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MATERIAIS NANOESTRUTURADOS E NANOTECNOLOGIAS

Photonic Crystals

Summary

Summary

- Natural Iridescent Materials
- Iridescence
- Artificial Opals
- Photonic Crystals
- Further Reading

Natural Iridescent Materials

Natural nanostructured materials, exhibiting iridescence

- Wings of butterflies
- Scales of fishes
- Soap bubles
- Hummingbird
- Peacock
- Bat
- Beetle
- Natural opals
- Fossil ammonite

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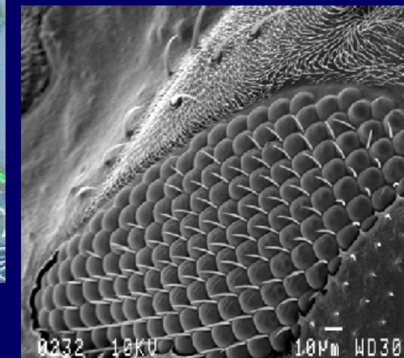
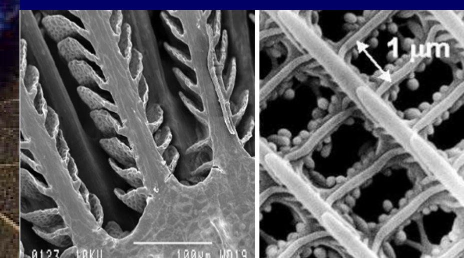
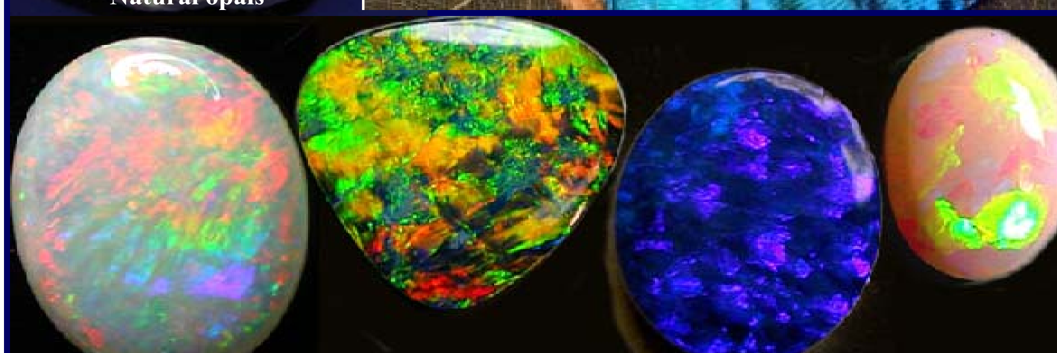
Natural Iridescent Materials

Scales of fishes



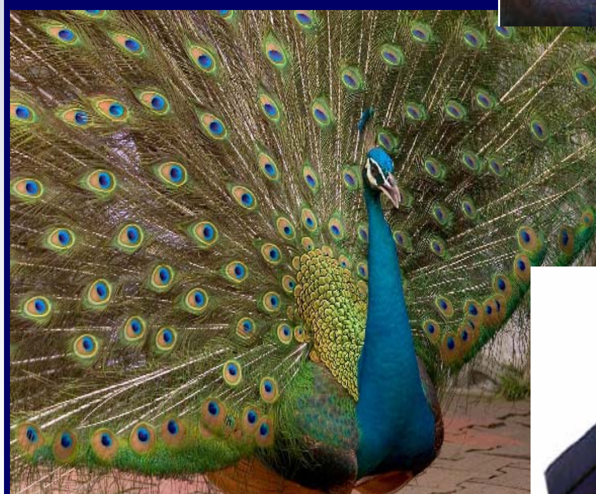
Wings of butterflies

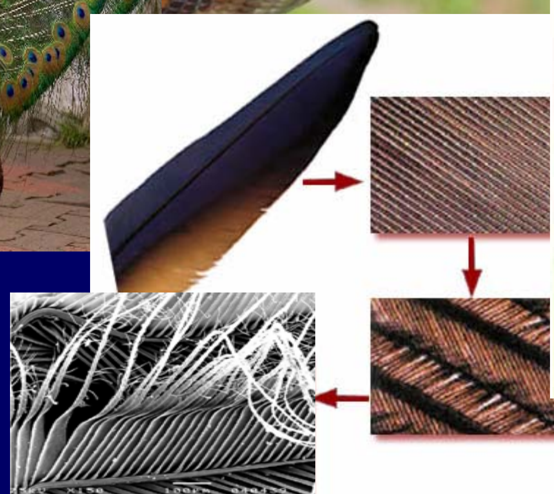




Natural Iridescent Materials

Beetle





Peacock

Peacock

Hummingbird

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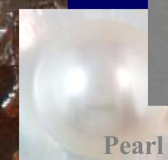
Natural Iridescent Materials

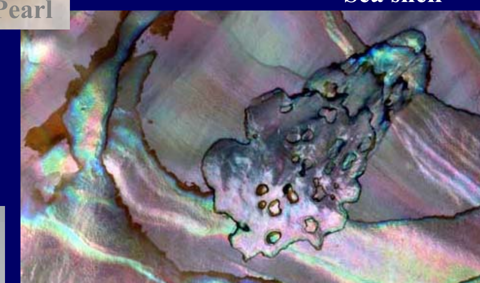

Roman glass


Sea shell

Fossil ammonite


Pearl


Sea shell


Sea shell


Roman glass

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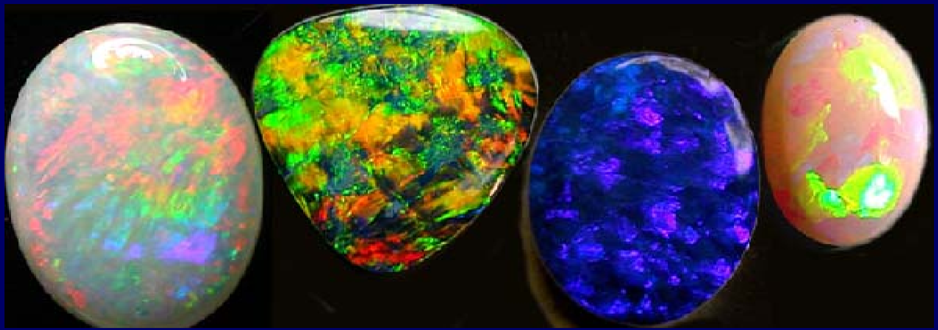
Natural precious opal

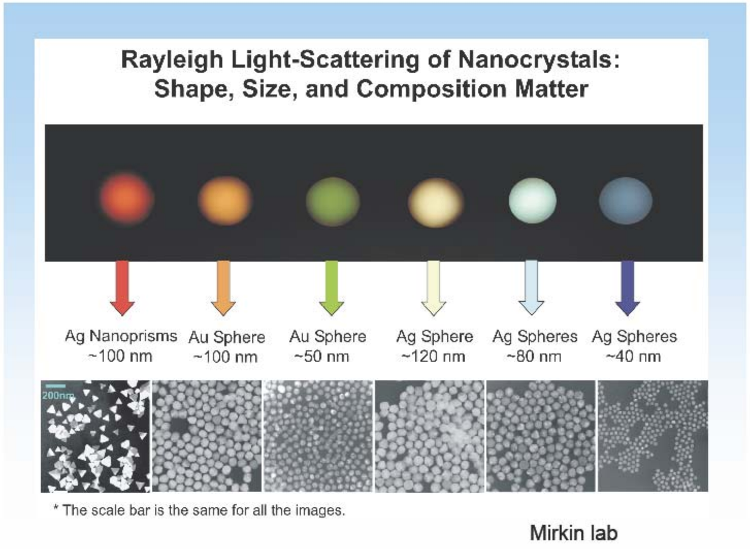
Precious opal is a **natural iridescent material**. In the gem opal, **nature spontaneously makes simple *fcc* crystals**, where **amorphous SiO_2 spheres** naturally self-assemble in regular ***fcc* globules**, cemented by a **disordered matrix of silica spheres** and **amorphous silica**. The amorphous silica spheres are ordered like the atoms in a crystal lattice, but on a scale a thousand times larger.



Natural Iridescent Materials

Natural precious opal

The **diameter of the spheres** is **comparable** with the **wavelength of visible light** and the **colours** of the opal are determined by the **diameter of the spheres** and the **effective refractive index**.



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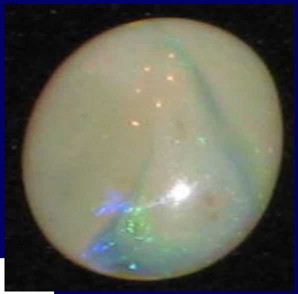
Iridescence phenomena



In nature, many colours cannot be explained simply by the absorption and reflection of light, but arise from physical mechanisms such as light and **scattering** **diffraction** from ordered structures with periodicities in the submicron range.

Wings of butterflies, peacock feathers, bat stars, fish scales, precious opals, or the multilayered structure of pearls, are examples of such natural structures. Compact disks are synthetic structures with the same optical characteristics.

The **iridiscent colours** of these materials show angle dependence, determined by the periodic structure of each material; in addition to strong multiple scattering of light, unexpected forbidden wave propagation in certain frequency ranges of normally transparent materials is observed.

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Iridescence phenomena

Iridescence phenomena refer to the optical effects that generate **colors** very **sensitive** to the **viewing** and **lighting directions**. Such colors are called **iridescent colors**.

The **physical mechanisms** causing iridescences include:

scattering

diffraction
(Bragg's law)

interference

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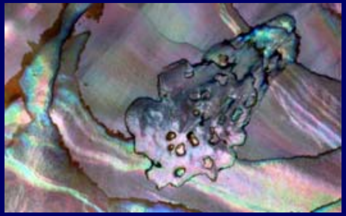
Iridescence phenomena

scattering

Rayleigh

$$\sigma_s \propto \frac{1}{\lambda^4}$$



Tyndall

$$\sigma_s = \frac{2\pi^5}{3}\frac{d^6}{\lambda^4}\left(\frac{n^2-1}{n^2+2}\right)^2$$

Mie

$$\sigma_s \approx \lambda$$

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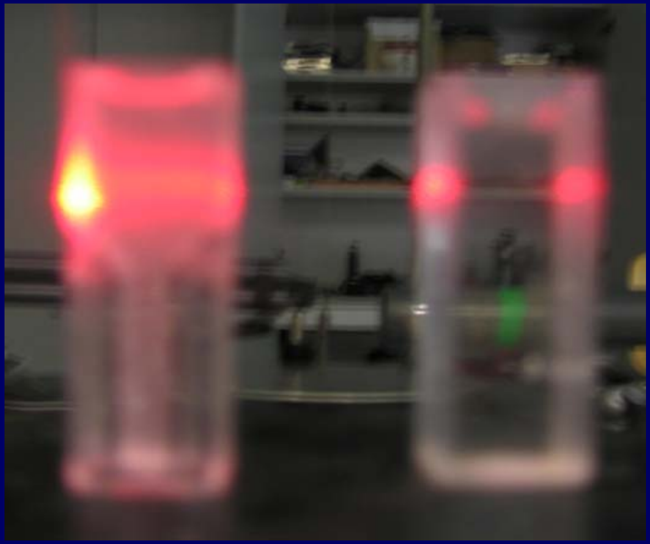
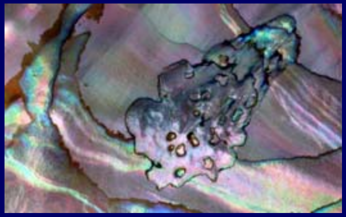
Iridescence phenomena

scattering

Tyndall

$$\sigma_s = \frac{2\pi^5}{3}\frac{d^6}{\lambda^4}\left(\frac{n^2-1}{n^2+2}\right)^2$$





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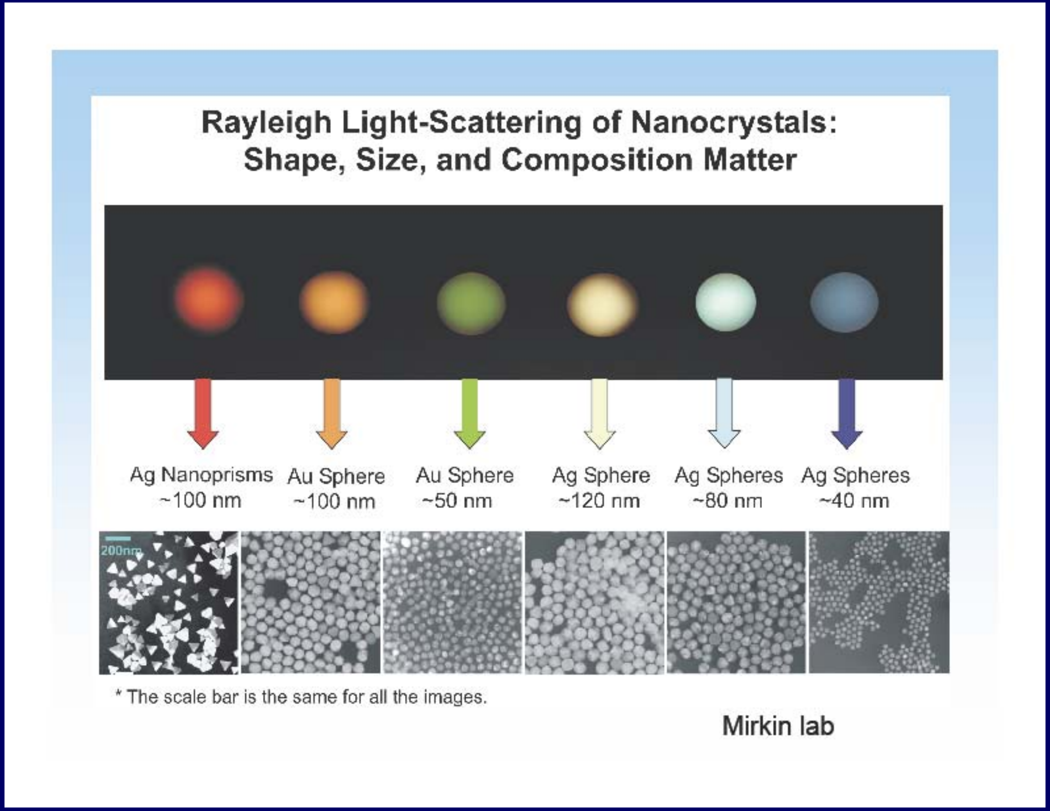
Iridescence phenomena

