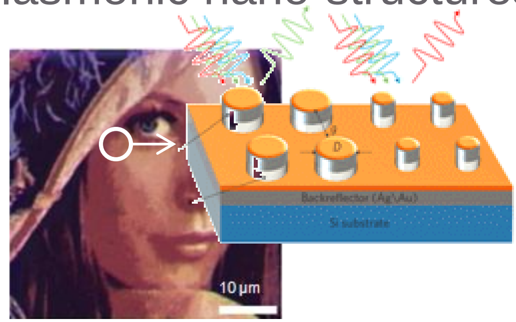
By NIL, wide range of structures can be made:

CDs

Anti-reflection coatings

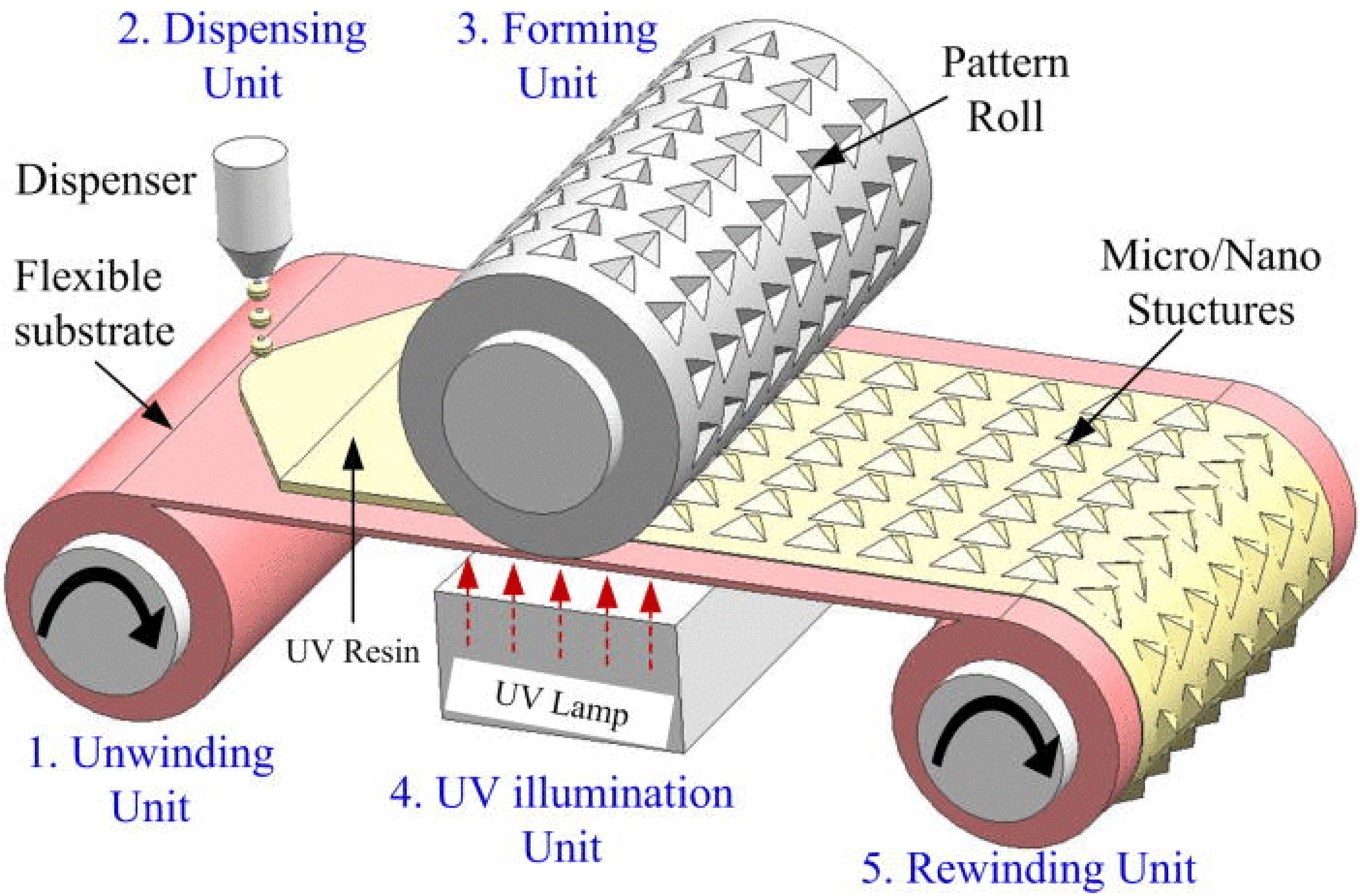


Plasmonic nano-structures



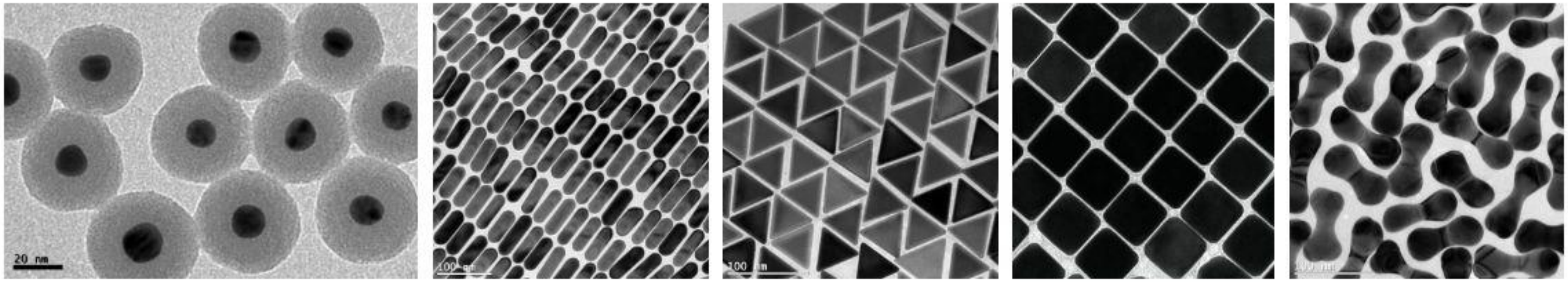
http://www.nilt.com

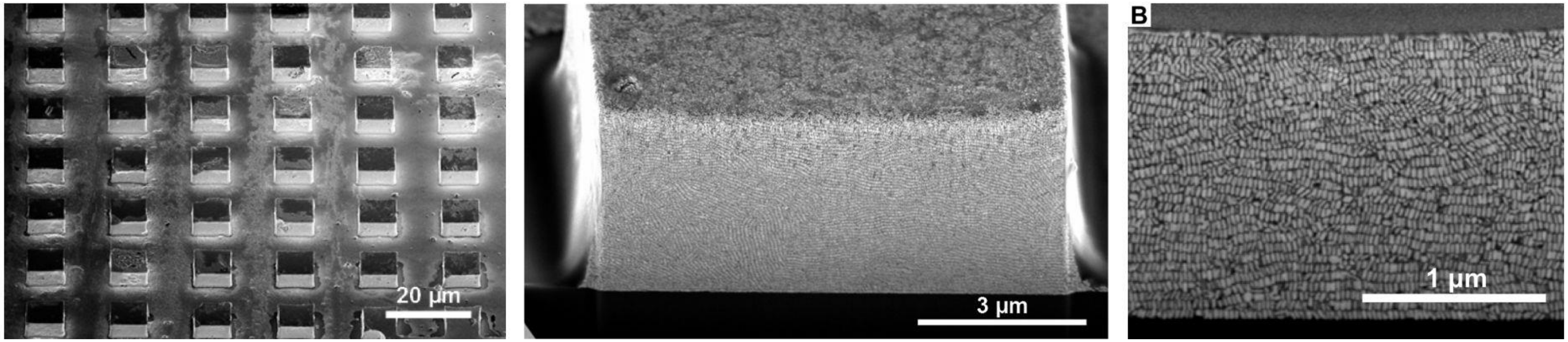
Roll-to-roll UV-NIL



