Institute of Electronic Materials Technology

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Manufacturing of electromagnetic materials

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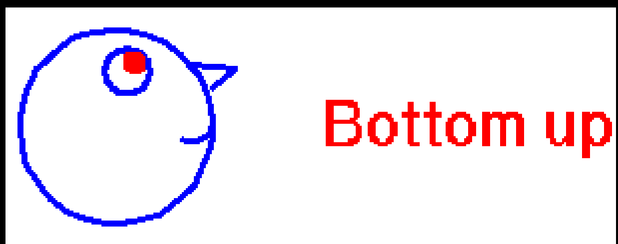
SEVENTH FRAMEWORK PROGRAMME

UNIA EUROPEJSKA
EUROPEJSKI FUNDUSZ
ROZWOJU REGIONALNEGO

FNP
Fundacja na rzecz Nauki Polskiej

INNOWACYJNA
GOSPODARKA
NARODOWA STRATEGIA SPÓJNOŚCI

Bottom-up approach



METAMATERIALS via SELF-ORGANIZATION

Arrays of semiconductor/metallic nanoparticles

Yannopapas and Vitanov, Phys. Rev. B 74, 193304 (**2006**)

Rockstuhl and Scharf, J. Microsc. 229, 281 (Pt 2, **2008**)

Colloidal crystallization/ Photonic crystals

Yannopapas and Vitanov, Phys. Rev. B 74, 193304 (**2006**)

Liquid crystals

Rockstuhl and Scharf, J. Microsc. 229, 281 (Pt 2, **2008**)

Molecular chirality

A. Baev, et al., Optics Express 15, 5730, (**2007**)

Powder processing

C. Pecharromán, et al., Adv. Mater. 13, 1541 (**2001**).

Combined approaches

metallic metamaterial + liquid crystal

Q. Zhao, et al., Appl. Phys. Lett. 90, 011112 (**2007**).

E. Lidorikis, et al., J. Appl. Phys. 101, 054304, (**2007**)

Arrays of semiconductor/metallic nanoparticles

Magnetic metamaterial – strong magnetic activity within and below the optical region *Yannopapas and Vitanov, Phys. Rev. B 74, 193304 (**2006**)*

Semiconductor nanoparticles CuCl and Cu_2O

Magnetism due to strong exciton resonance

In the case of CuCl the Re(μ_{eff})<0 has been calculated to exist close to exciton resonance ω_0 at 386.93 nm wavelength, which is around 19 times larger than the radius of the spheres for which it has been calculated.

Magnetic activity → **not affected by the disorder** ← Result of the interactions of the spheres with the closest neighbours

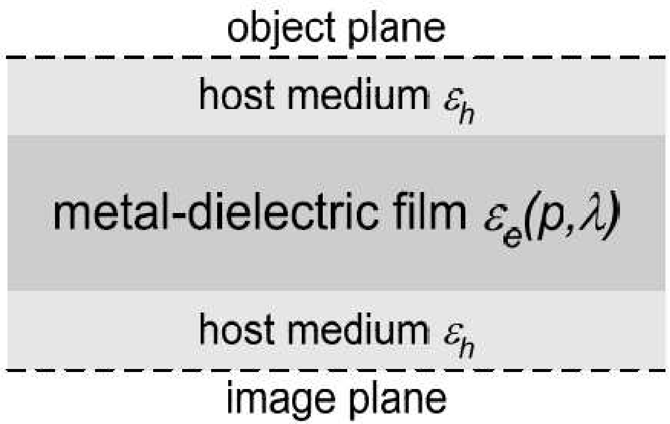
Electric activity → **affected by the disorder** ← The activity arise also from interaction with distant spheres, which is more sensitive to the disorder

The disorder seems to shift the region of Re(ε_{eff})<0 along the wavelength

Page from lectures of V. Shalaev

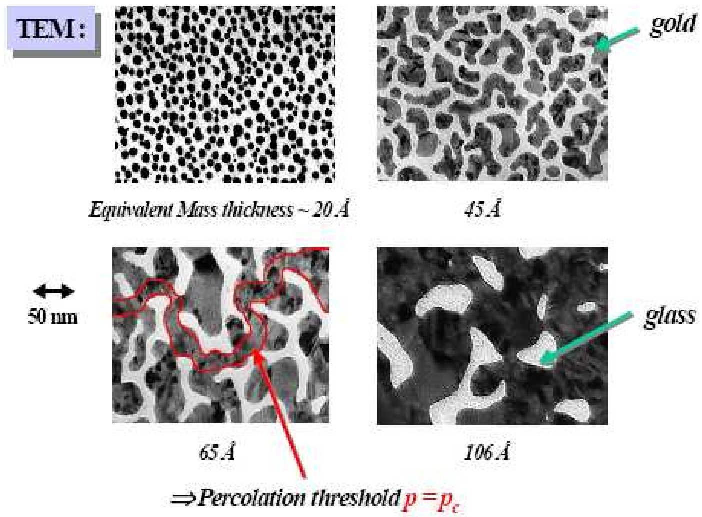
Near-Field Tunable Super-Lens Based on Metal-Dielectric Composites

Here we demonstrate that by employing metal-dielectric composites instead of bulk metals, one can develop a *tunable* NFSL that can operate at any desired visible or near-infrared (NIR) wavelength with the frequency controlled by the metal filling factor of the composite.

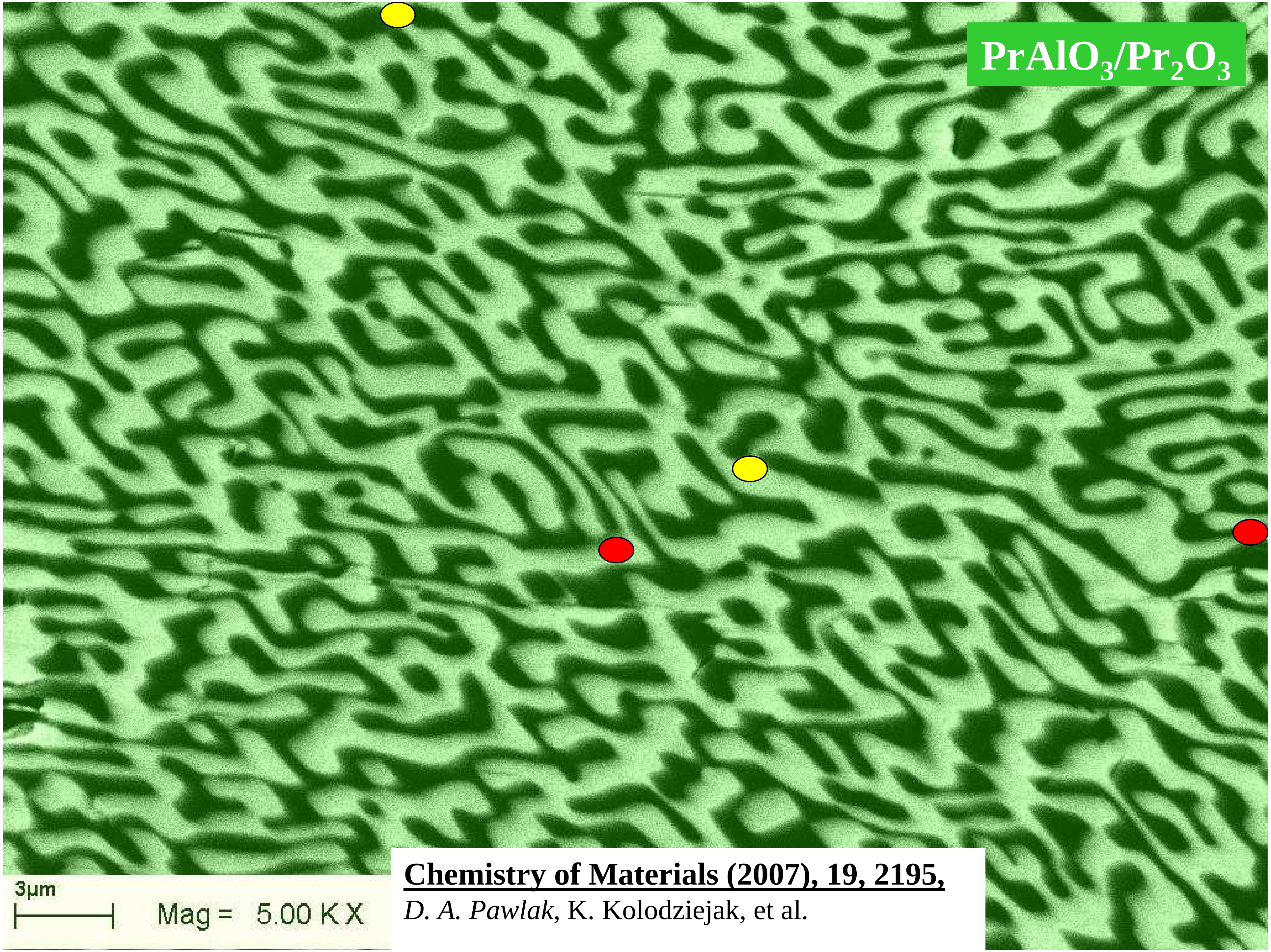


- For a metal-dielectric composite the NFSL can work <u>at any desired wavelength</u>

$$\mathrm{Re}[\varepsilon_e(\varepsilon_m, \varepsilon_d, p, \lambda)] = -\varepsilon_h$$



PRB 72, 193101 (2005)



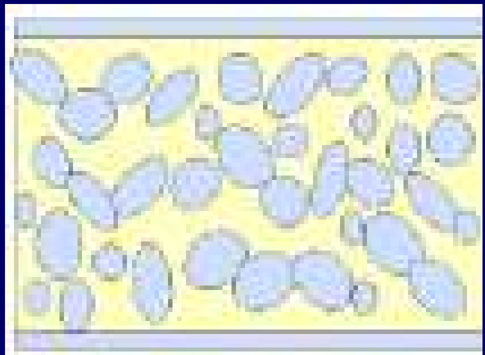
Chemistry of Materials (2007), 19, 2195,

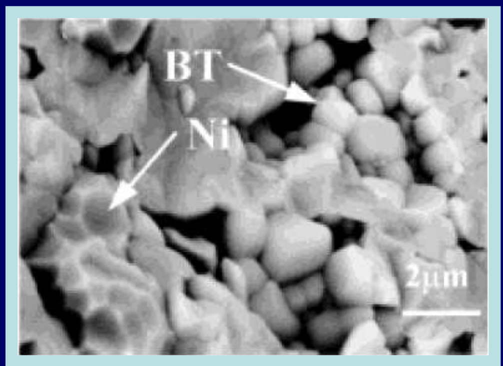
D. A. Pawlak, K. Kolodziejak, et al.