scattering



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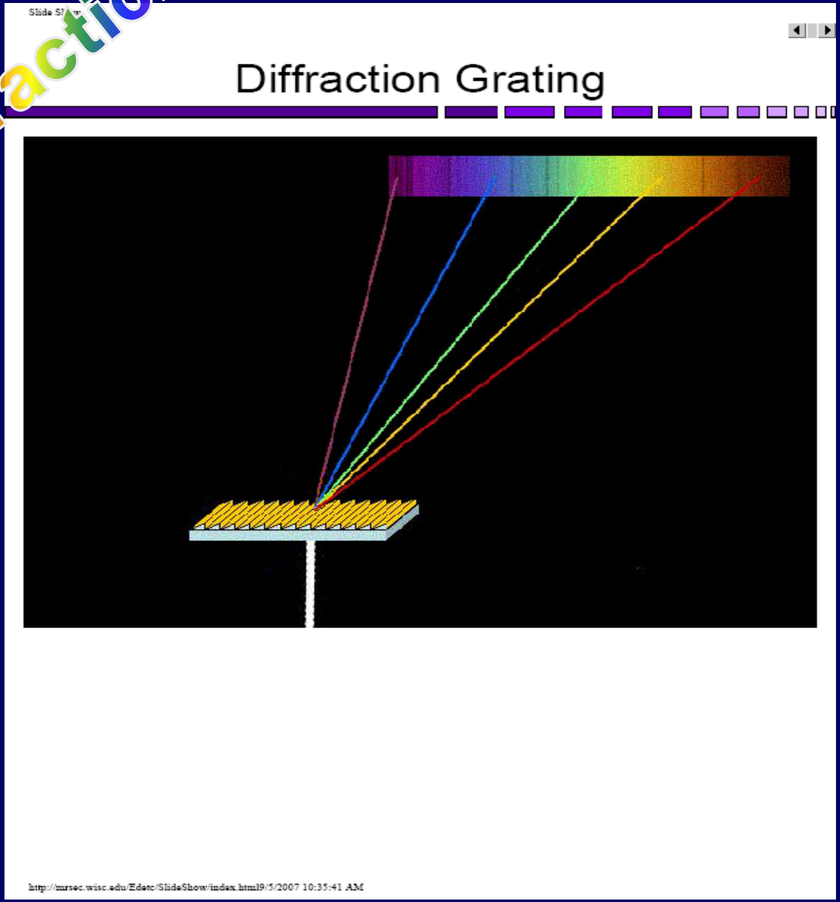
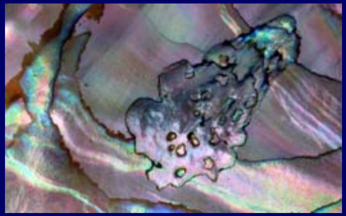
Iridescence phenomena

diffraction





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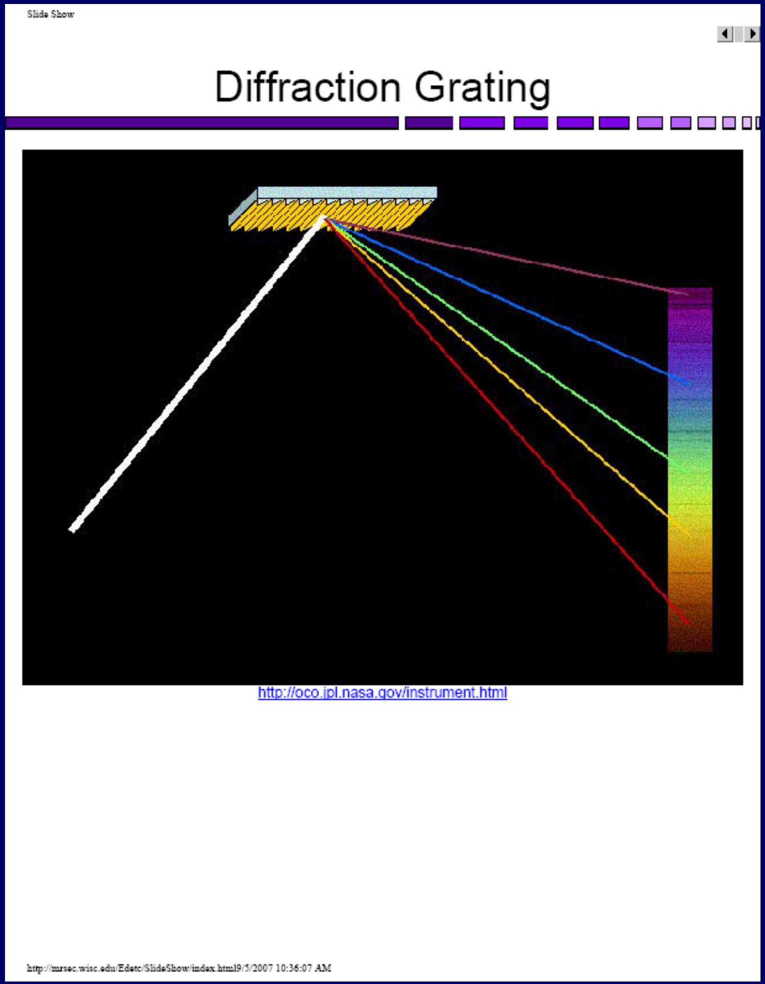
Iridescence phenomena

diffraction



Bragg's Law

interference

Bragg's Law applies to **any wave** in any **periodic object**. Usually this happens for X-rays in crystals, because X-ray wavelengths are of the order of the special period of the crystal.

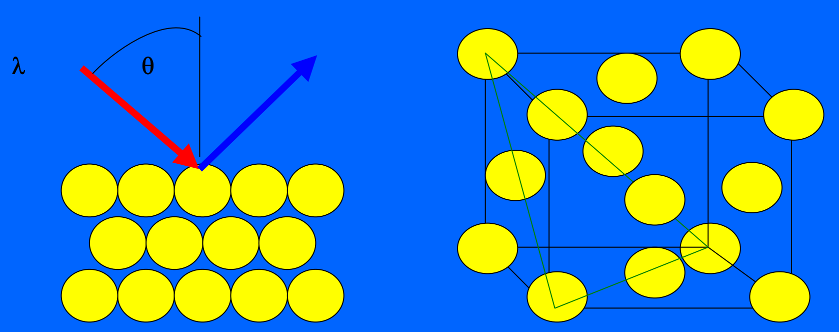
Periodic objects reflect incident waves when the **wavelength** and **interplanar spacing** satisfy **Bragg's Law**. Under these conditions waves do not penetrate very far and are reflected from the object.

but PBG can also diffract white light creating a similar effect. There are many occurring materials that have much longer periods that the atomic dimensions of crystals.

Iridescence

Bragg's Law

interference



$$\lambda = 2d\sqrt{n_{eff}^2 - \sin^2\theta}$$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$n_{eff}^2 = f_1 n_1^2 + f_2 n_2^2$$

$$d = \sqrt{2/3}\,D$$

Diffraction of white light by ***fcc* colloidal crystals** at the **(111)** crystal **planes**. The (111) crystal plane is the **most densely packed** in the *fcc* arrangement, with a spacing d(111), related to the sphere diameter, D.

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Iridescence phenomena

By analogy with X-ray diffraction **white light shines** upon the **colloidal crystal**. From this white light the **wavelength is selectively reflected** from the **(111) plane** of the **colloidal crystal**. The colloidal crystal appears **colored** upon **reflection**; the remaining transmitted light generates the complementary color.

The **angle dependent colors** of these systems are dependent upon the **diameter of the spheres**, which can be about a hundred nanometers or more, and upon the **effective refractive index** of the system.

Colloidal crystals reflect light of a particular wavelength (i.e., inhibition of the propagation of light within the colloidal crystal) which falls onto the crystals at a particular angle according to **Bragg's law**, and so **generate decorative iridescent angle-dependence color effects** (*play of color*).

Inverted opals, within particular limits, can completely inhibit the propagation of light within the crystalline inverted structure irrespective of the angle of the incidence. In this case the structure shows a so-called complete photonic bandgap.

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Bragg's Law

By analogy with X-ray diffraction, the interaction of white light with the PC is described by the modified form of **Bragg's law** for the optical region, which takes into account **Snell's law** of refraction:

$$\lambda = 2d\sqrt{n_{eff}^2 - \sin^2\theta}$$

where ***l*** is the free space wavelength of the light, ***d*** the interplanar spacing between the scattering planes, ***θ*** is the angle between the incident radiation and the normal to the set of planes and ***n2eff*** is the effective dielectric constant of the composite PC.

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$, where $$d_{(111)} = \frac{a}{\sqrt{3}}$$ and $$a = \frac{2D}{\sqrt{2}}$$

Since the (111) plane is the most densely packed in the *fcc* arrangement, with spacing

and D is the sphere diameter in a colloidal PC, the longest wavelength diffracted by the *fcc*-packing, for an observer perpendicular to the surface, will be:

$$\lambda_{\max} = 2n_{eff}\frac{D\sqrt{2}}{\sqrt{3}} = 1.633 n_{eff} D$$

The diameter of the spheres is comparable to the wavelength of visible light, so the *opal* acts as a 3-D diffraction lattice for visible light and its colours are determined by the diameter of the spheres and the RI of the composite.

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B) **Bottom-Up** (*scaling up*, smaller to larger size)

Self-Assembly

Mimic natural nanostructured materials

This approach is simply one of letting molecules find their own lowest states of energy. Molecules are subject to forces that orient them and / or move them in such a way that their final positions exhibit a lower state of energy than the original position. Forces that are taken advantage of by nanosciences in this way include hydrogen bonding, magnetic attractions, and hydrophobic and hydrophilic interactions.

1) Amphiphilic aggregate structures

2) PS, SiO_2, … nanoparticles self-assembly

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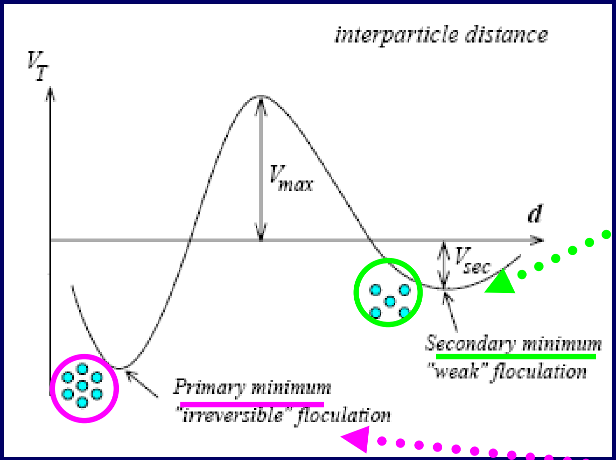
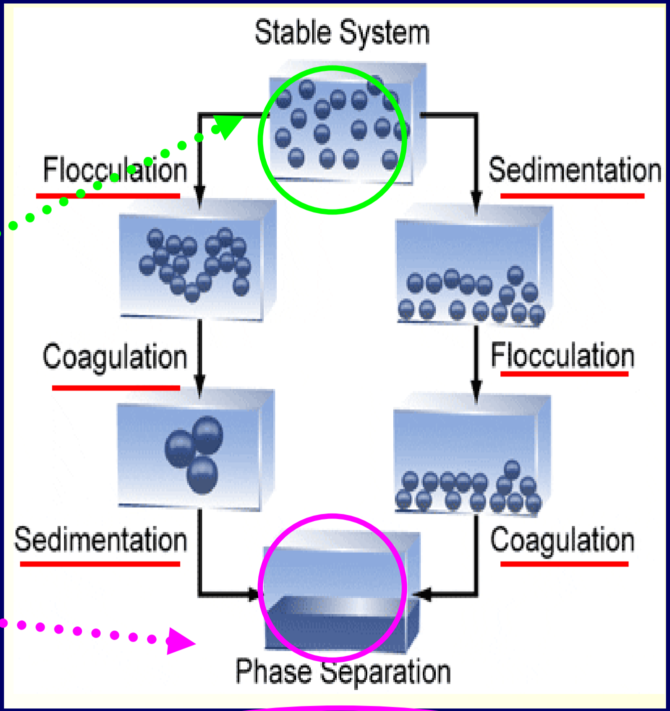
•IN COLLOIDAL SUSPENSIONS THE SURFACE ENERGY CAN BE REDUCED THROUGH

AGGREGATION / FLOCULATION / COALESCENCE

THERMODINAMIC METASTABLE KINETIC STABLE SYSTEM





THERMODINAMIC STABLE SYSTEM

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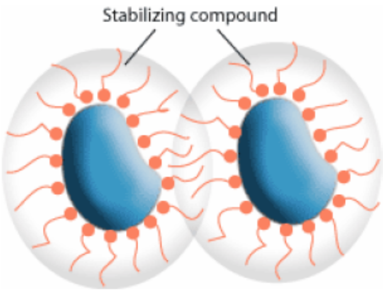
Important factors in colloidal dispersions

- Brownian motion
  Constant, random motion of particles due to collisions with the other molecules in the solution. Displacement of particles is given by the Einstein relation.
- Gravity
  Density differences between the solute particles and the external phase lead to sedimentation or creaming of the solutes.
- Steric stabilization (e.g., by polymer grafting)
  Lyophilic molecules chemically or physically attached to the solute surface prevent aggregation of colloidal particles. Overlap of the stabilizing molecules results in an osmotic pressure in the overlap region and the stabilized solutes are pushed apart.



- Depletion interactions
  Depletion of other solutes (intermediate in size with respect the colloidal particles and the solvent molecules) in a region between two colloidal particles results in an (osmotic) pressure difference. The pressure difference in the depletion region and bulk solvent results in an effective attraction between the colloidal particles.
- Electrostatics
- van der Waals interactions

} **Electrostatic Stabilization**
DLVO theory

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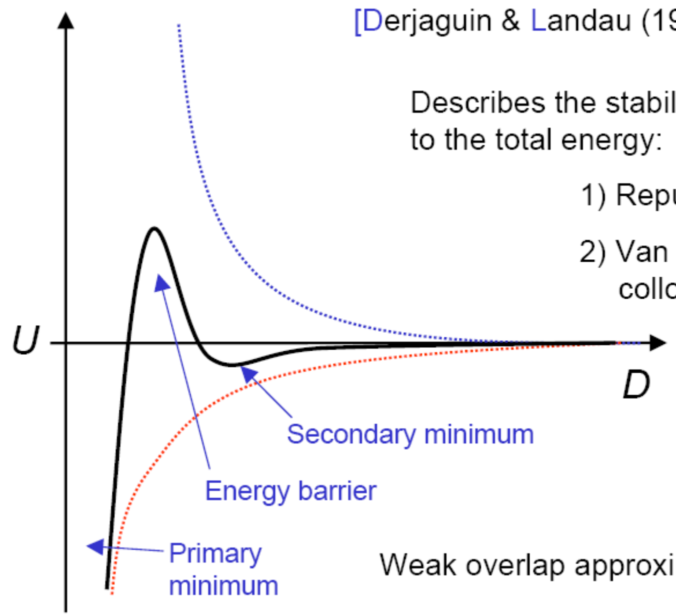
COLOIDAL STABILITY: DLVO theory

i) ATRACTIVE INTERACTIONS + **ii) REPULSIVE INTERACTIONS**

DLVO theory

[Derjaguin & Landau (1941) / Verwey & Overbeerk (1948)]



Describes the stability of colloids with two contributions to the total energy:

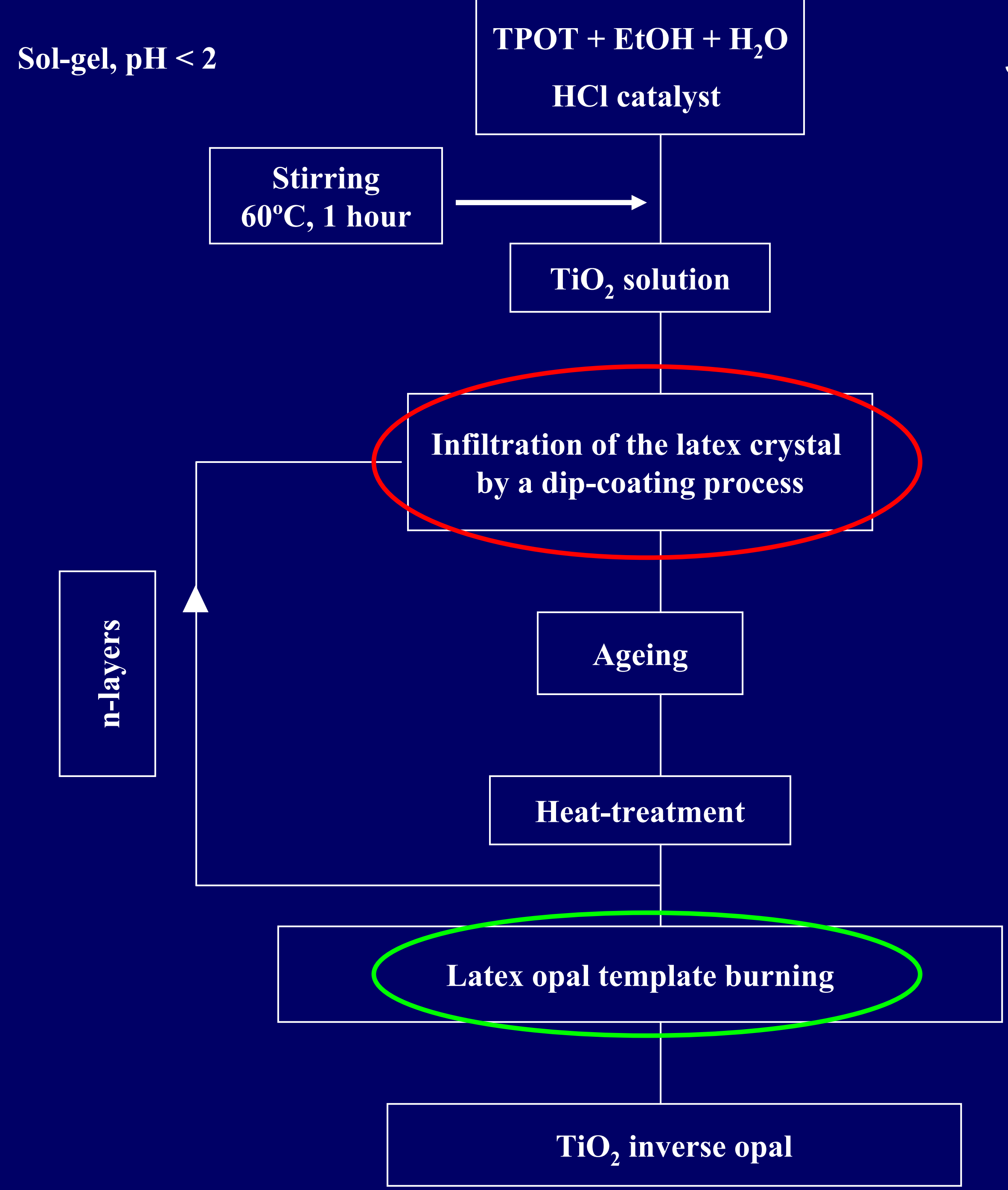
1) Repulsion of the ionic double layers U_R
2) Van der Waals attraction between the colloidal particles U_A

Weak overlap approximation:

$$\begin{aligned} U_{\mathrm{DLVO}} &= U_{\mathrm{R}} + U_{\mathrm{A}} \\ &= (64\pi k_{\mathrm{B}} T R c_0 \Gamma_0^2/\kappa^2) e^{-\kappa D} - AR/12D \end{aligned}$$

[J. Israelachvili, *Intermolecular & Surface Forces* (Academic Press, 1992)]

Self-Assembly



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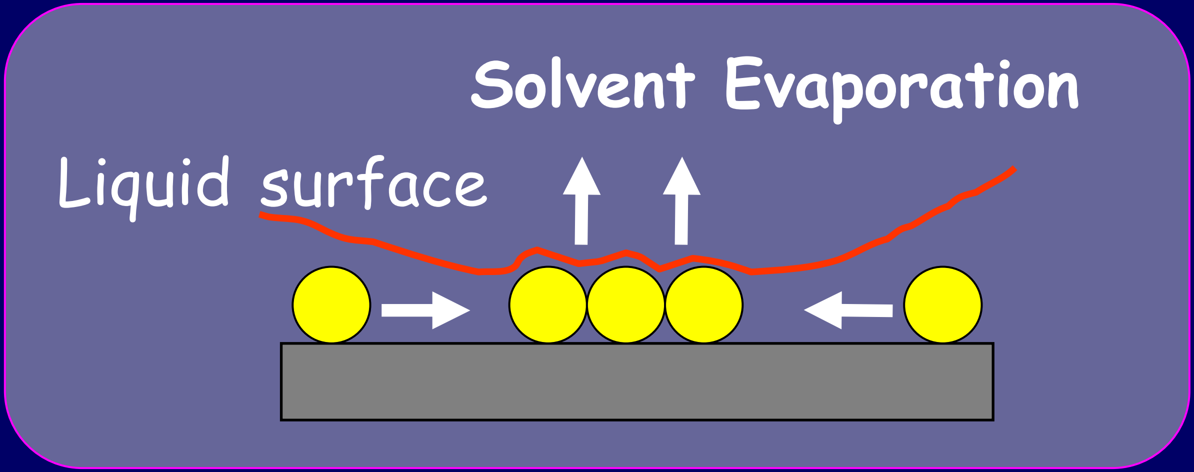
SELF-ASSEMBLY BY:

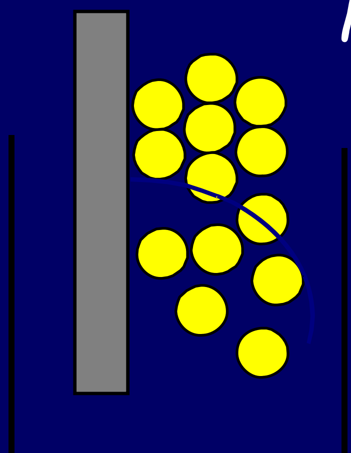
Sedimentation



SELF-ASSEMBLY BY:

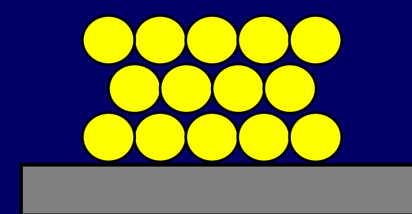
Convective self-assembly

Meniscus



Suspension of PS colloidal spheres in water **0.1 %**

Latex (PS) opal



FCC arrangement

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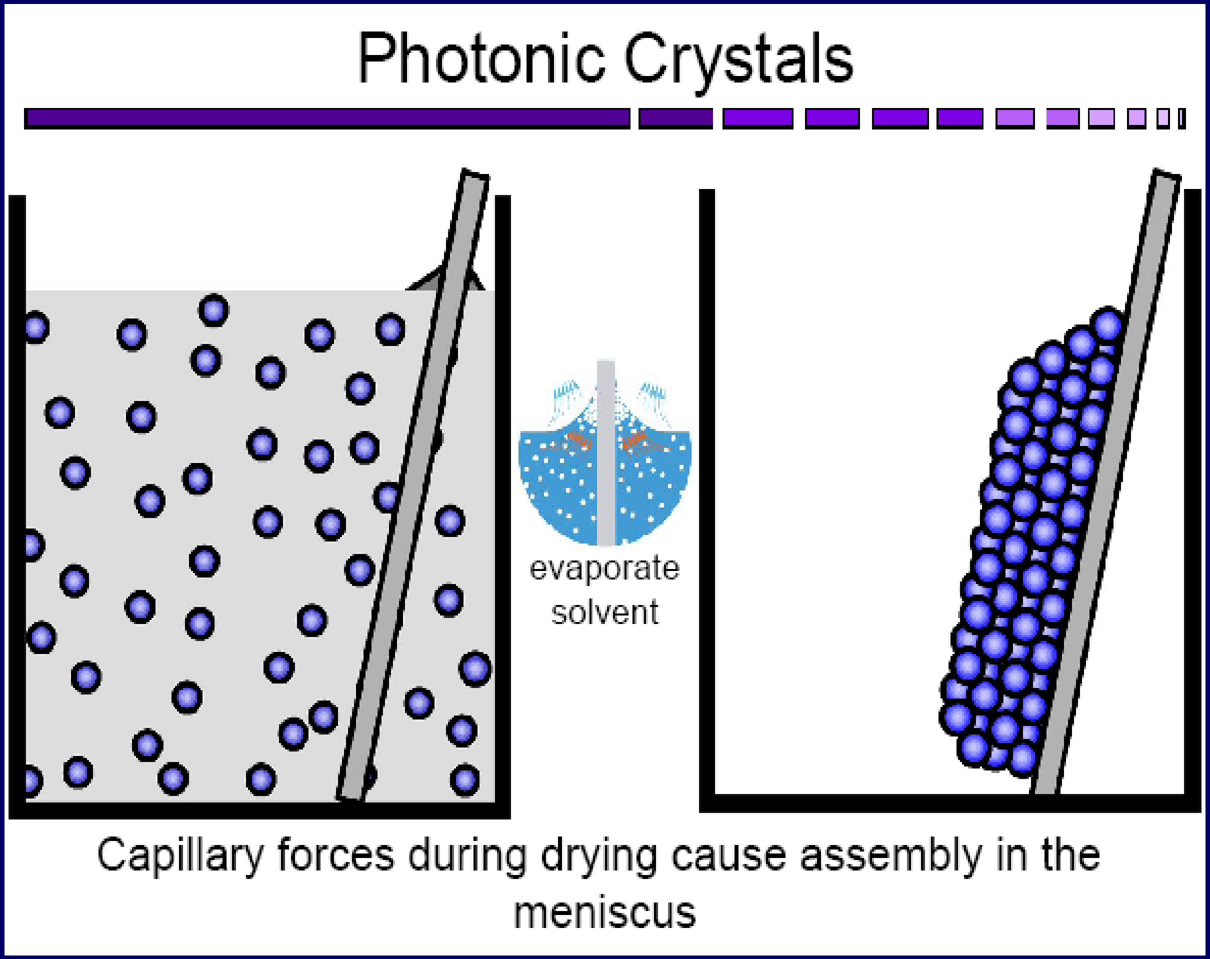