https://doi.org/10.1116/1.4933347

Chemical Synthesis



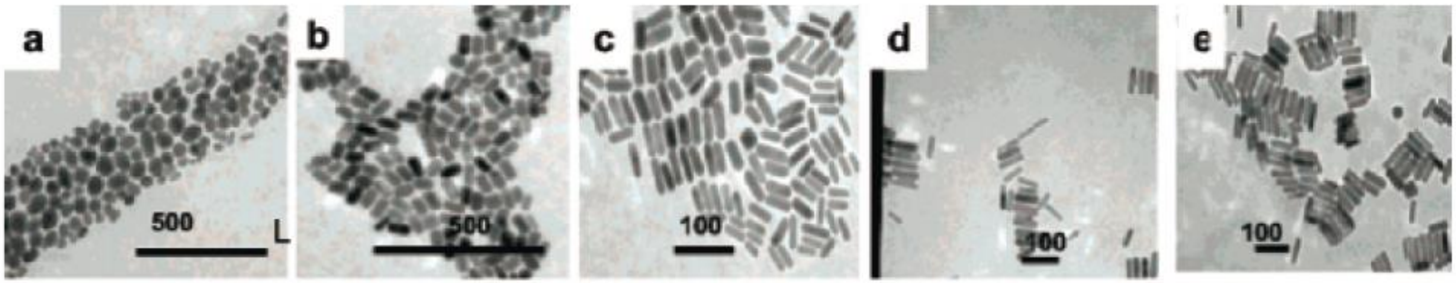


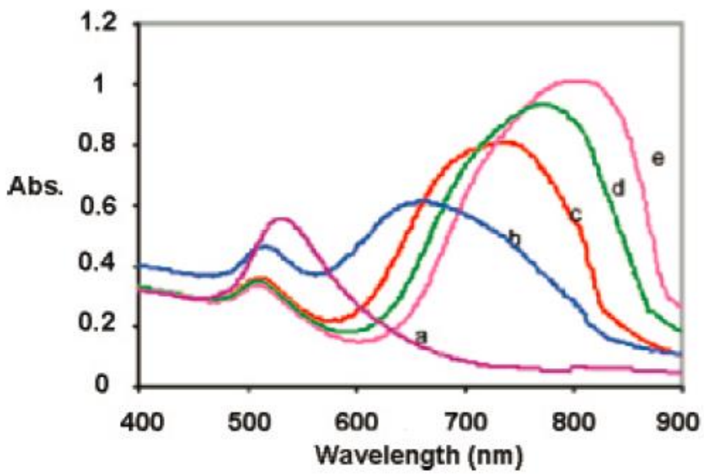
Rich spectrum of mono-crystaline metallic nanoparticles can be prepared by wet chemical routes and latter arranged e.g. lattices by self-assembly.

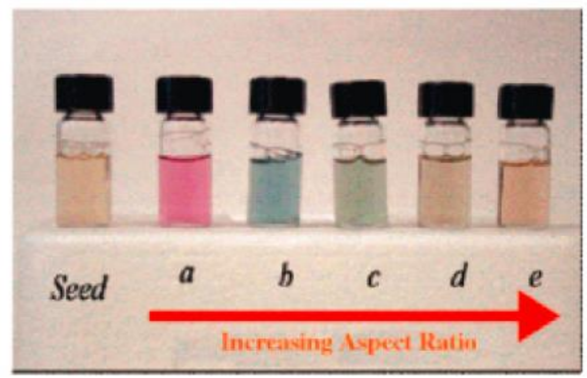