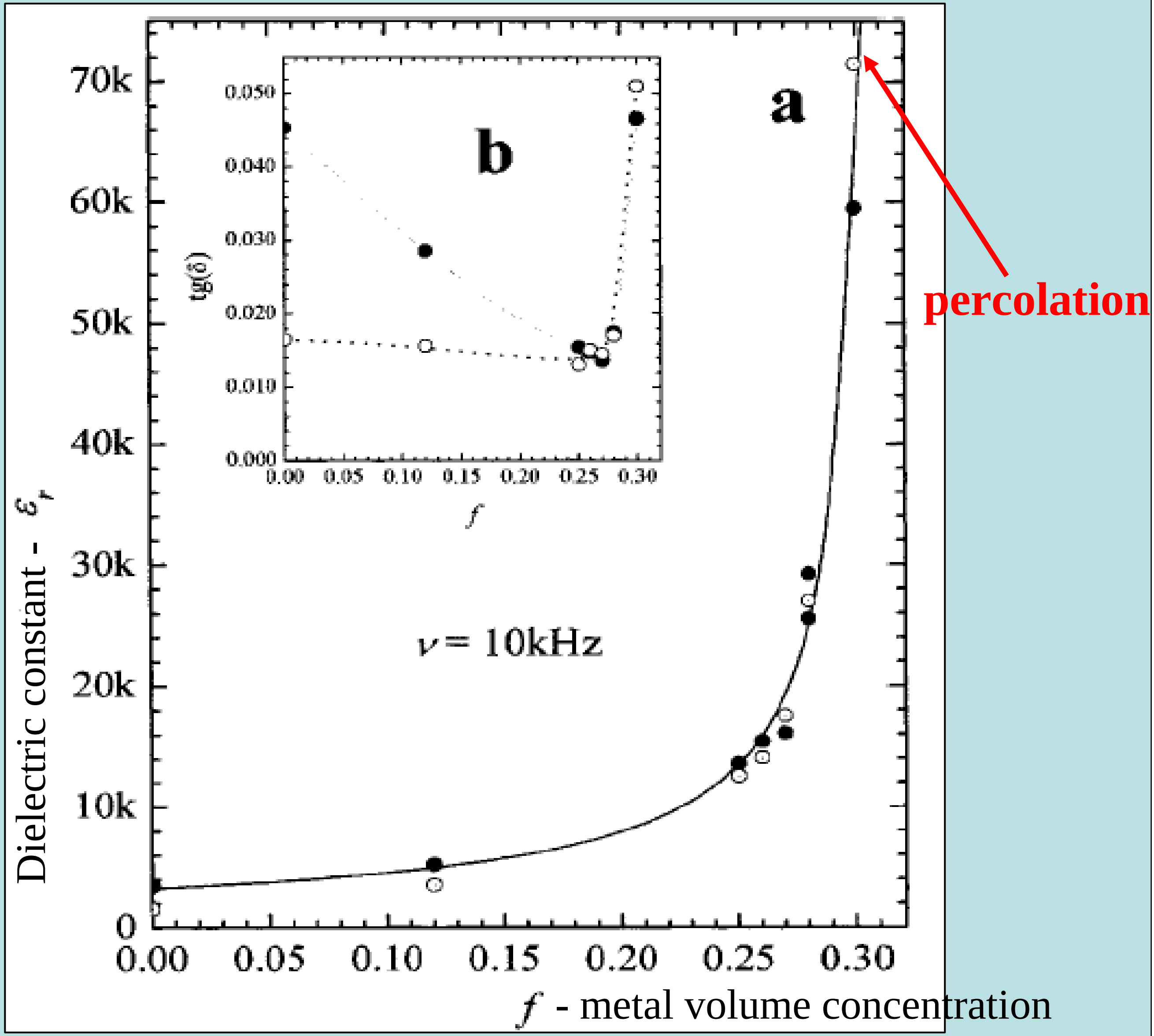
Percolated materials with giant dielectric constant