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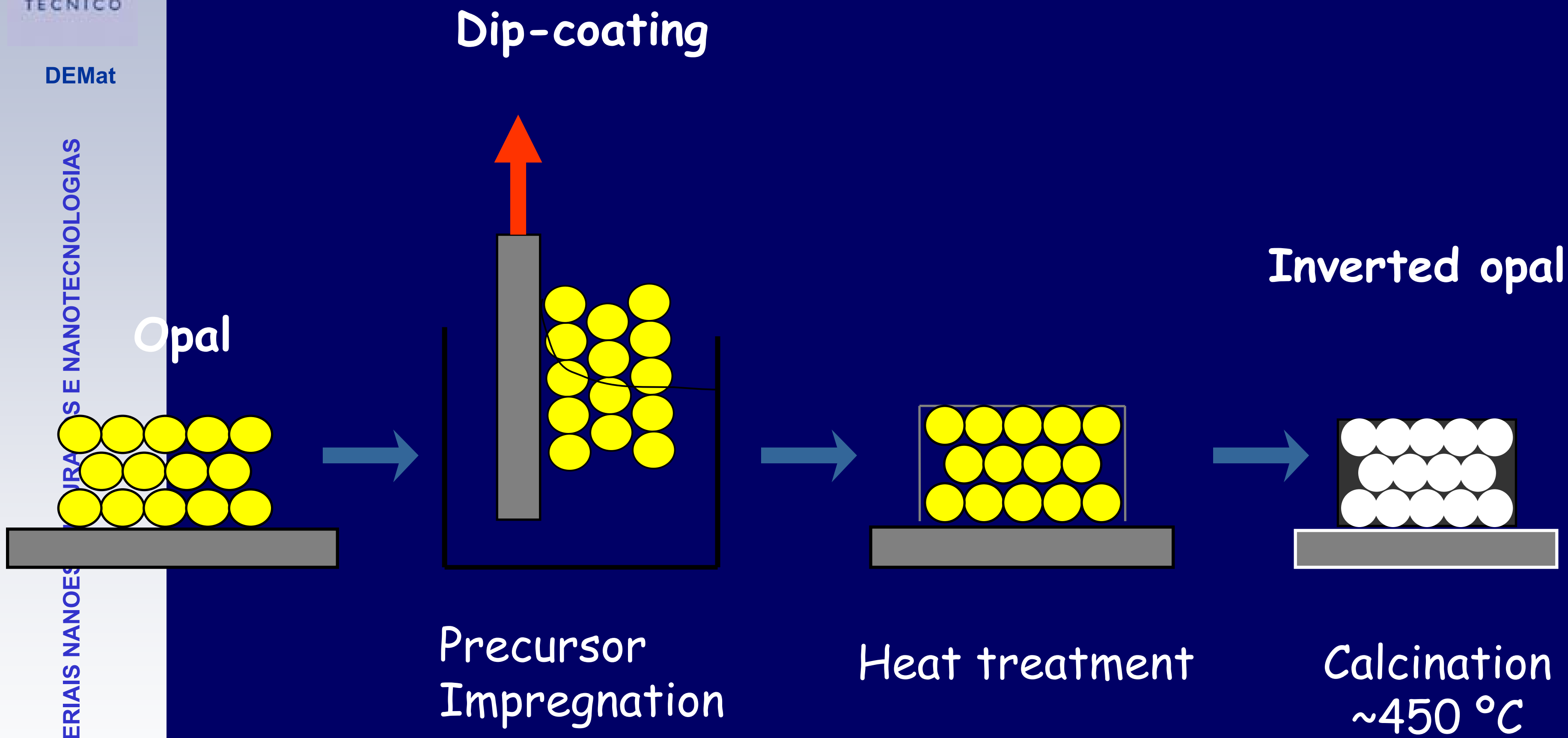
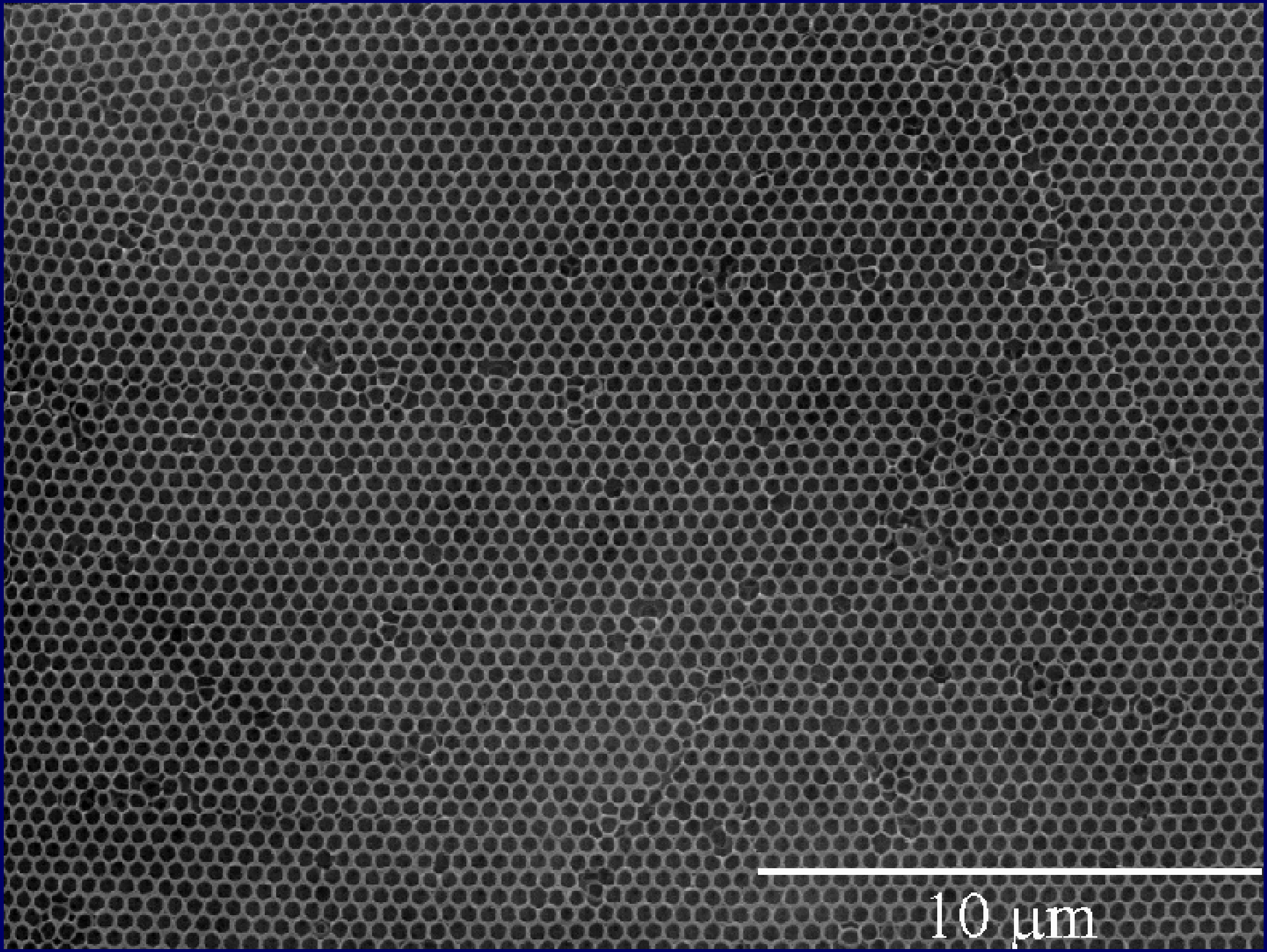
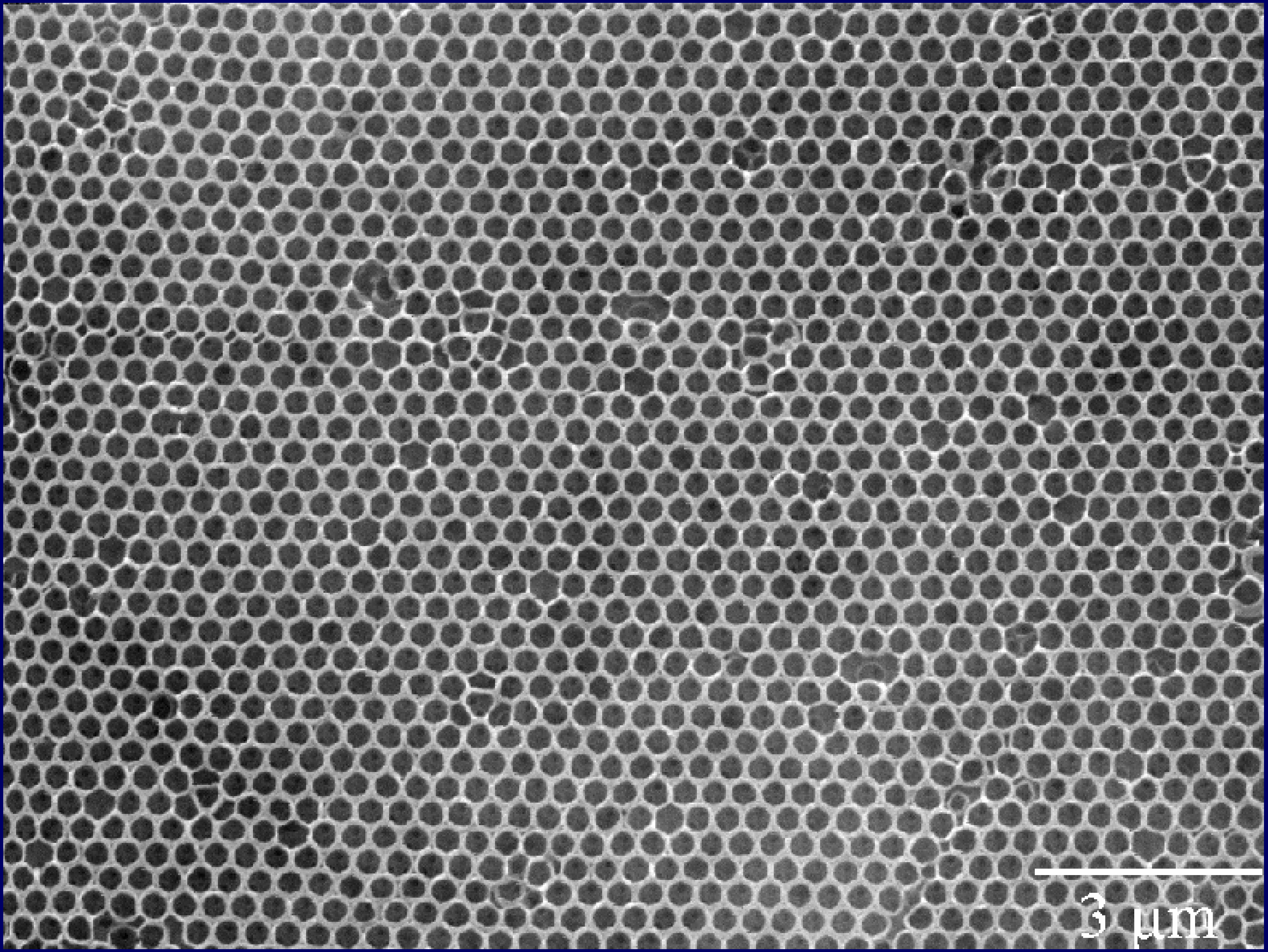


80 silica-20 titania / air inverted opal



80 silica-20 titania / air inverted opal



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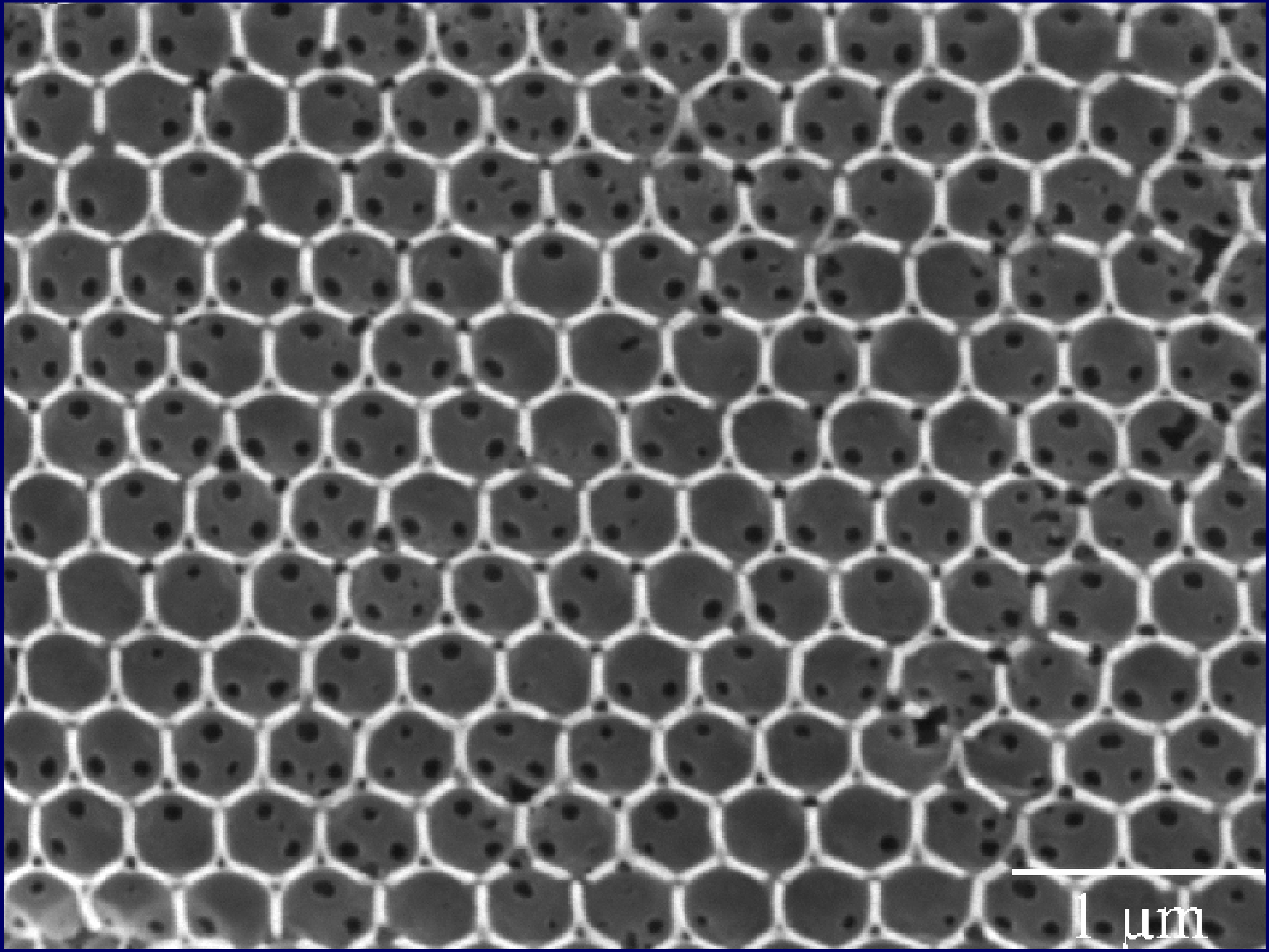
80 silica-20 titania / air inverted opal



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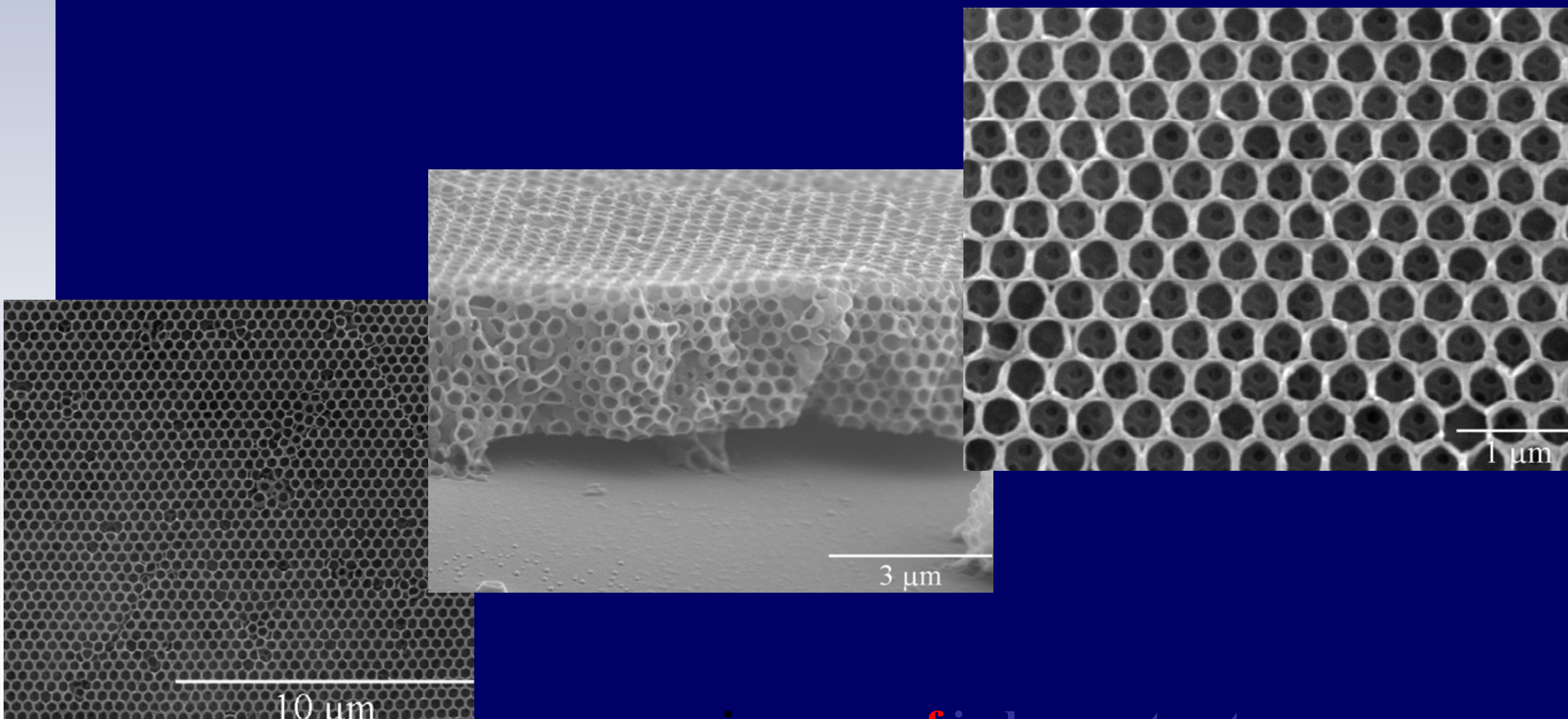
Titania inverted opal

SEM micrograph of a titania/air inverted opal, prepared by convective self-assembly of PS spheres (dia = 460 nm), at different magnifications.