http://www.bionanoplasmonics.com/research.php

Localized Surface Plasmons (LSPs)

Synthesized metallic nanorods - tuning of λ_{LSPR} by changing the aspect ratio.







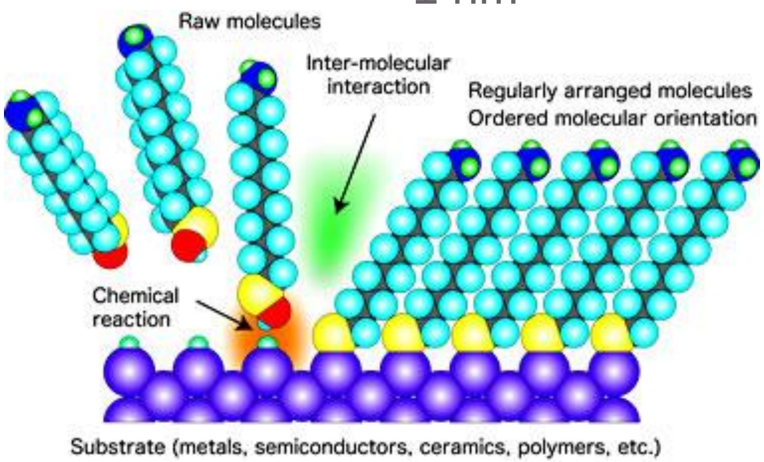
Watt, F.; Bettiol, A. A.; Van Kan, J. A.; Teo, E. J.; Breese, M. B. H.
Int. J. Nanosci. ***2005, 4, 269.***