$\varepsilon_r \approx 80\ 000$

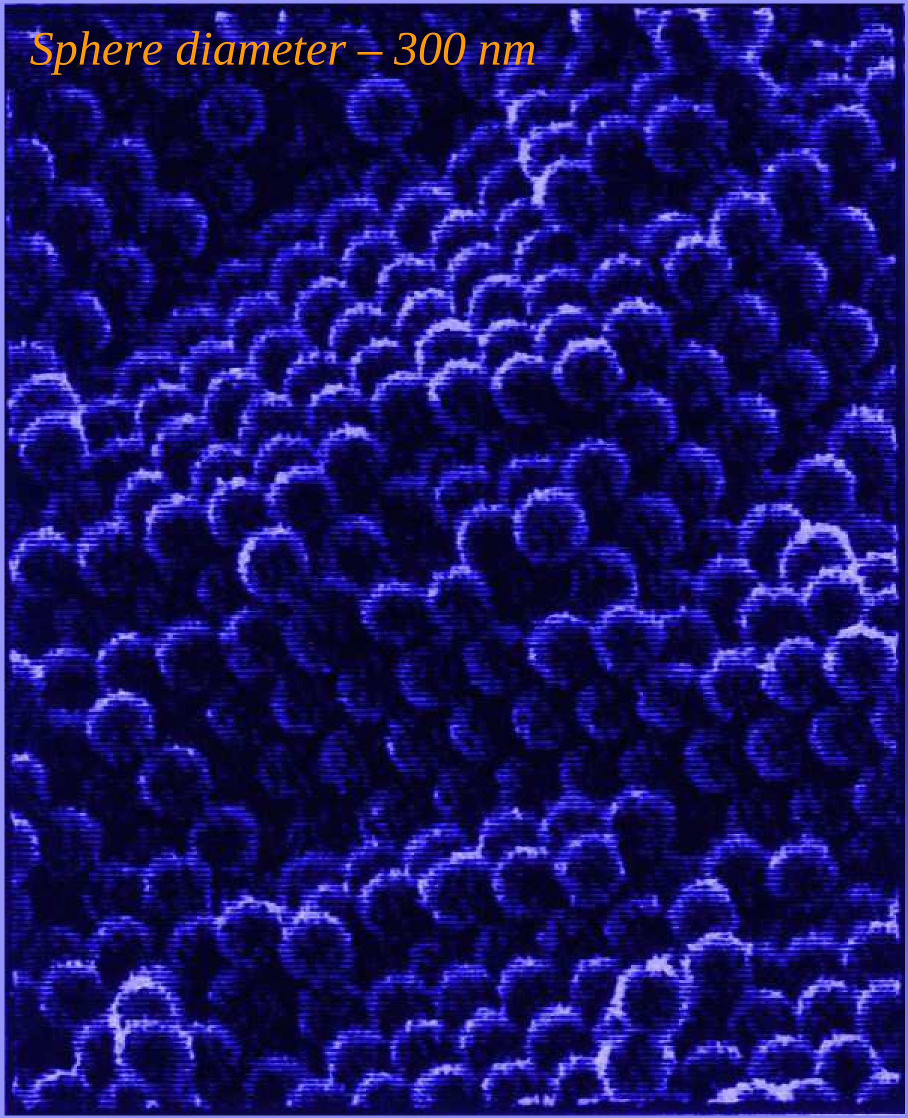
$BaTiO_3$-Ni





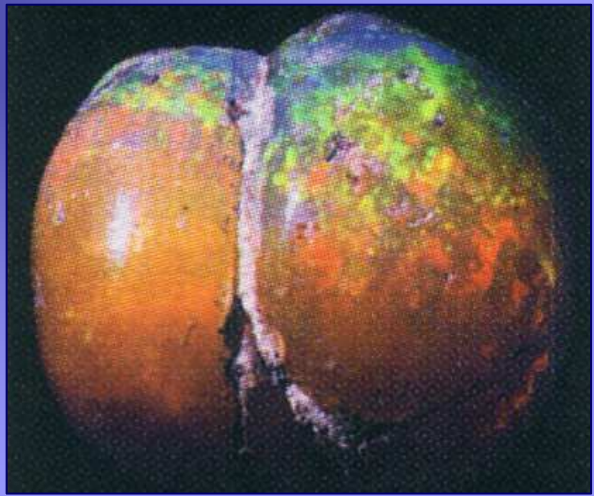


C. Pecharroman, et al. Adv. Mater. 2001, 13, 1541.



OPAL

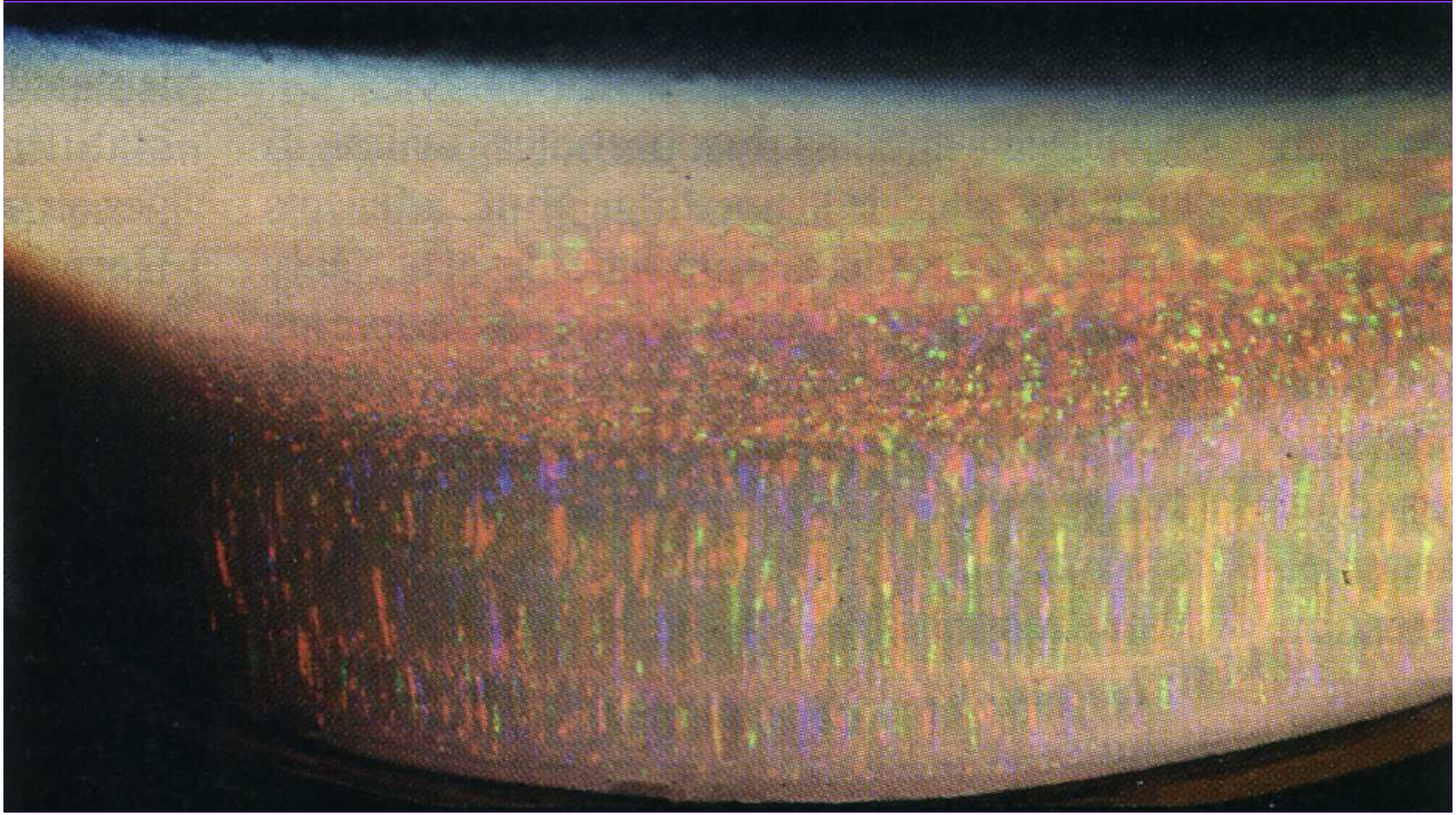
Natural opals consist of a regular three dimensional crystalline array of colloidal silica spheres, several hundred nanometers in size



***A. van Blaaderen, SCIENCE, 282 (1998) 887-888.**

A van Blaaderen, Science 282 (1998) 887

Artificial opal grown from a dispersion of silica spheres



Methods to make high quality colloidal crystals

→ **Electrostatically induced crystallization**

E. A. Kamenetzky et al., Science 1994, 263, 207.
N. A. Clark et al., Nature 1979, 281, 57.
Z. Cheng et al., Nature 1999, 401, 893.

→ **Gravity sedimentation**

P. N. Pusey et al., Nature 1986, 320, 340.
H. Miguez et al., Adv. Mater. 1997, 10, 480.

→ **Electro-hydrodynamic deposition**

M. Trau et al., Science 1996, 272, 706.
R. C. Hayward et al.,Nature 2000, 404, 56.

→ **Colloidal epitaxy**

A. van Blaaderen et al., Nature 1997, 385, 321.

→ **Physical confinement**

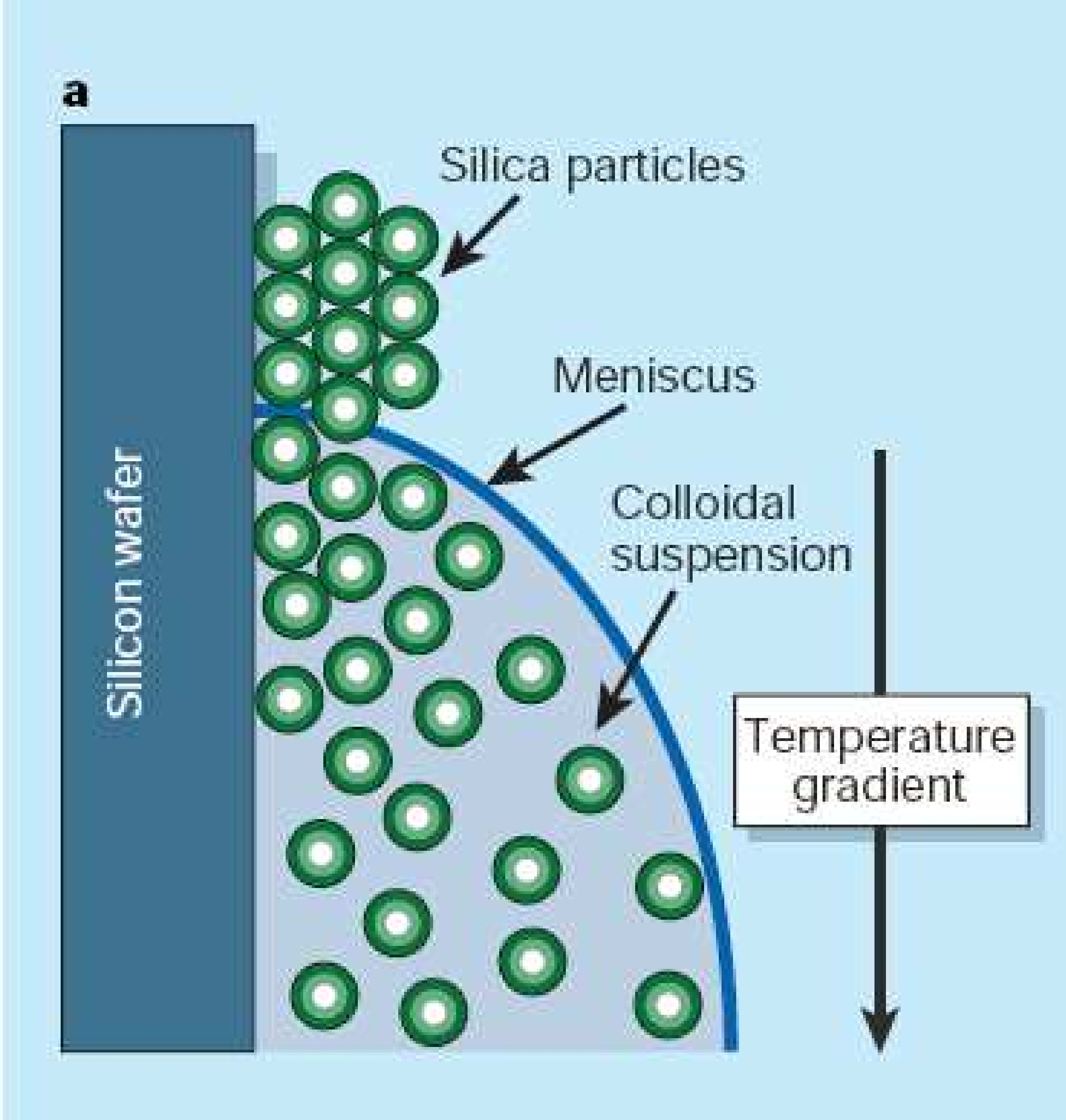
Y. Xia et al., Adv. Mater. 2000, 12, 693.
S. H. Park et al., Adv. Mater. 1998, 10, 1028.

→ **Convective self-assembly**

P. Jiang et al., Chem. Mater. 1999, 11, 2132.
A. S. Dimitrov et al., Langmuir 1994, 10, 432.

Y. A. Vlasov et al., Nature, 414 (2001) 289

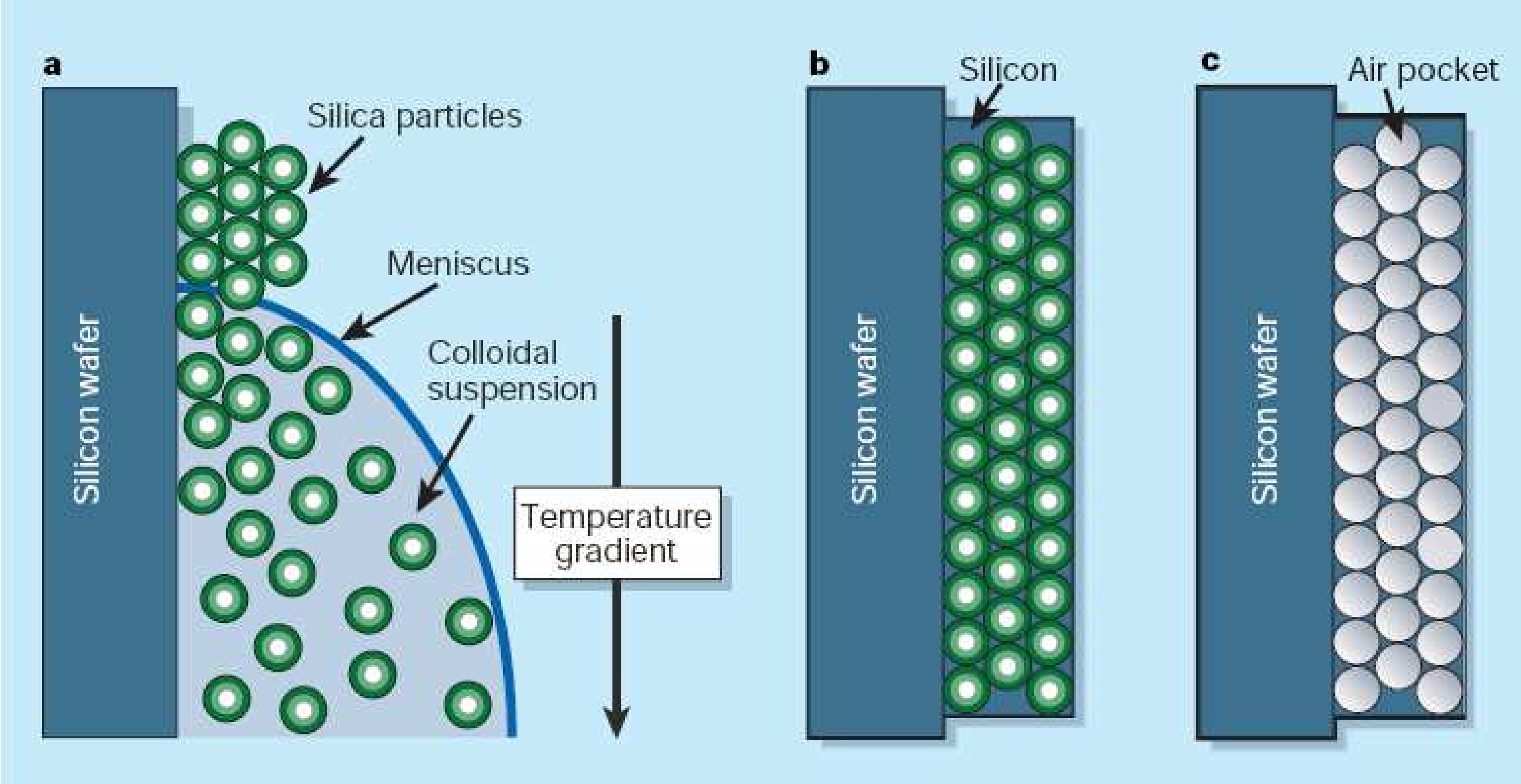
J. D. Joannopoulos et al., Nature, 414 (2001) 257



The convective flow combats sedimentation and provides a continuous flow of particles to the meniscus region.
Strong capillary forces at a meniscus between a substrate and a colloidal sol can induce crystallization of spheres into a 3D array of controllable thickness.