increase of index contrast

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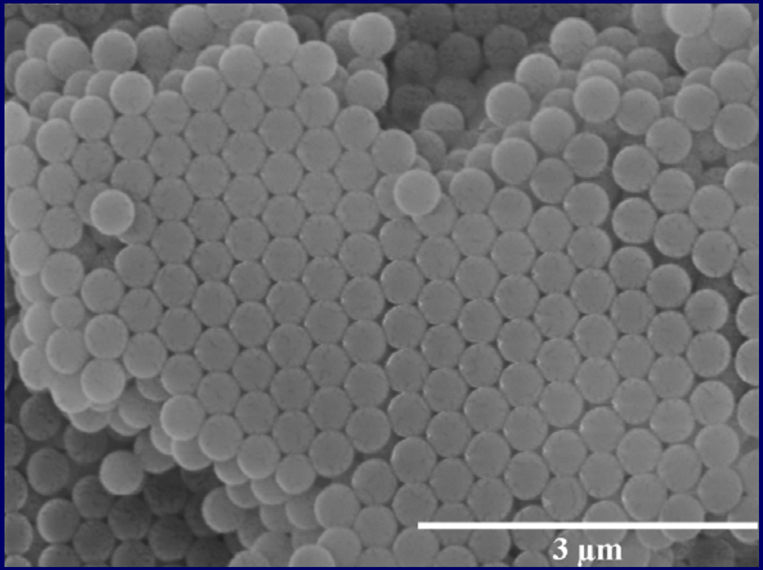
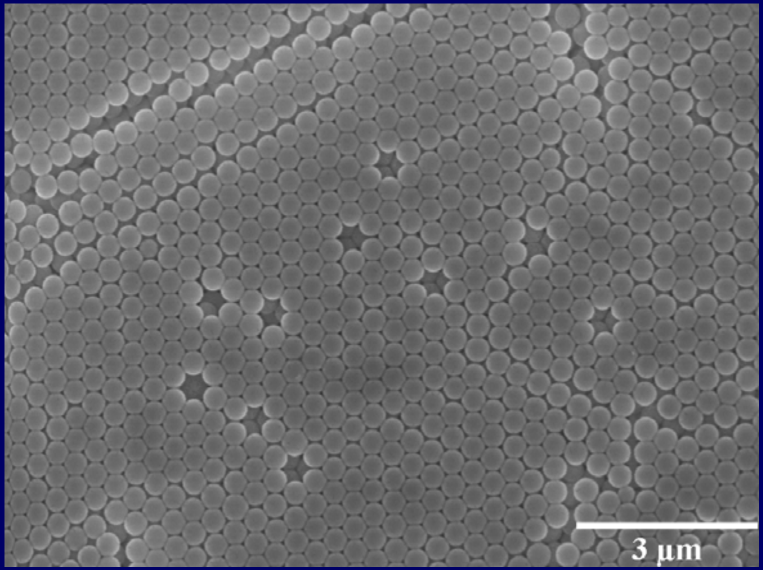




Natural sedimentation on horizontal substrate

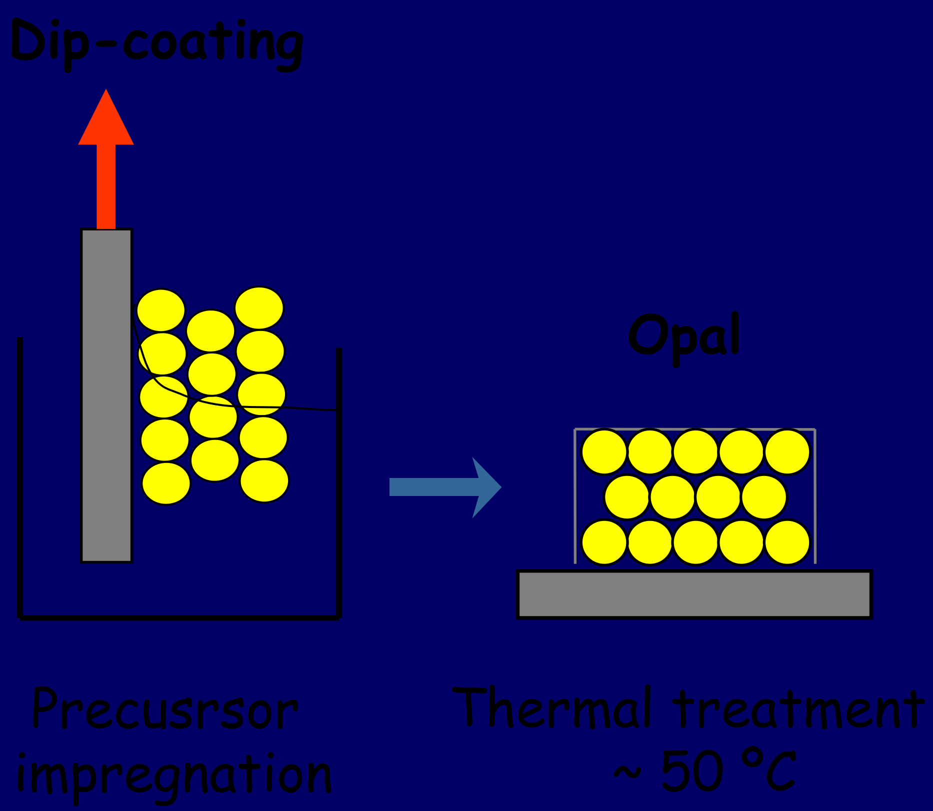
↓

PS synthetic opal

(sphere dia = 460 nm)

(FCC (111) planes)

Self-Assembly



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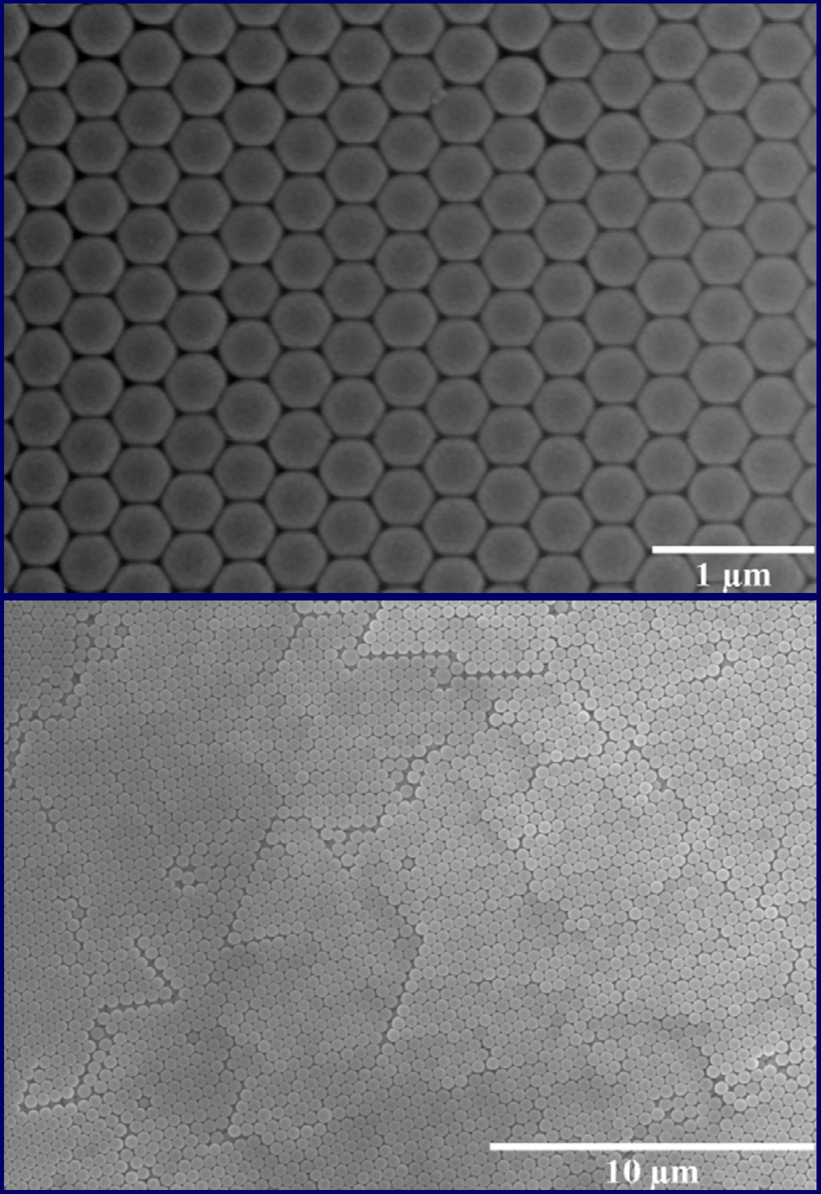

dip-coating

PS synthetic opal
(dia = 460 nm)

(FCC (111) planes)

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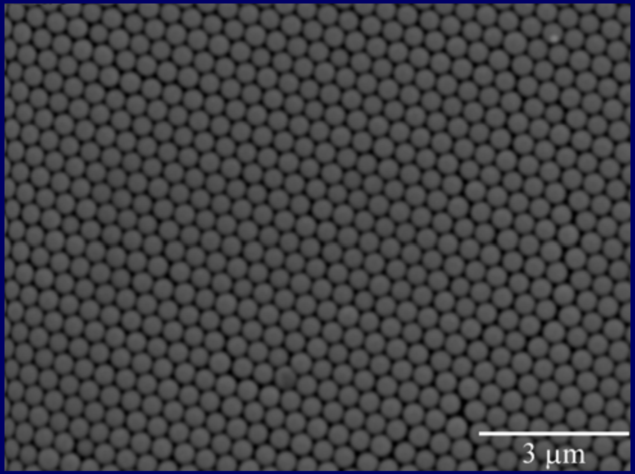
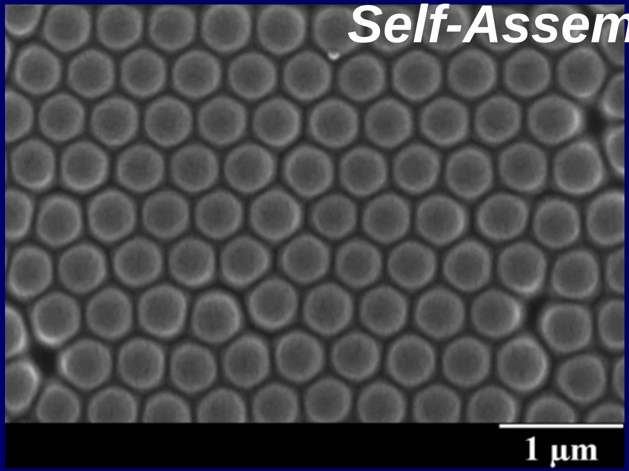
Self-Assembly



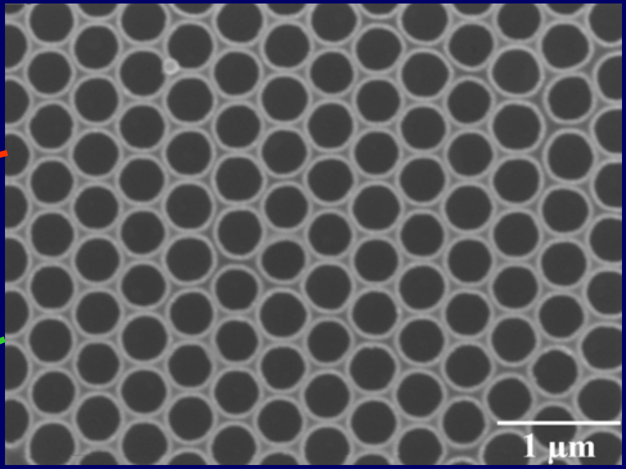
PS opal

(convection, dia = 460 nm)

(~ 120 µm², few defects)



Opal infiltrated with TiO_2



air spheres

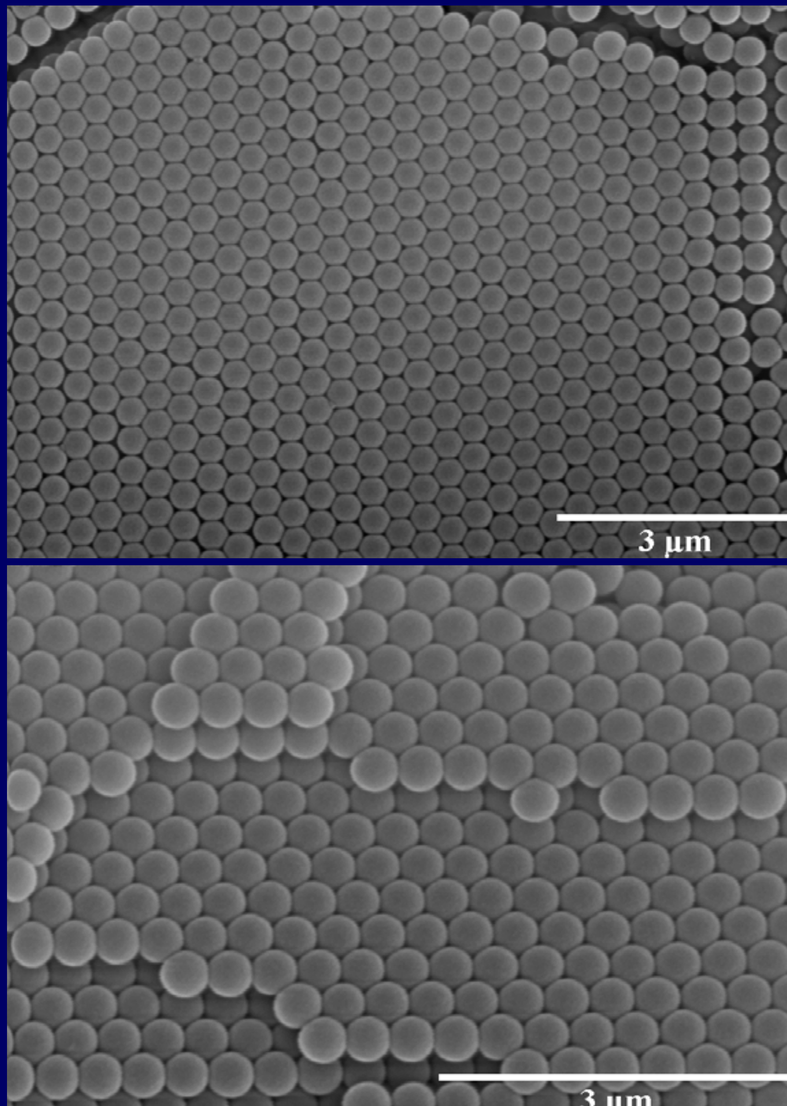
(~ 74% vol.)

TiO_2 skeleton

(~ 26% vol.)