Self Assembly

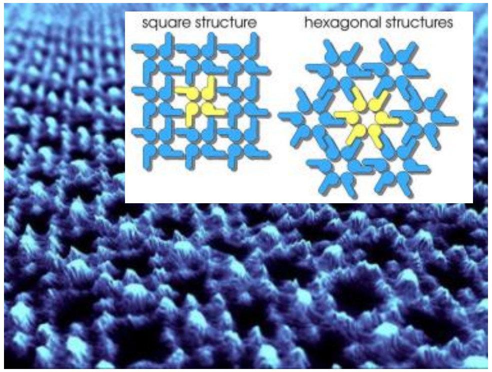
Molecules or micro/nanoparticles can self-arrange in well defined structures. Creates a high quality layer of material. Layers are deposited one layer at a time over large areas. Self assembled monolayer (SAM).

Building blocks with different characteristic size:

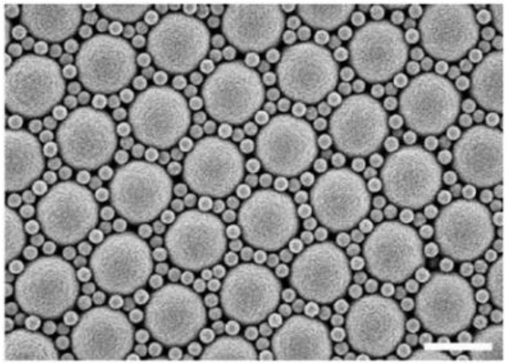
< 1 nm	several nm	> 100 nm



Thiol SAM



S-layer



Colloidal crystal

http://www.mtl.kyoto-u.ac.jp/english/laboratory/nanoscopic/nanoscopic.htm

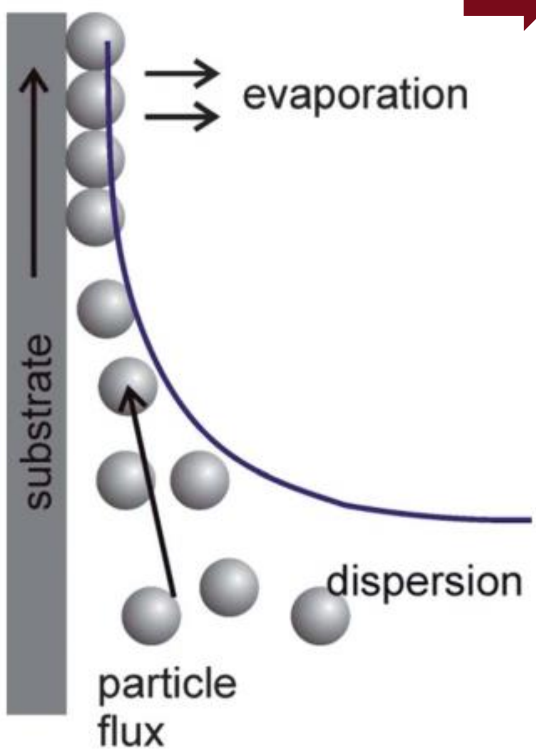
Sleytr, FEMS Microbiology Letters (2007), 267 (2), 131–144

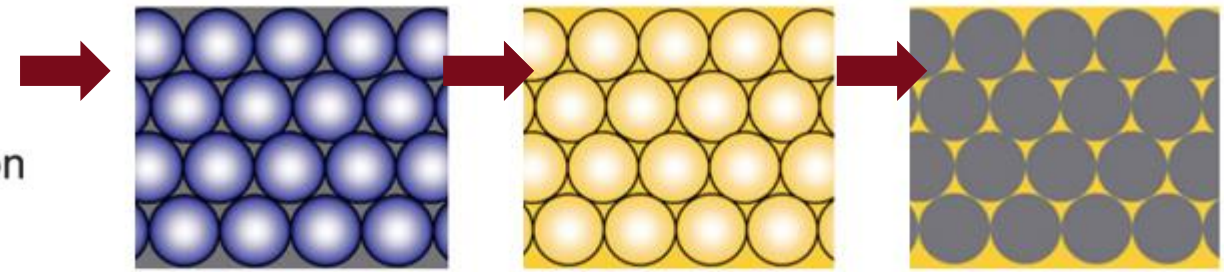
N. Vogel, et al., Adv. Funct. Mater., 2011, 21, 3064–3073.