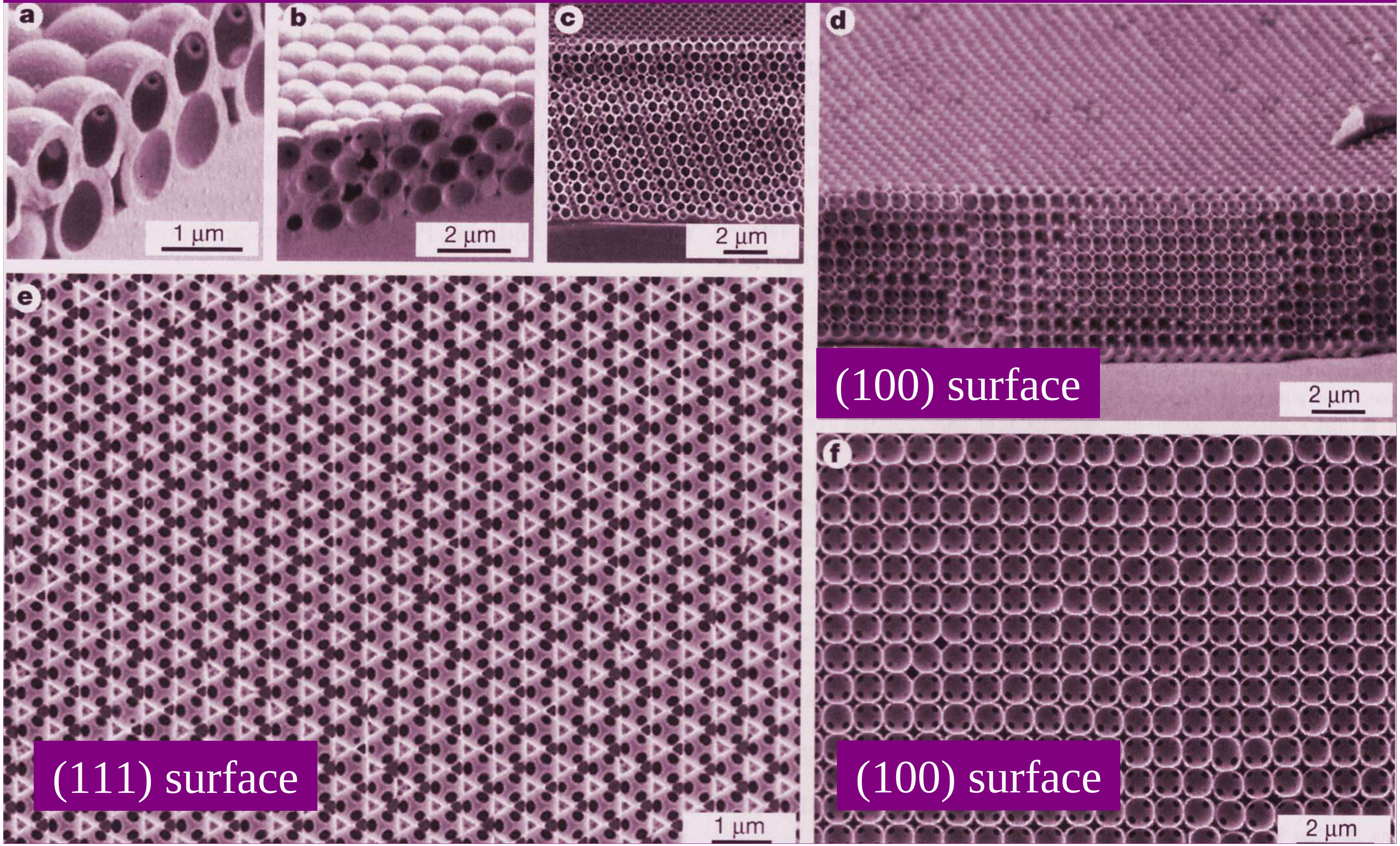
Y. A. Vlasov et al., Nature, 414 (2001) 289

J. D. Joannopoulos et al., Nature, 414 (2001) 257



Y. A. Vlasov et al., Nature, 414 (2001) 289

On-chip natural assembly of silicon photonic bandgap crystals



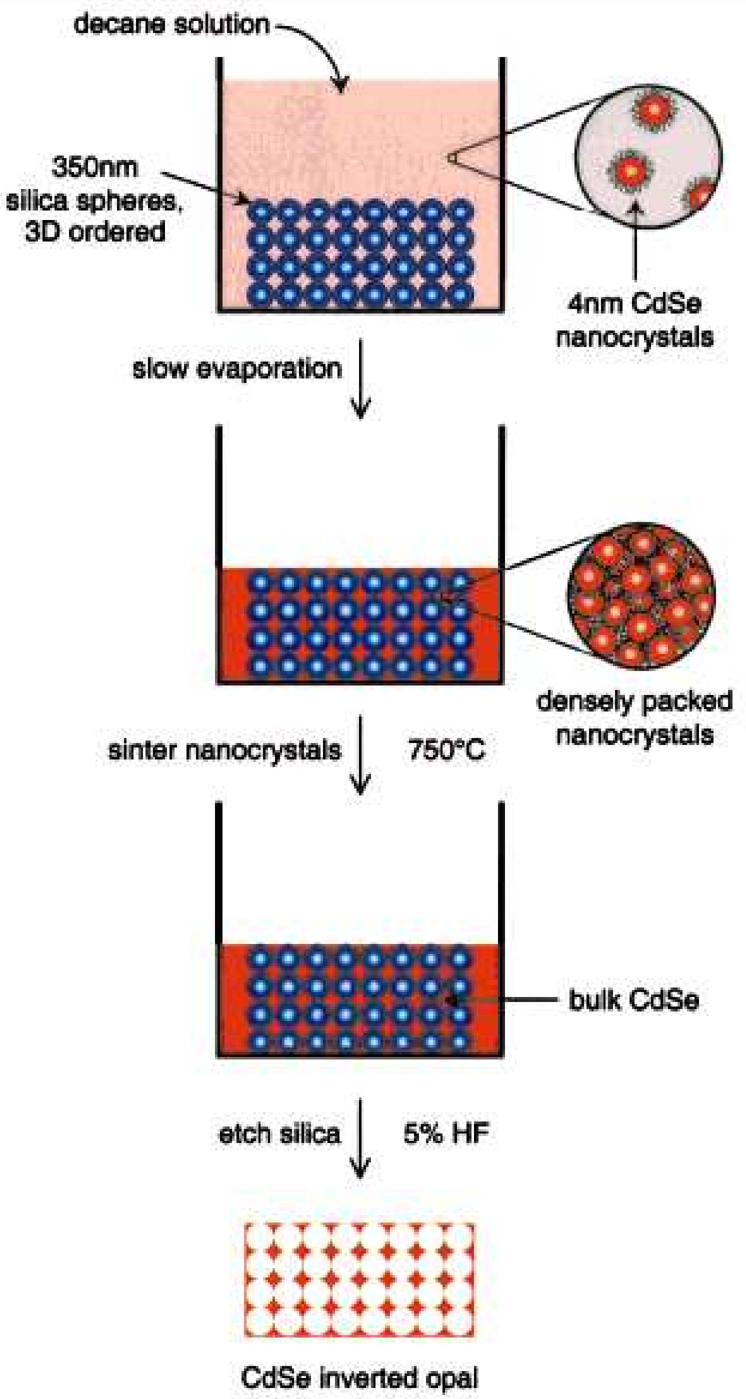
Methods to fill the pores with semiconductor