TiO_2 inverse opal

Self-Assembly



vertical convective self-assembly

PS synthetic opal

(dia = 460 nm)

(FCC (111) planes)

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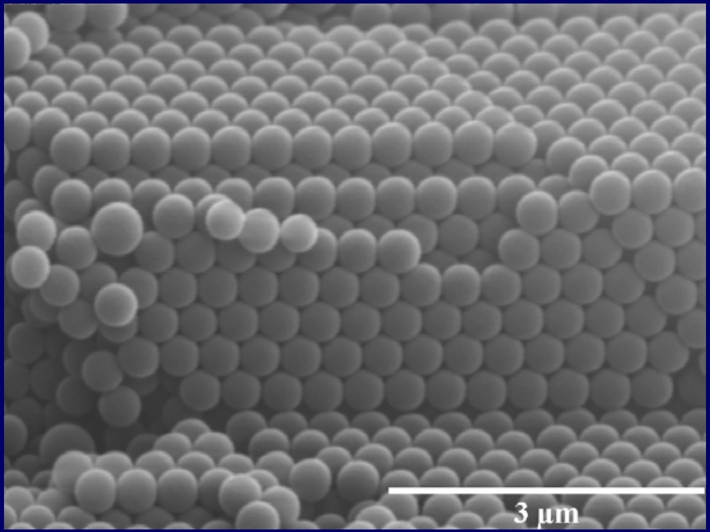
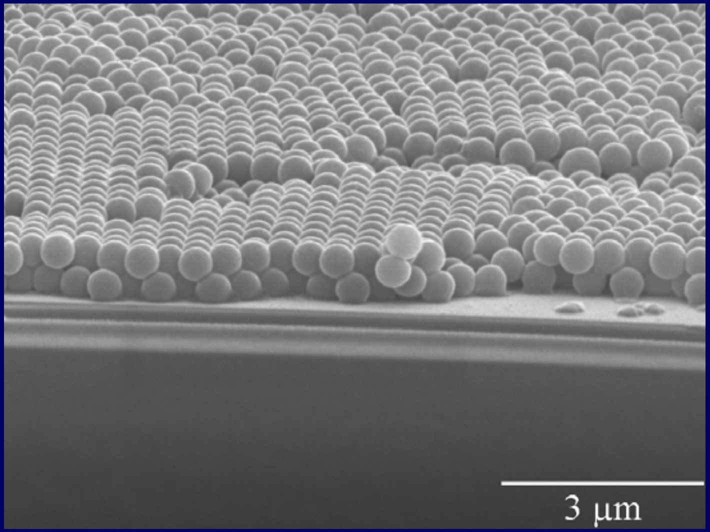


Convection



Dip-coating

SEM micrographs of PS synthetic opals

(FCC structures)

(dia = 460 nm)

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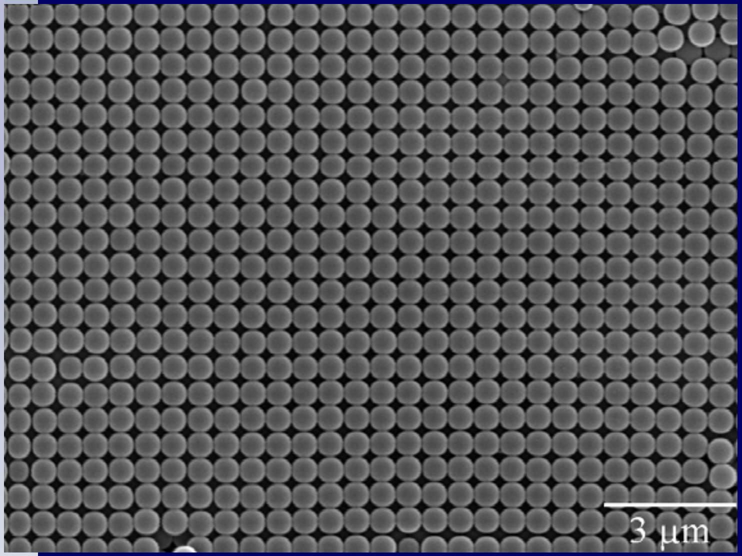
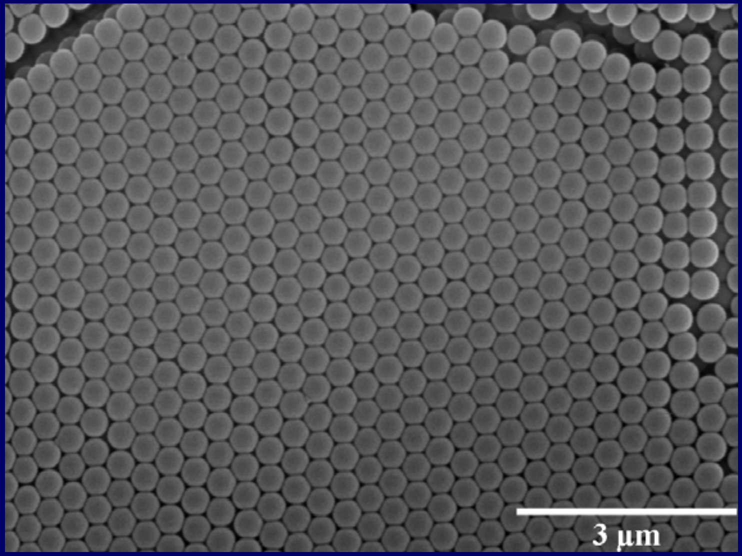
SEM micrographs of PS synthetic opals prepared by convection

(dia = 460 nm)



SC structure {100}

f = 52 %



FCC structure {111}

f = 74 %

R%

METAMATERIALS and PHOTONIC CRYSTALS (PCs)

Metamaterials: **composite artificial structures** with **unusual optical properties** impossible to obtain in natural materials.

PCs: a **particular case of metamaterials;** also **composite structures** with a **periodicity** (in 1-, 2- or 3-dimensions) **in the dielectric constant** (or **refractive index**), on a linear scale **~ λ** in the **optical region** of the spectrum (e.g. ~ 100 – 1000 nm).

Periodicity in the refractive index originates **optical gaps in the PCs**: **frequency ranges** in which **light does not propagate in the composite**, due to **Bragg reflection** (“**stop bands**”), although the **individual materials are transparent**.

PCs, or *photonic bandgap* (**PBG**) *materials*, are **metamaterials for the optical region of the spectrum** (near the visible).

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Near the end of the twentieth century, **E. Yablonovich** and **S. John** proposed the idea that an **artificial structure with a periodic modulation in refractive index** (RI) (or dielectric constant) **can prevent the propagation of light over a certain band of wavelengths**, where the isolated materials are otherwise transparent, while allowing other bands to propagate.

The periodicity prevents light from propagating through the material due to Bragg reflection, in a wavelength range of the order of the spatial period of the PBG structure, or simply, PC.

When the **RI periodicity** is on a **millimetre scale**, the PBG confines and controls the light in the **microwave regime**, while in the **infrared (IR) scale** the PBG does the same in the **optical regime**; when the periodicity is of the order of a **few angstroms**, the PBG operates in the **X-ray regime**, thus being a common solid-state crystal formed by atoms, ions or molecules.

Self-Assembly

When white light shines upon the PC, certain wavelengths do not penetrate very far and are selectively reflected from the periodic scatterers of the PC, like the highest density plane (111) in a face-centred cubic (*fcc)* structure (Figure 2). Each wavelength is reflected exactly at the same frequency as the incident light, regardless of its direction or polarization state, for a full PBG structure. Then, wherever in space the radiation interferes constructively, by adding scattered rays with phase differences multiple of 2π, a coloured crystal will be observed. The wavelength (or frequency) range which is forbidden to propagate through the periodic structure is called a *stop band* and corresponds to a *photonic bandgap* in the optical density of states. The remaining transmitted light generates the complementary colour.

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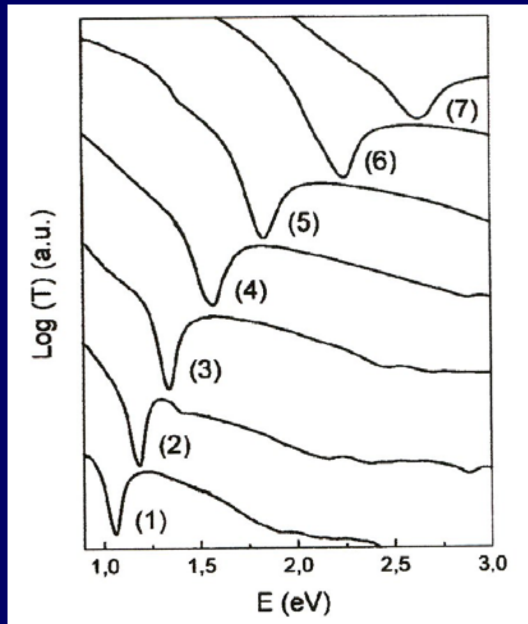
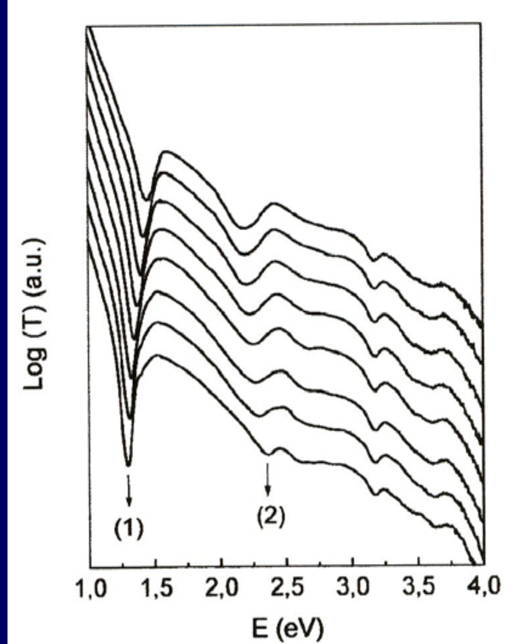
MATERIAIS NANOESTRUTURADOS E NANOTECNOLOGIAS





(a) Optical transmission at normal incidence (θ = 0º) for opal-like structures made of

(b) spheres with different diameters: (1) 535 nm, (2) 480 nm, (3) 415 nm,

(c) (4) 350 nm, (5) 305 nm, (6) 245 nm, and (7) 220 nm. The spectra have been vertically shifted for the sake of clarity.

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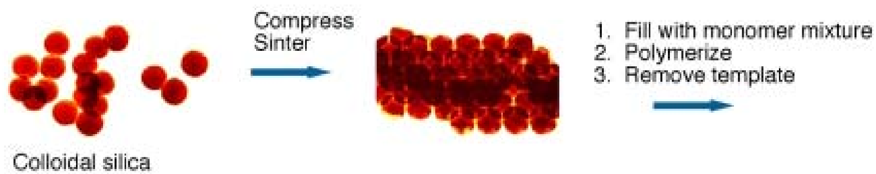
Colloidal crystals

Interesting for applications in optics, sensors, separations

So far, building blocks are spheres and high symmetry polyhedra

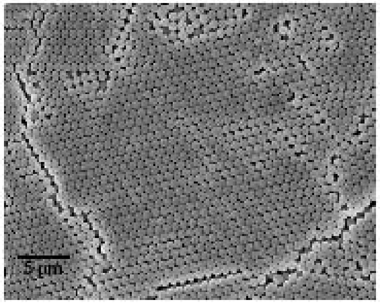
➡ limited structural variety

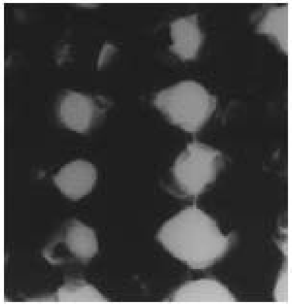


polymer "inverse opal"

Johnson, et al., *Science* 1999, *283*, 963.

860 nm silica opal thin film





Pt inverse opal with 12 nm "necks"

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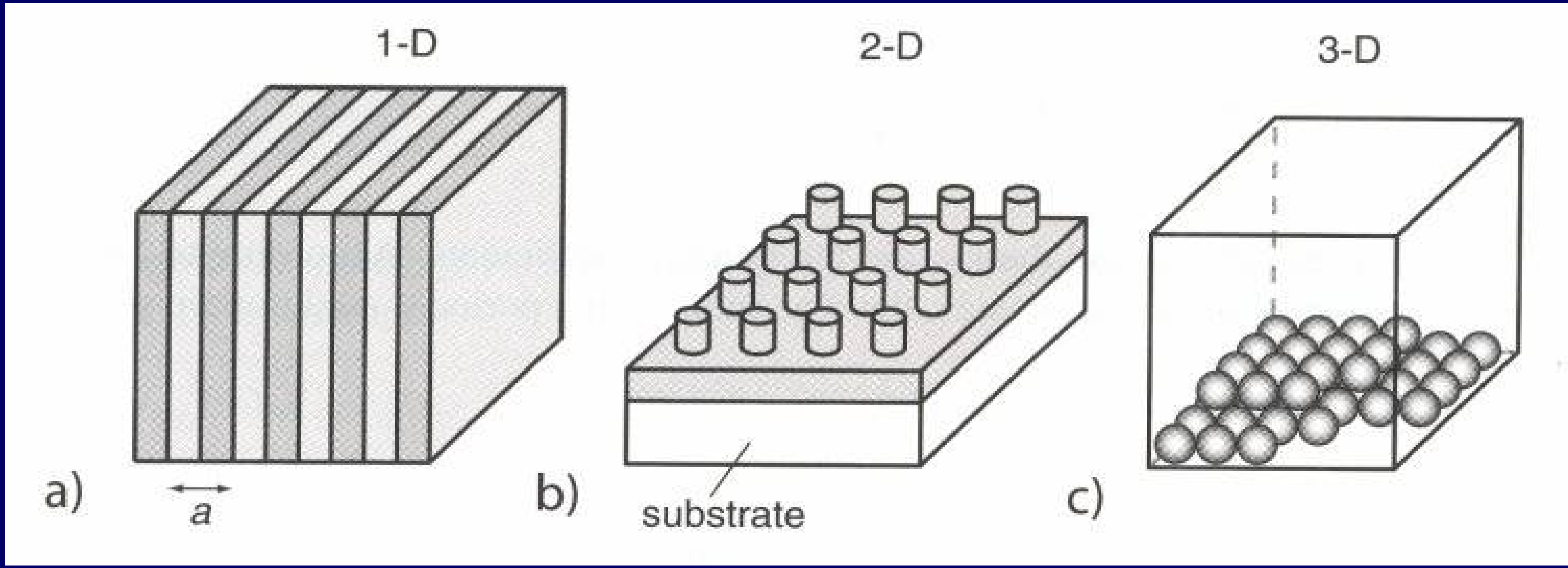
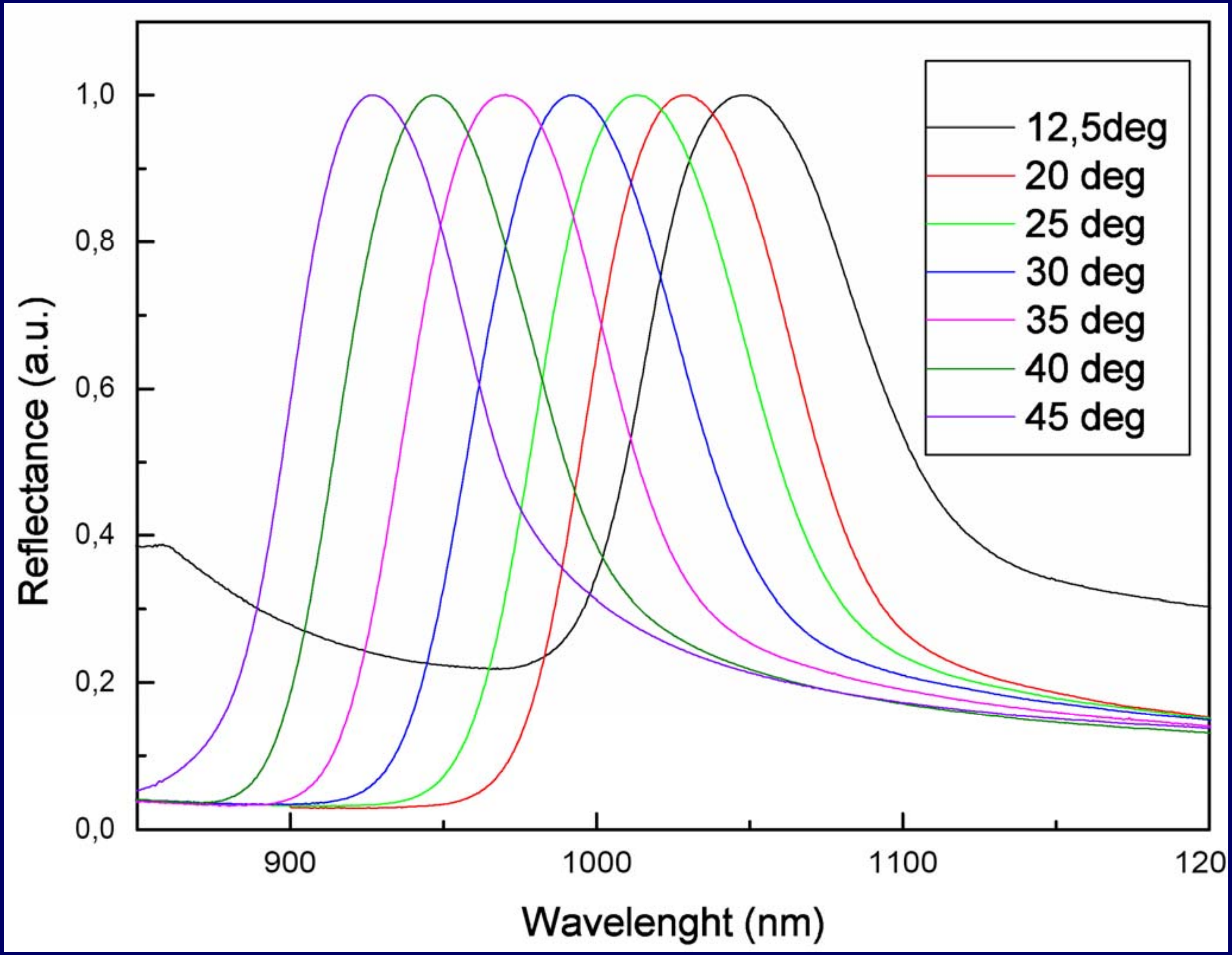
PCs: 1-D, 2-D and 3-D



Schematic of 1-, 2-, and 3-D periodic lattices consisting of two materials of different dielectric constants. The lattice constant is denoted **a**.