Colloidal Lithography

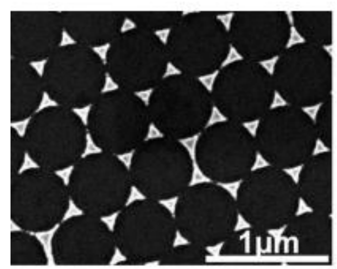
Colloidal crystal monolayer is employed as a mask for further fabrication of desired structures.

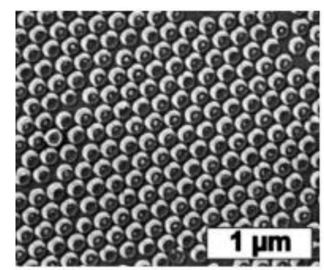
Colloid mask assembly / Metal deposition / Removal of colloid





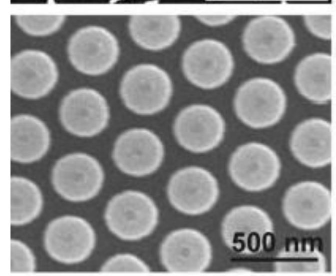
Triangles

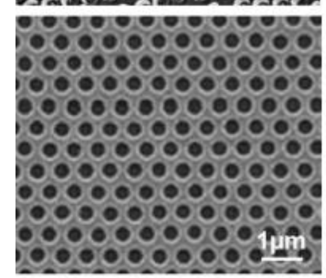




Crescents

Nano disks





Nano holes

N. Vogel et al ***Soft Matter***, 2012,**8**, 4044-4061
DOI: 10.1039/C1SM06650A

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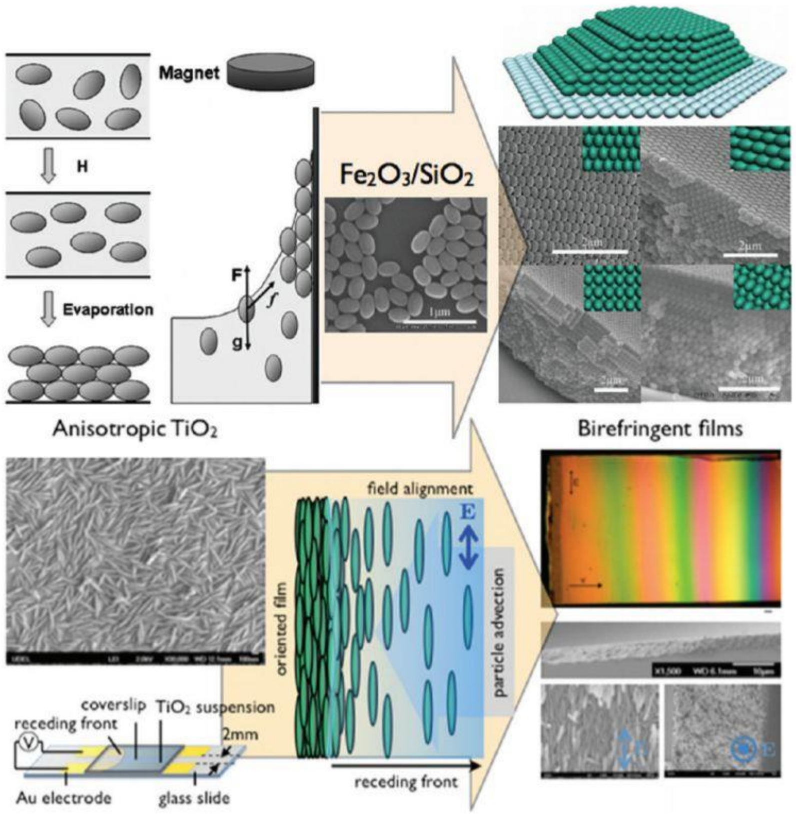
Self Assembly of Chemically Synthesized Nanostructures



Watt, F.; Bettiol, A. A.; Van Kan, J. A.; Teo, E. J.; Breese, M. B. H. *Int. J. Nanosci.* ***2005, 4, 269.***