→ Nanocrystals sintering

→ Chemical electrodeposition

→ Chemical vapor deposition

→ Oxide reduction



NANOCRYSTALS SINTERING

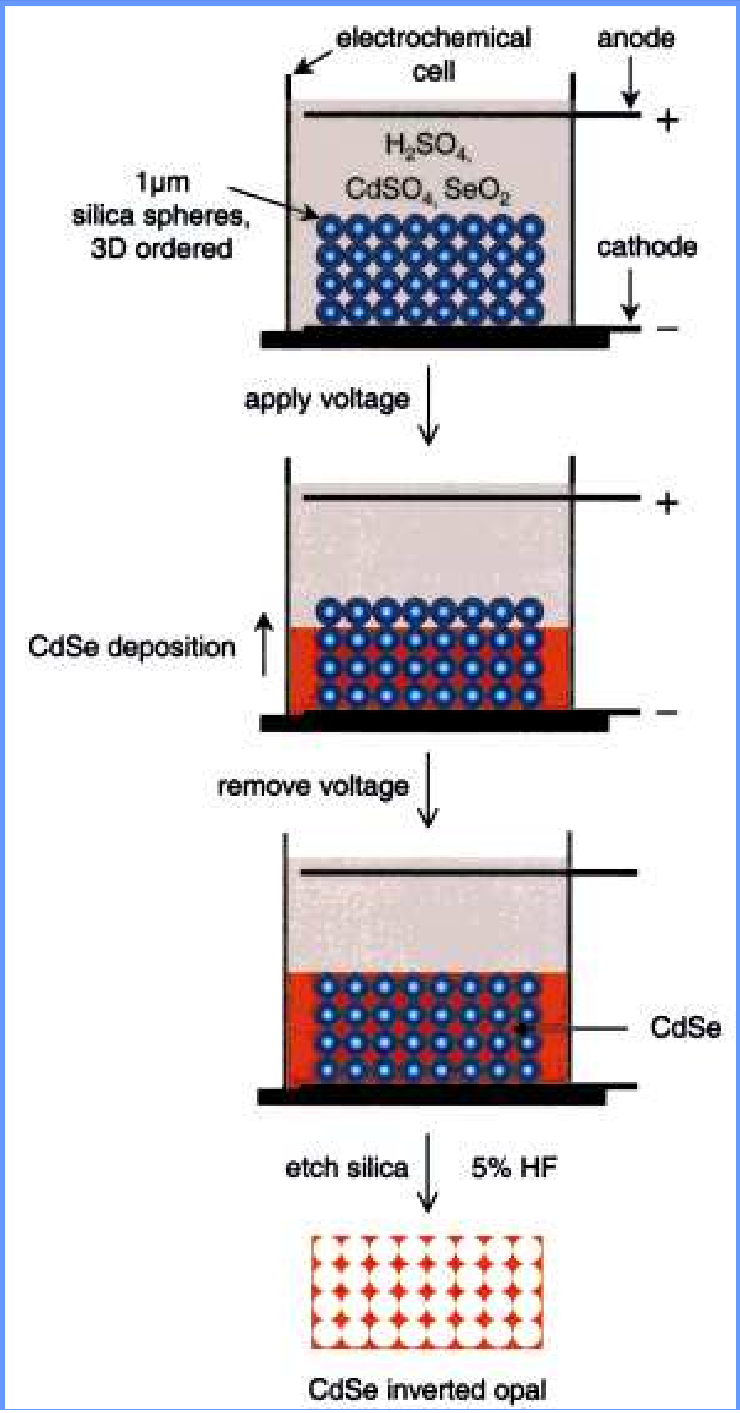
Advantage →

completely general to any of the materials that can be synthesized as colloidal nanoparticles

Potential problem →

difficulties in obtaining infiltration of the high refractive index material greater than 50 % (nanocrystals get condensed during sintering)

Yu. A. Vlasov,et al., Adv. Mater. 1999, 11, 165.
A. N. Goldstein et al., Science 1992, 256, 1425.
O. D. Velev et al, Nature 1999, 401, 548.
O. D. Velev et al., Adv. Mater. 2000, 12, 531.



CHEMICAL ELECTRODEPOSITION

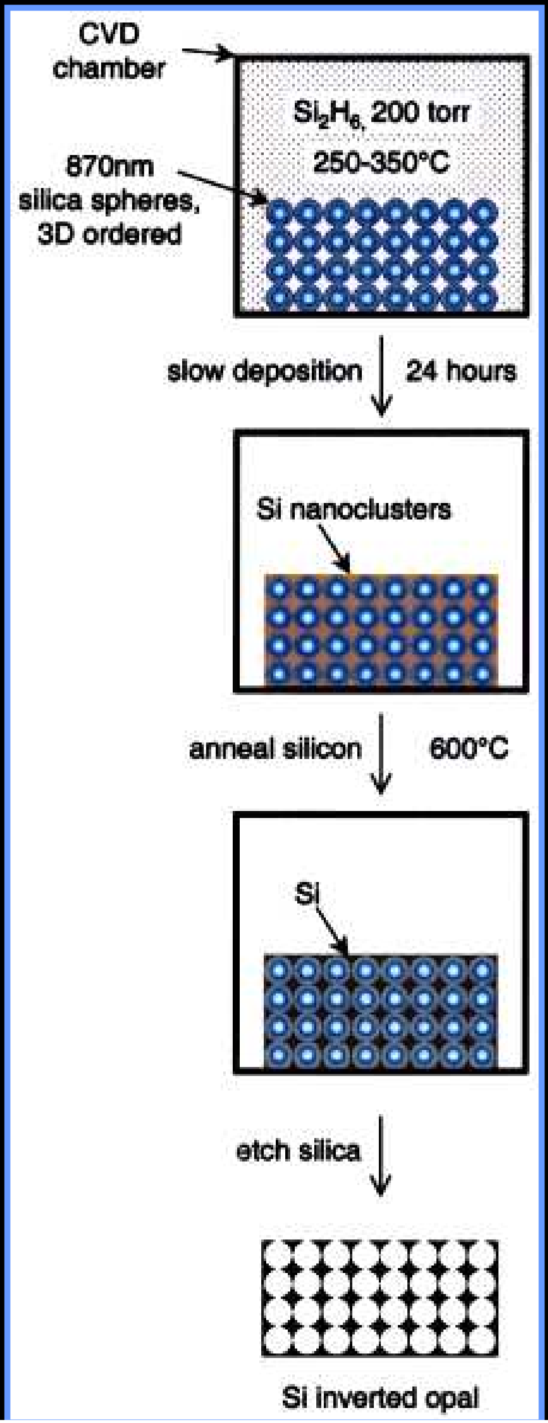
Advantage →

deposition proceeds sequentially from the bottom to the top of the template - so the voids can be completely filled

Potential problem →

maybe not all important materials can be electrodeposited

P. V. Braun, P. Wiltzius, Nature 1999, 402, 603.



CHEMICAL VAPOR DEPOSITION

Advantage → **the resulting infill is extremely homogeneous, and could be 100%**

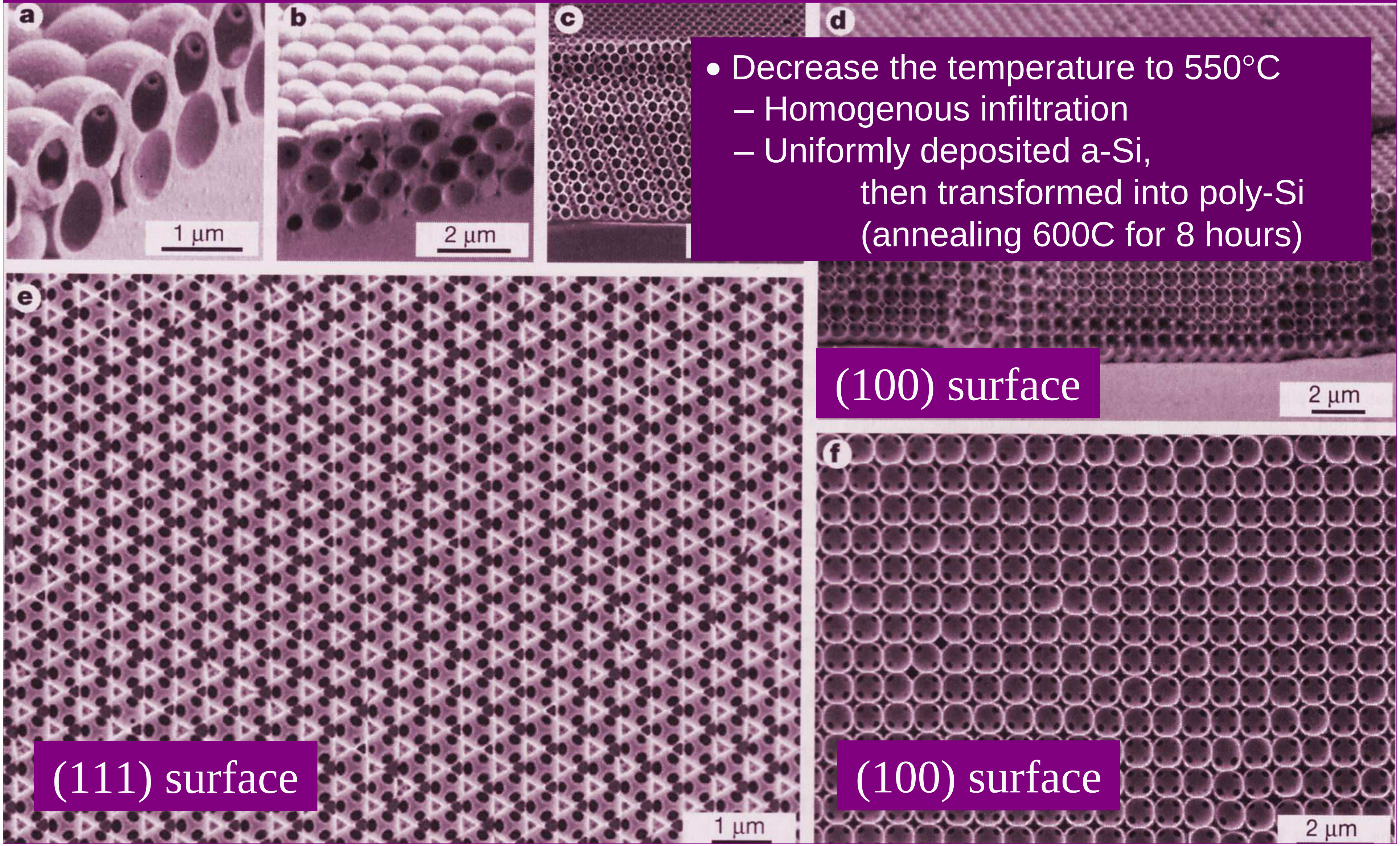
Potential problem → **not sure if it can be extended to wider bandgap semiconductors**

A. Blanco et al., Nature 2000, 405, 437.

Y. A. Vlasov et al., Nature, 414 (2001) 289

LPCVD - Low-Pressure Chemical Vapor Deposition – standard Si deposition technique for the microelectronics industry