Stop bands as a function of incidence angle (dia = 460 nm)



$$\lambda = 2\, d\, (n_{eff}^2 - \sin^2\theta)^{1/2} \iff \sin^2\theta = n_{eff}^2 - \lambda^2/4\, d^2$$

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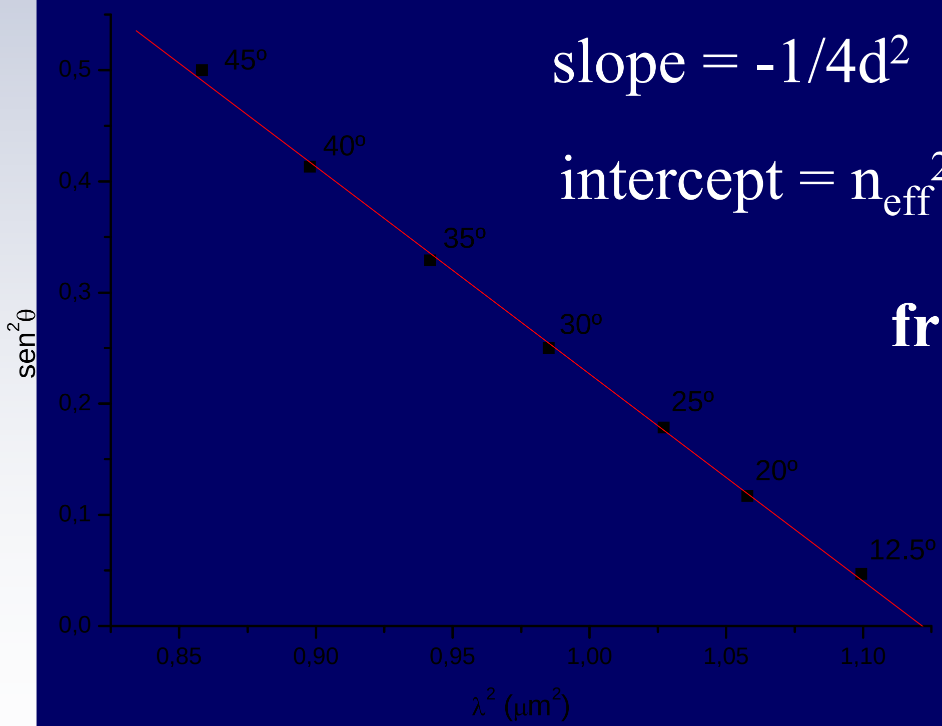
Latex sphere opal (PS, n ~ 1.59 @ 588 nm)
Convective self-assembly

D = 460 nm **n_{eff} = 1.46**



slope = $-1/4d^2$

intercept = n_{eff}^2

$d_{hkl} = a / (h^2 + k^2 + l^2)^{1/2}$

$d_{111} = a / \sqrt{3} = 0.817$ D

from plot: D = 450 nm

n_{eff} = 1.45

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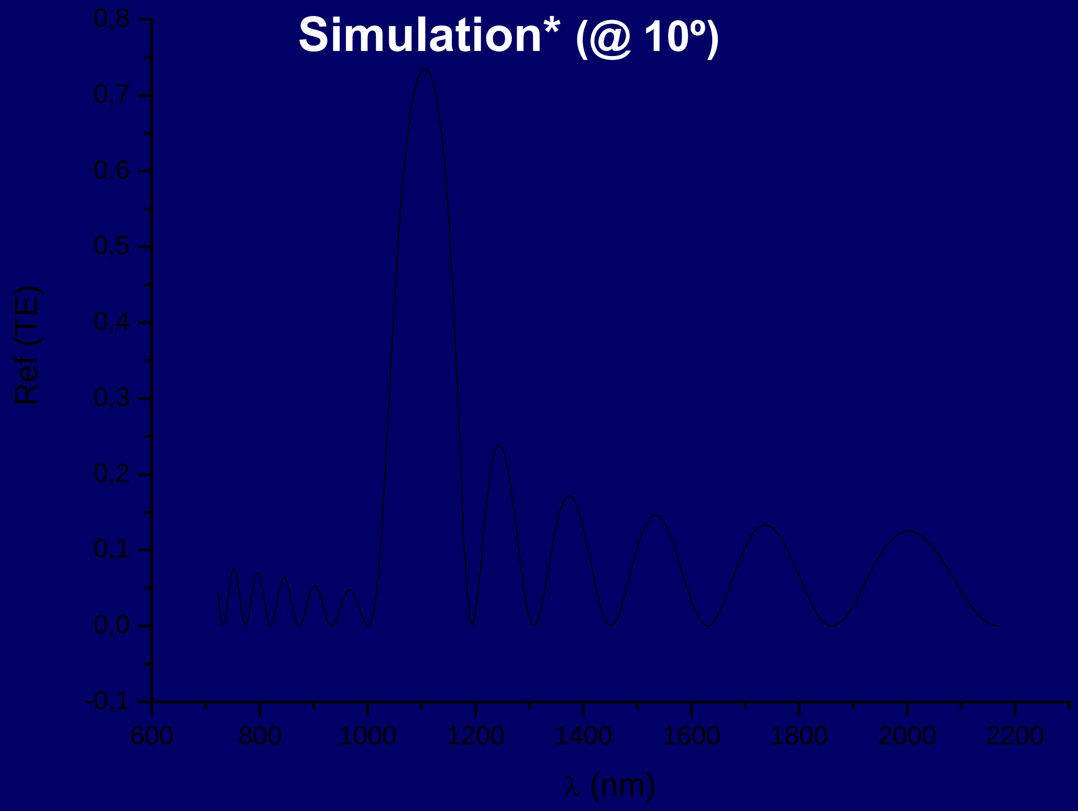
PS opal (dia = 460 nm)

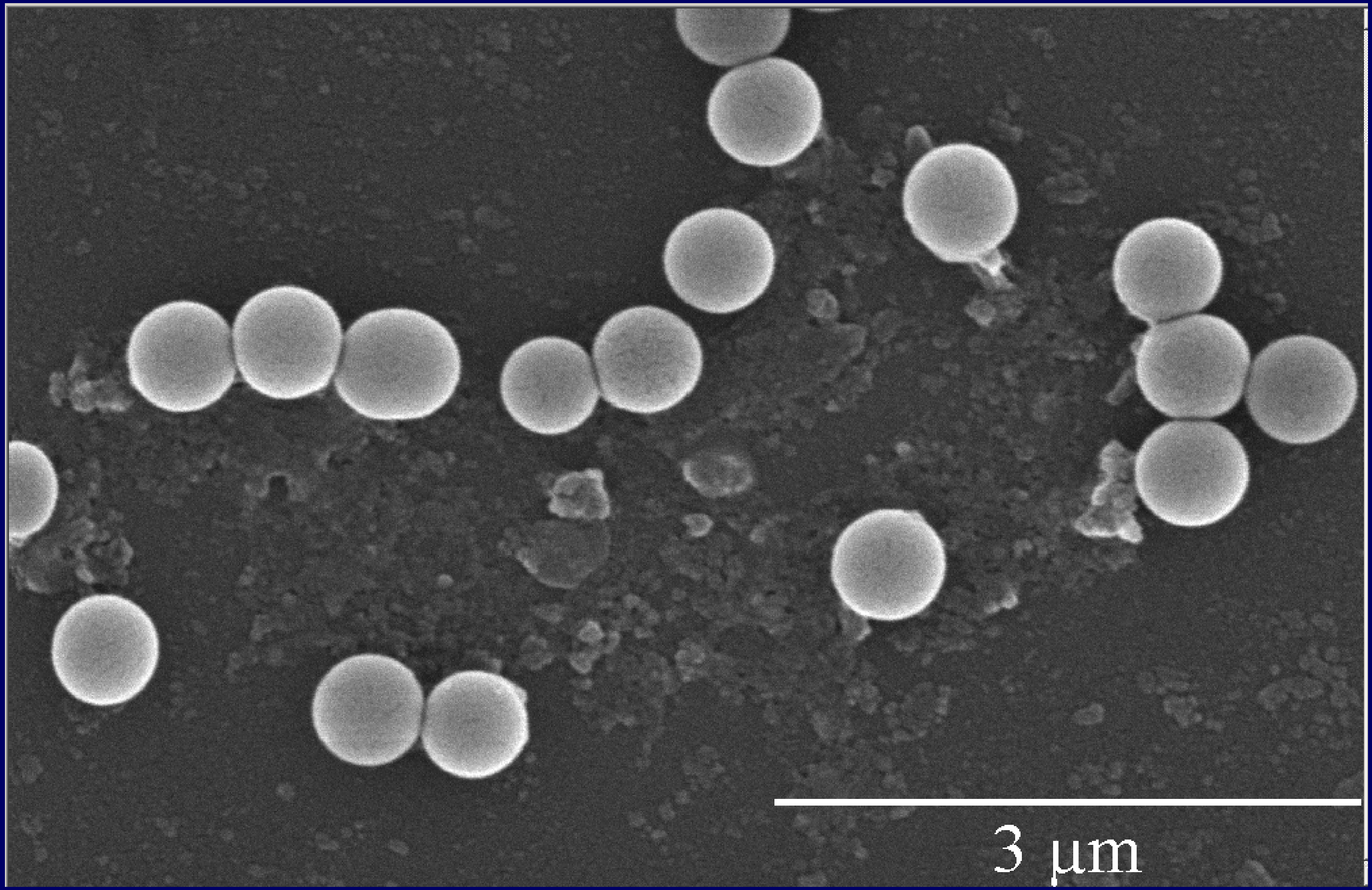
Simulation* (@ 10º)



*** Translight Software code (transfer matrix)**

M. Clara Gonçalves

TEM: SiO_2 Stober spheres, dia ~ 570 nm (15,000 X)



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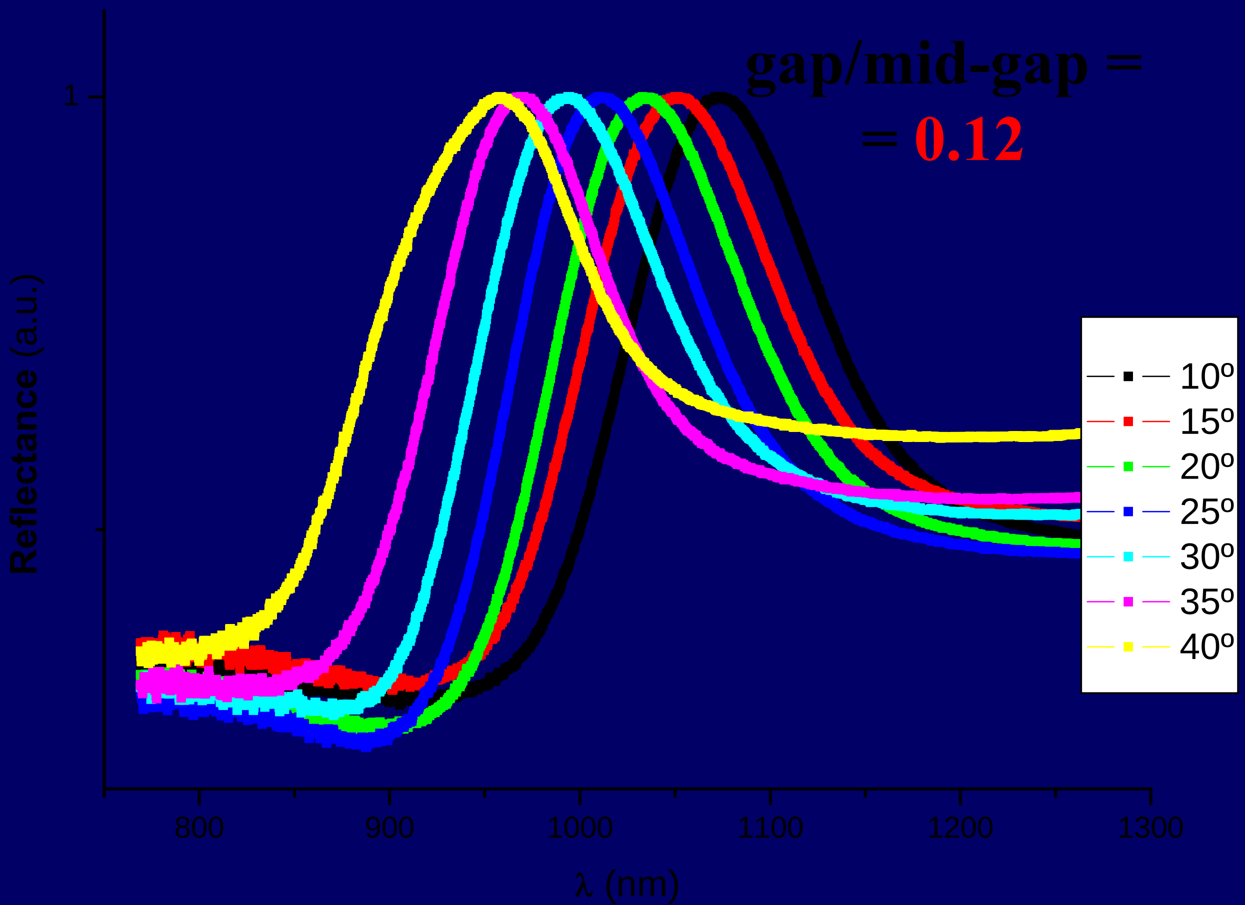
SiO_2 – infiltrated PS opal