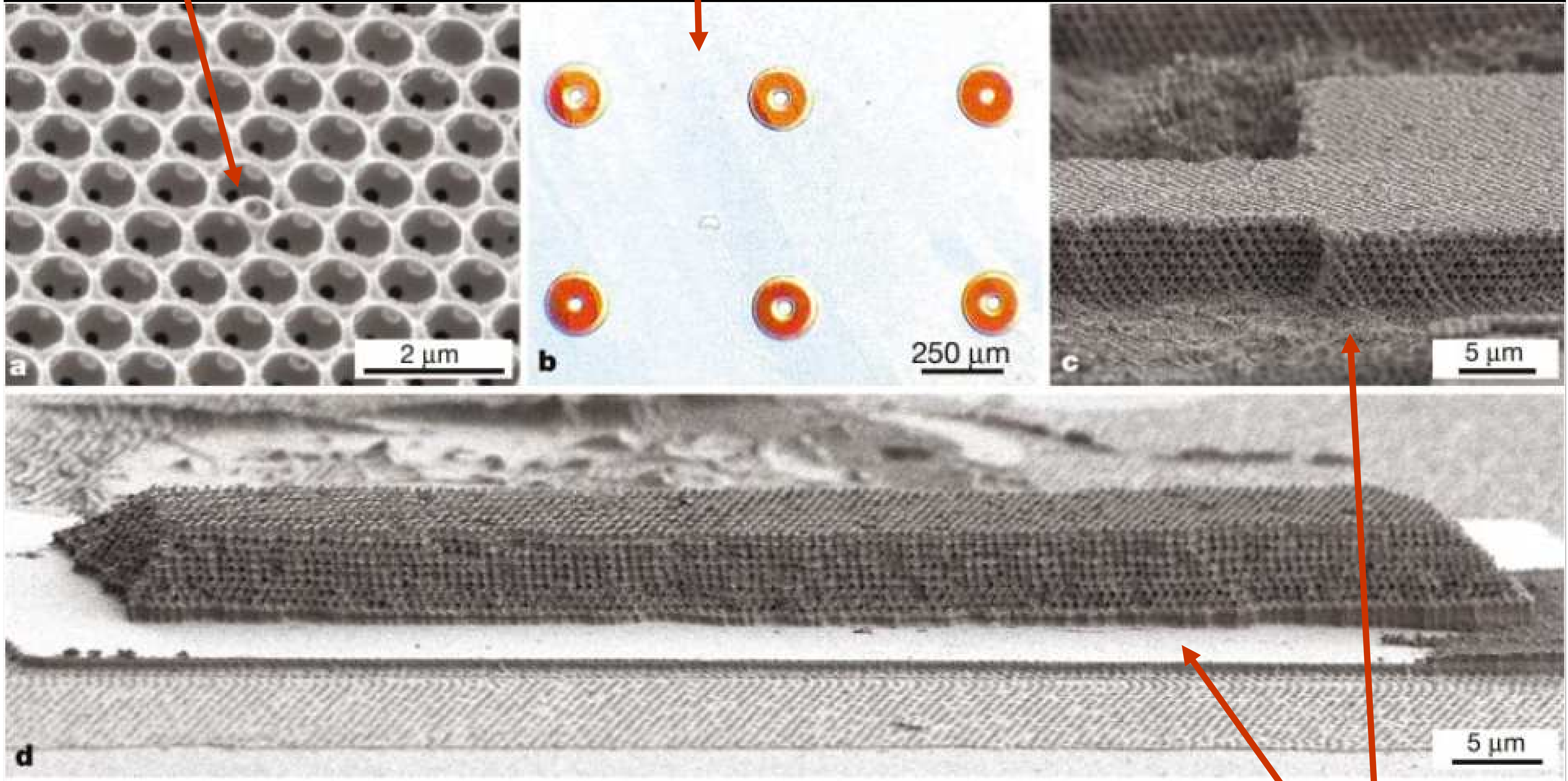
- Decrease the temperature to 550°C
  - Homogenous infiltration
  - Uniformly deposited a-Si, then transformed into poly-Si (annealing 600C for 8 hours)



Patterning using standard photolithography

Introduction of an interstitial defect

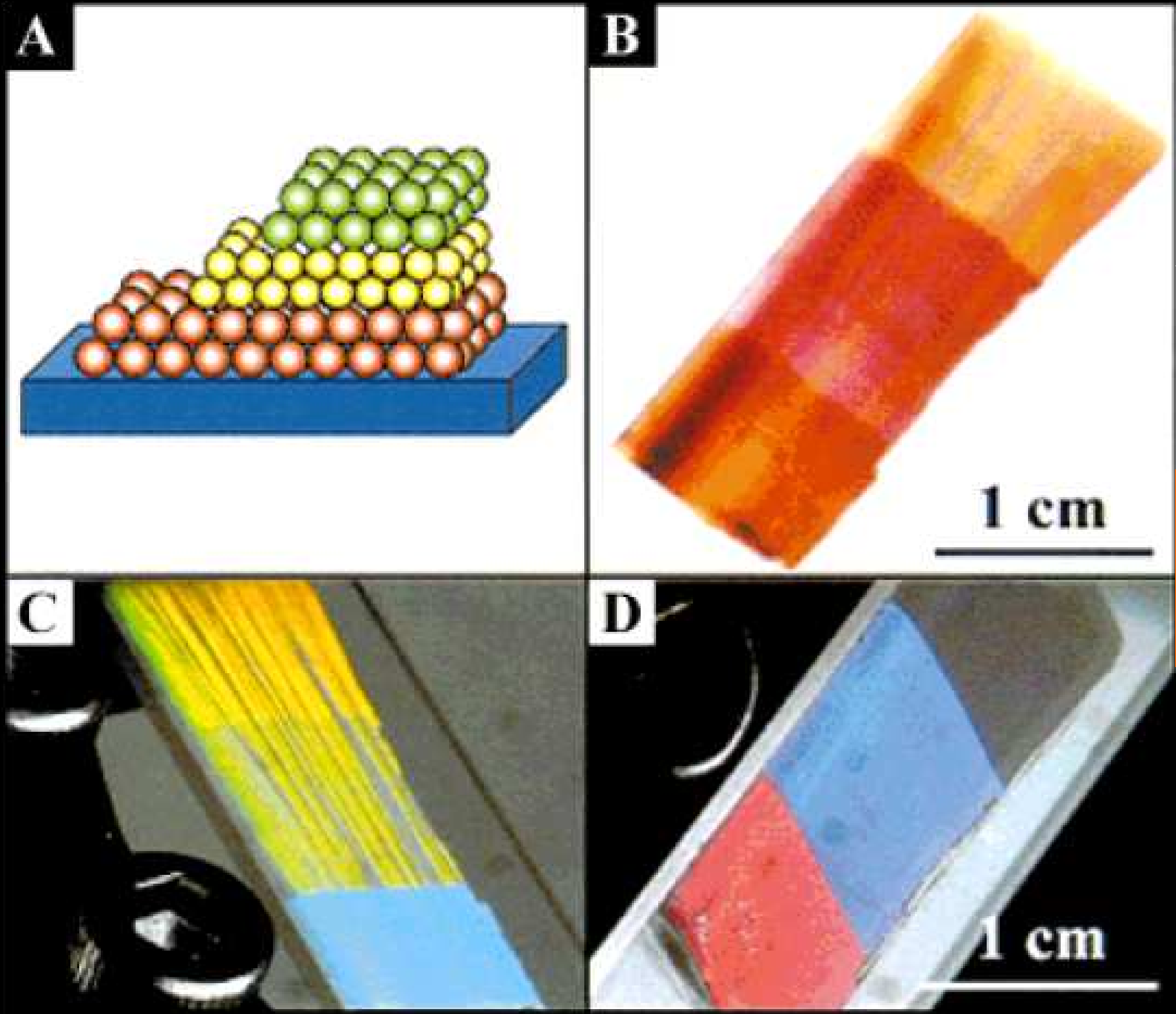
PC rings patterned into large-area crystal via photolitography and etching



Patterned photonic crystals

Y. A. Vlasov et al., Nature, 414 (2001) 289

Multilayer colloidal crystal made by consecutive deposition of colloidal crystals from colloids of three different sizes

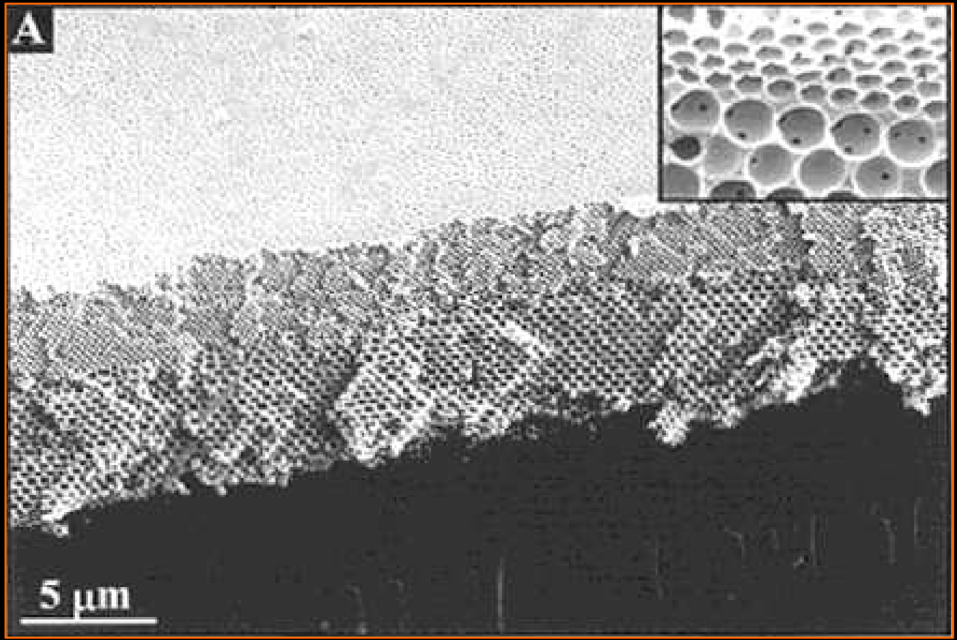


Transmitted colors

430 /253/338 nm
silica superlattice crystal

Reflected colors

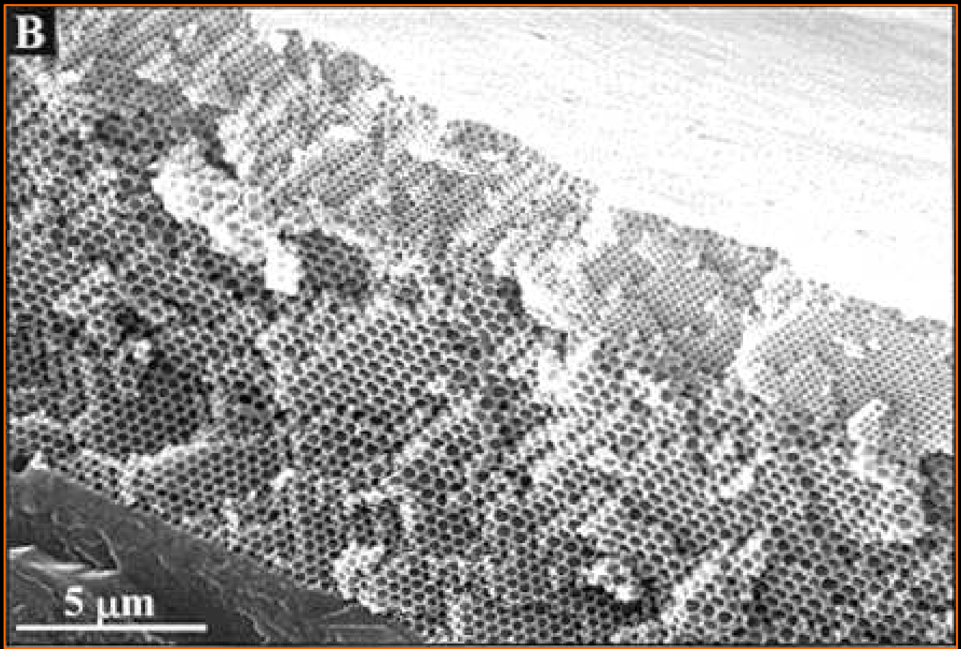
Adv. Mater. 13 (2001) 389, P. Jiang et al.



Macroporous polystyrene

made by templating from silica multilayer crystals

253/430 nm voids



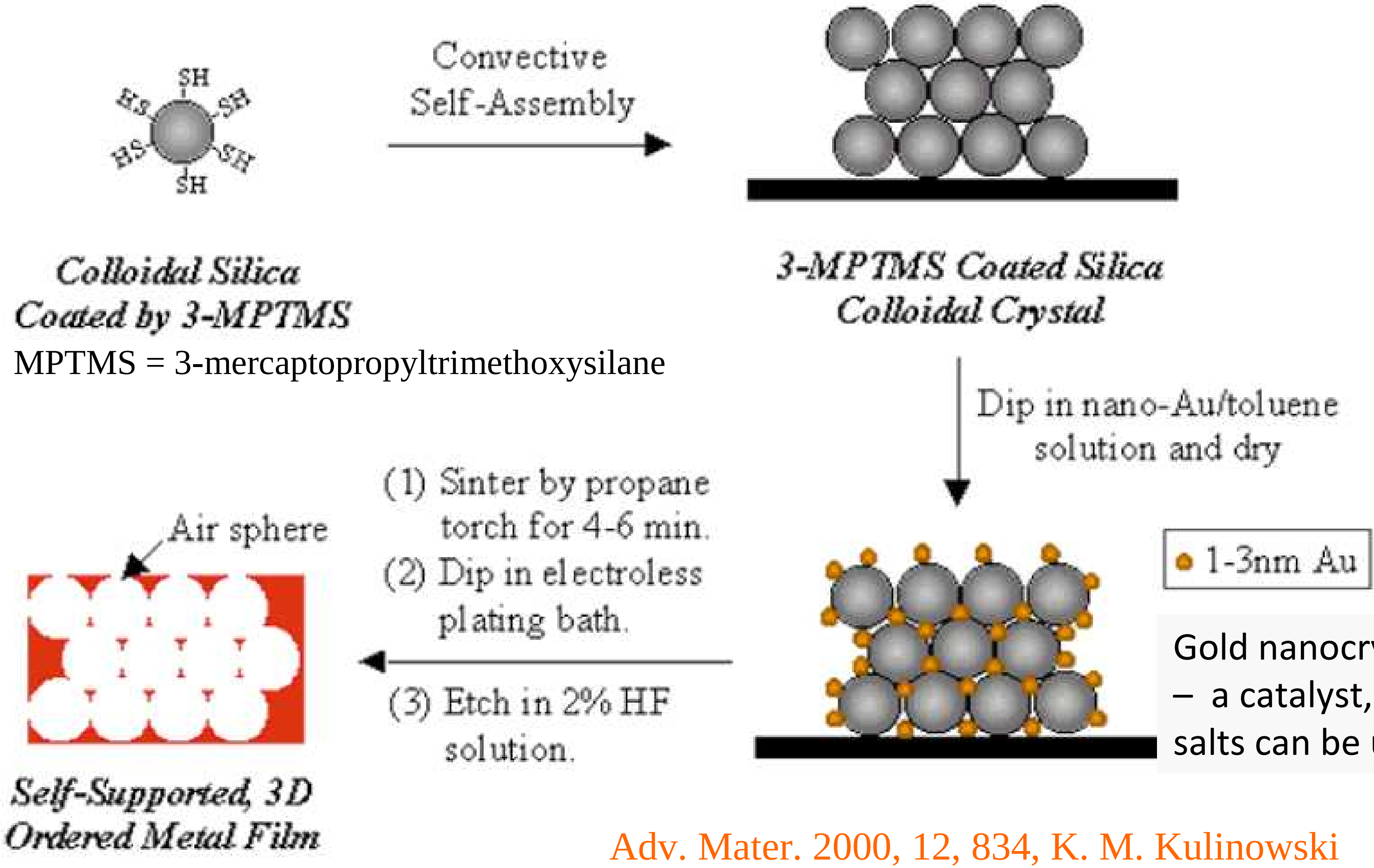
253/ 430 / 338 nm voids

Adv. Mater. 13 (2001) 389, P. Jiang et al.

Porous Metals from Colloidal Templates

Reaction scheme for the formation of macroporous metals by gold nanocrystal-catalyzed electroless deposition

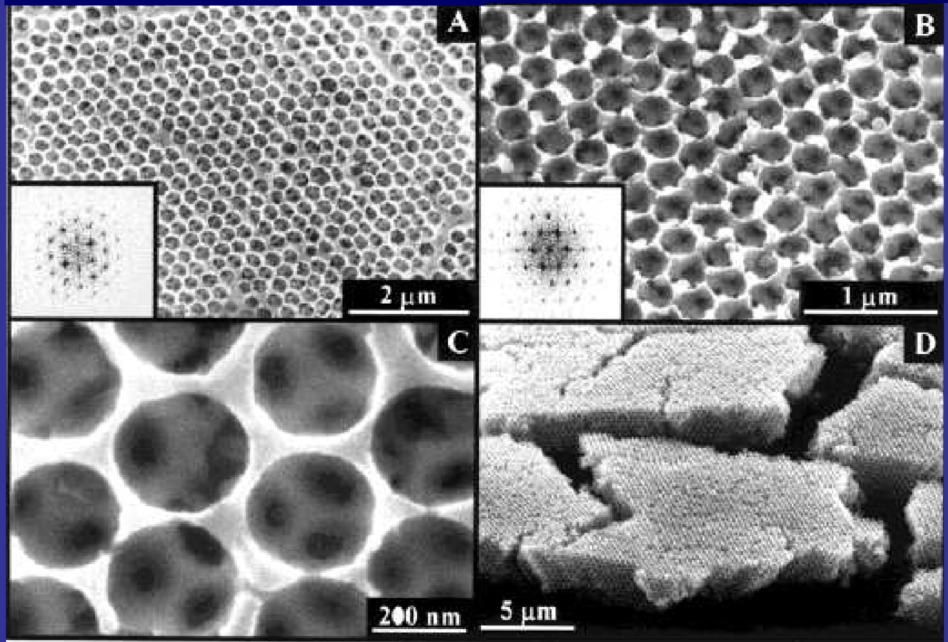
Electroless plating process (industrial process) can produce many types of porous metals, including nickel, cobalt, copper, silver, gold, and platinum



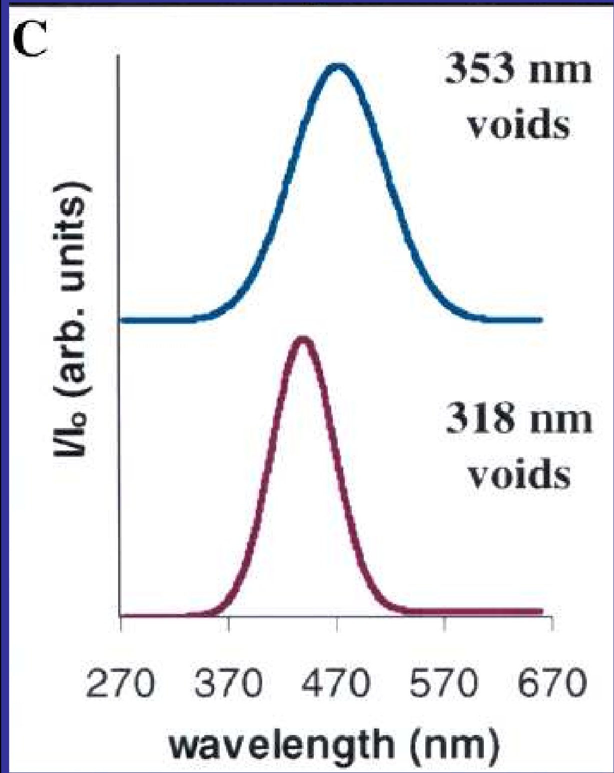
MPTMS = 3-mercaptopropyltrimethoxysilane

Gold nanocrystals – a catalyst, tin salts can be used

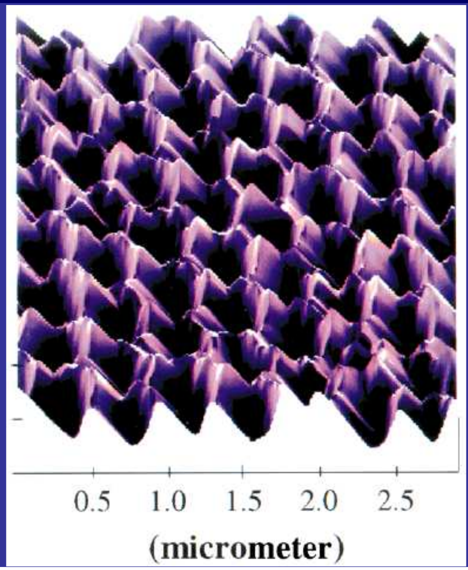
Adv. Mater. 2000, 12, 834, K. M. Kulinowski copper, 325 ± 15 nm voids silver, 353 ± 17 nm voids