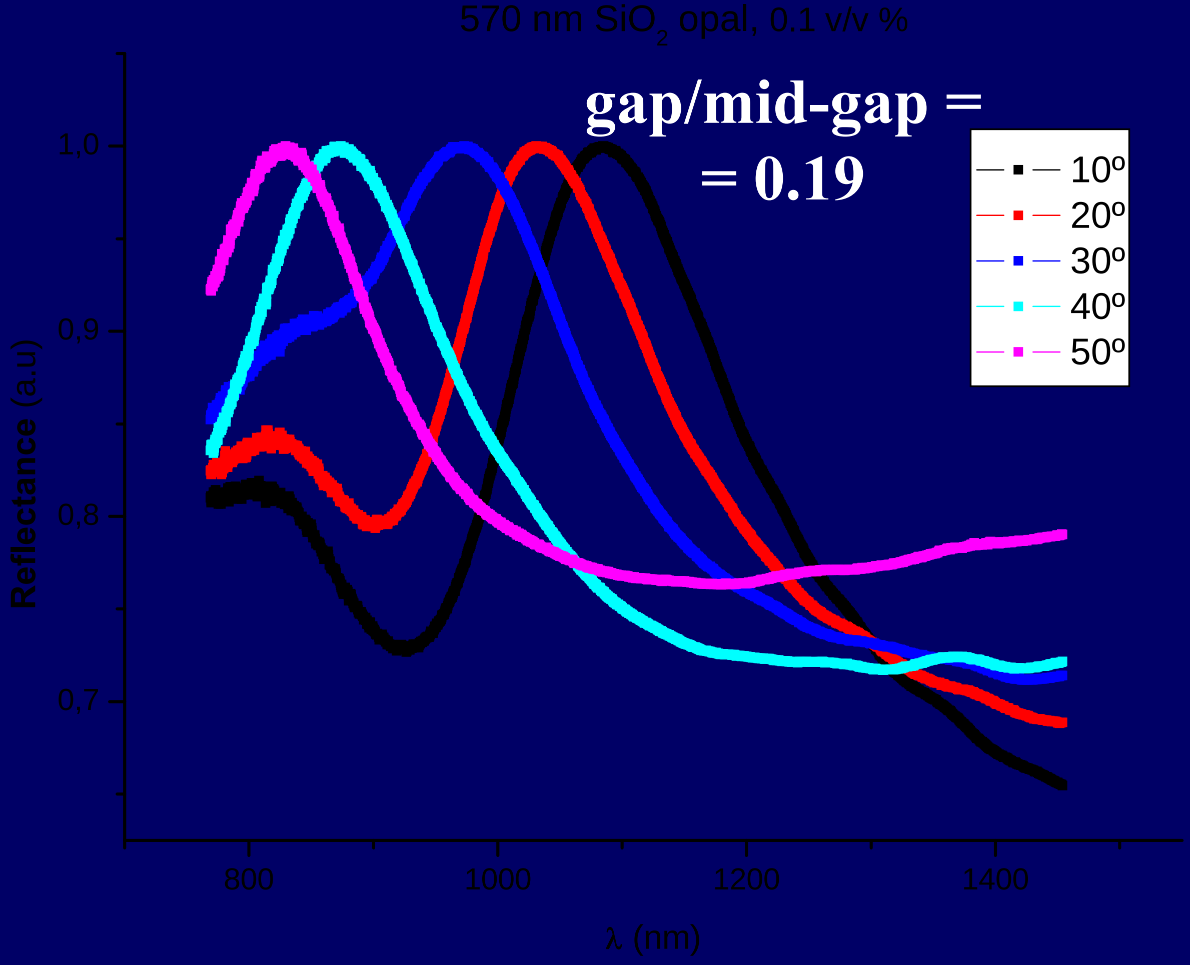
D = 460 nm $n_{eff} = 1.55$



SiO_2 sphere opal (n ~ 1.35 @ 600 ºC)

Self-Assembly

D = 570 nm n_{eff} = 1.27



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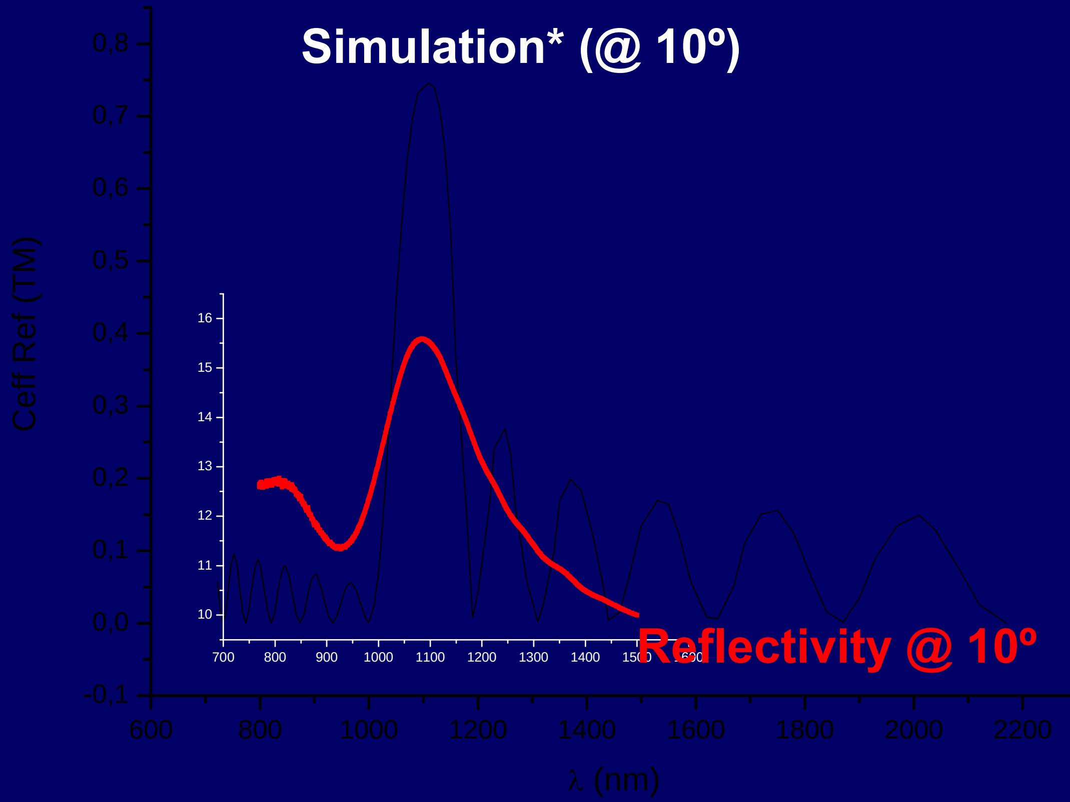
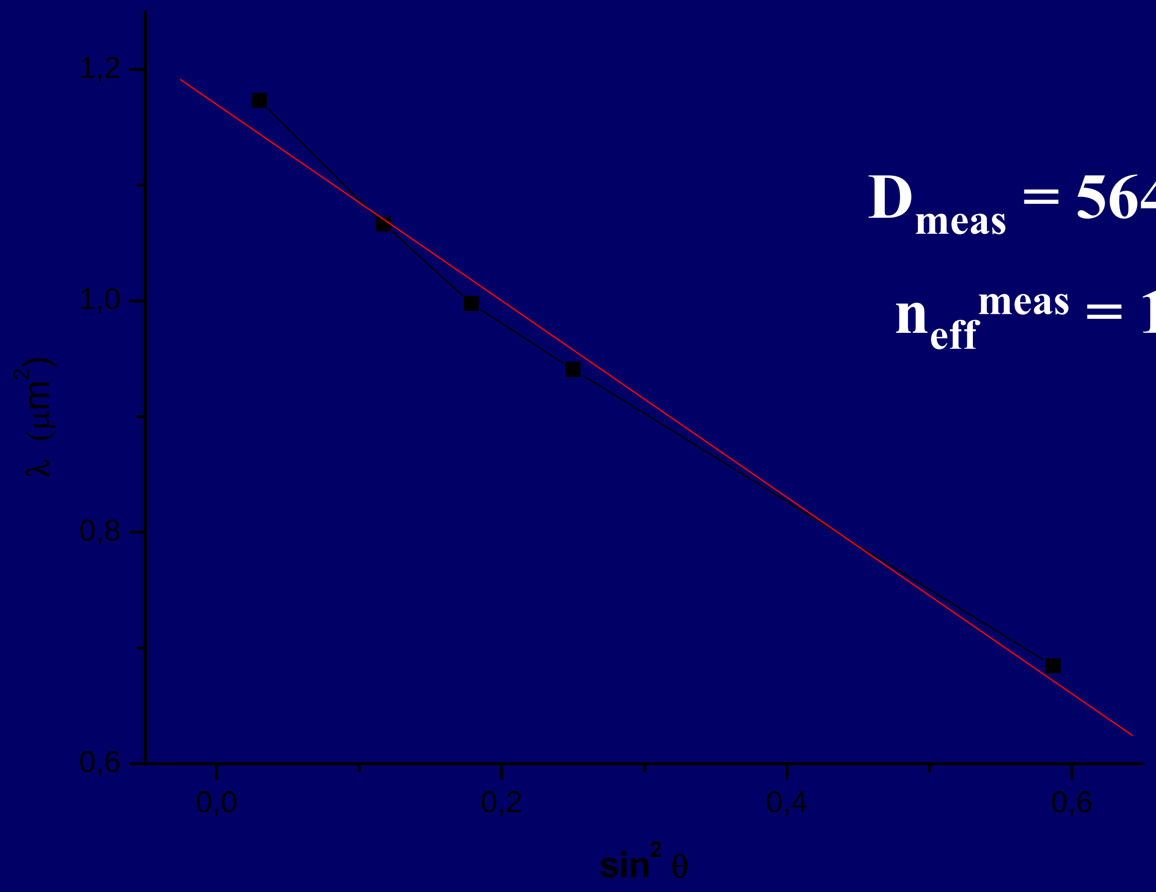
Silica opal (dia = 570 nm)



SiO_2 sphere opal (n ~ 1.35 @ 600 ºC)

D = 570 nm n_{eff} = 1.27

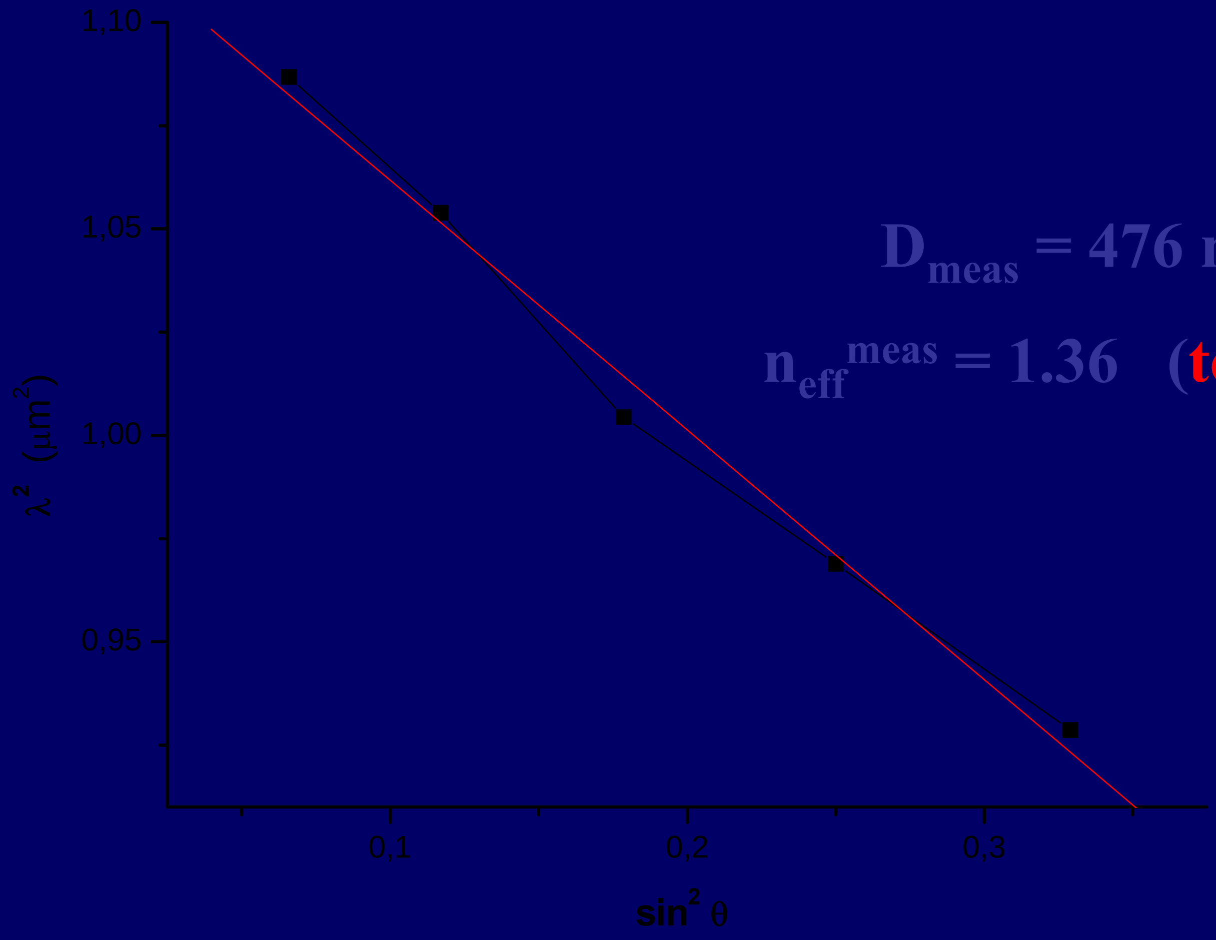


D_{meas} = 564 nm

n_{eff}^{meas} = 1.17

TiO_2 infiltrated PS opal

D = 460 nm $n_{eff} = 1.77$



$D_{meas} = 476$ nm

$n_{eff}^{meas} = 1.36$ (**too low**)

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Comparison between measured and calculated $n_{eff} = \varepsilon_{eff}^{1/2}$

		$\varepsilon_{eff} = \varepsilon_1\left(\frac{2\varepsilon_1+\varepsilon_2+2f(\varepsilon_2-\varepsilon_1)}{2\varepsilon_1+\varepsilon_2-f(\varepsilon_2-\varepsilon_1)}\right)$ Maxwell-Garnett	$(n_{eff}^2-1)/(n_{eff}^2+2) = f(n_2^2-1)/(n_2^2+2) + (1-f)(n_1^2-1)/(n_1^2+2)$ Lorentz-Lorenz	$n_{eff} = (1-f)n_1 + fn_2$ Additive n	$n_{eff}^2 = (1-f)n_1^2 + fn_2^2$ Additive ε
	n_{eff}^{meas}		n_{eff}		
PS opal	1.33	1.19	**1.41**	1.44	1.46
SiO_2 opal	1.17	**1.13**	1.32	1.33	1.35
PS opal + TiO_2	1.36	**1.31**	1.68	1.70	1.71
PS opal + SiO_2	1.51	1.24	**1.55**	**1.55**	**1.56**
TiO_2–inverse opal		1.11	1.20	1.26	1.33
SiO_2–inverse opal		1.05	1.11	1.12	1.13