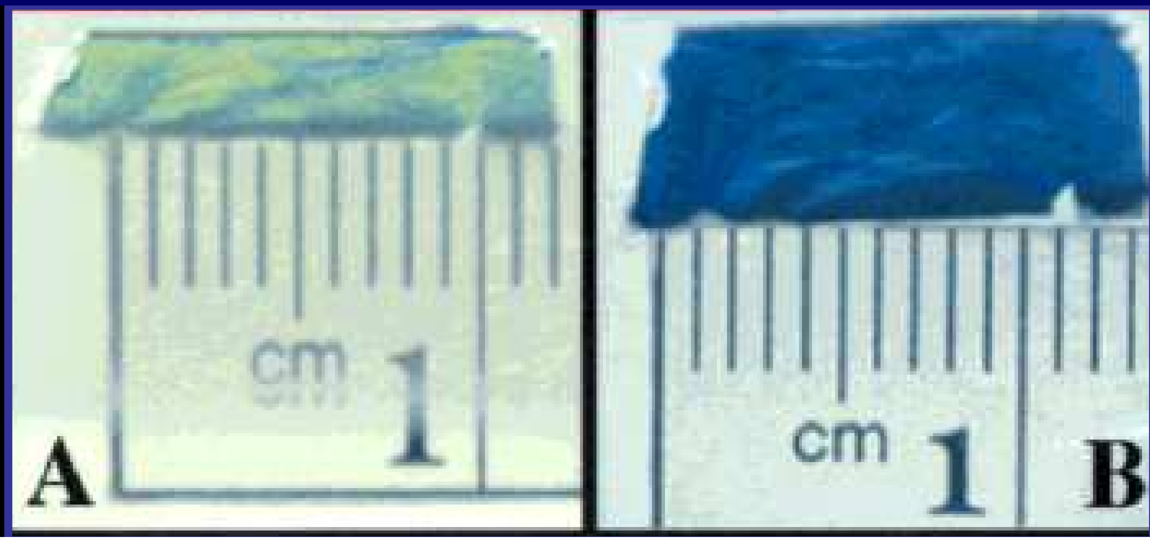
nickel copper, 325 ± 15 nm voids



AFM of macroporous platinum



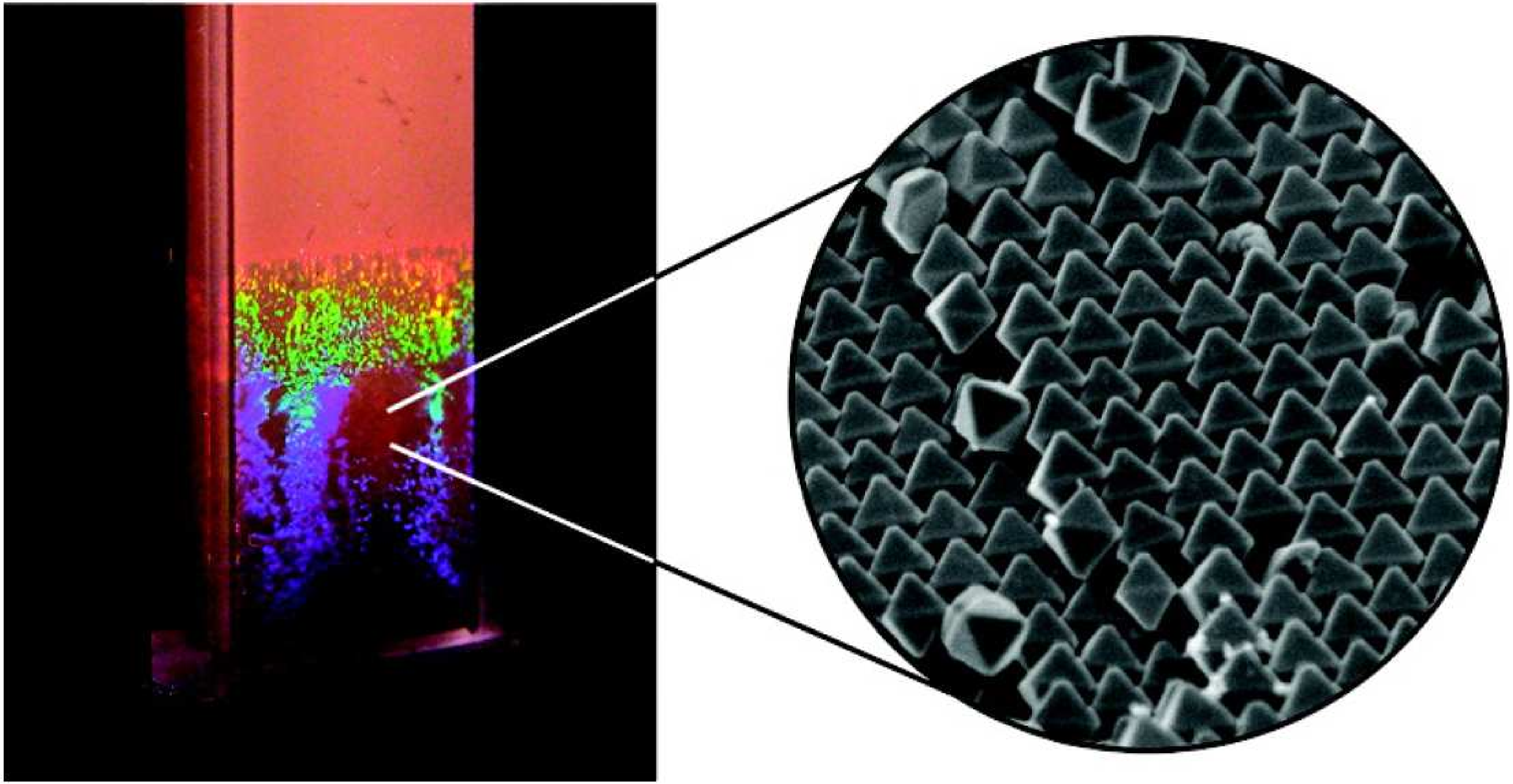
macroporous platinum film (pore size = 353 nm) at two different angles



Self-organized silver nanoparticles for 3D plasmonic crystals

Nanoparticles are passivated with a bulky polymer so crystallization is dominated by repulsive steric interactions that favor close-packed structures.

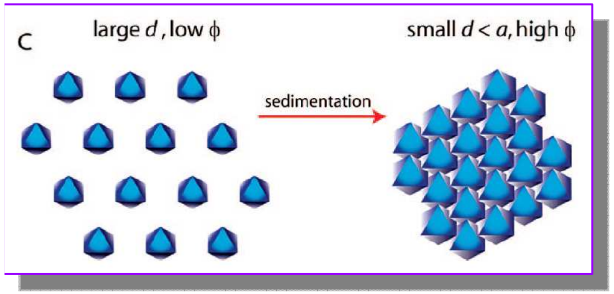
The nanocrystals precipitate from the suspension and settle layer-by-layer before the final stage of drying (~12h for a suspension volume of ~1cm^3).



Nano Lett., 8, (2008), 4033, A. R. Tao et al.

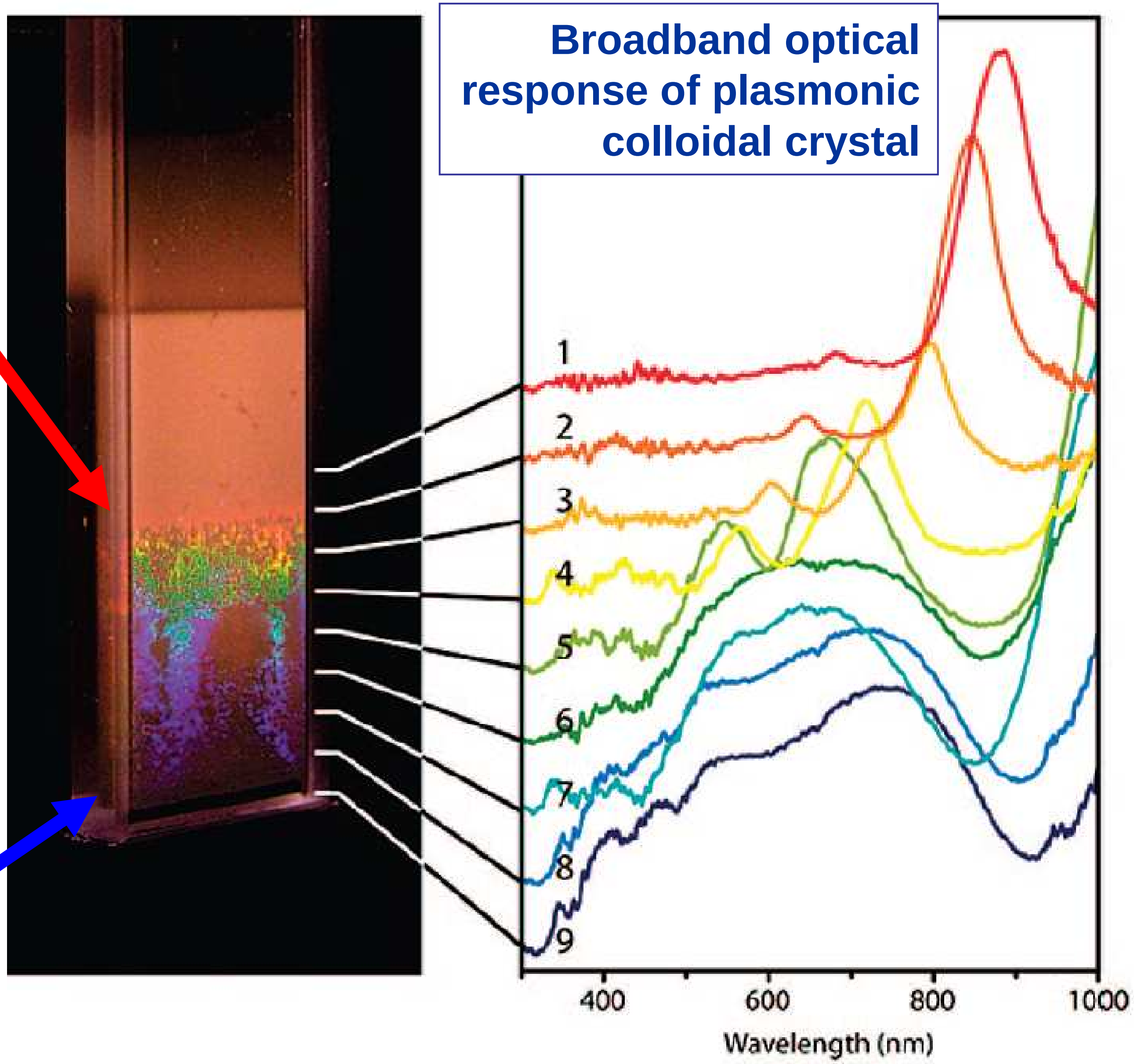
Self-organized silver nanoparticles for 3D plasmonic crystals

At low volume densities
- Long-range hexagonal order stabilied by repulsive steric interactions

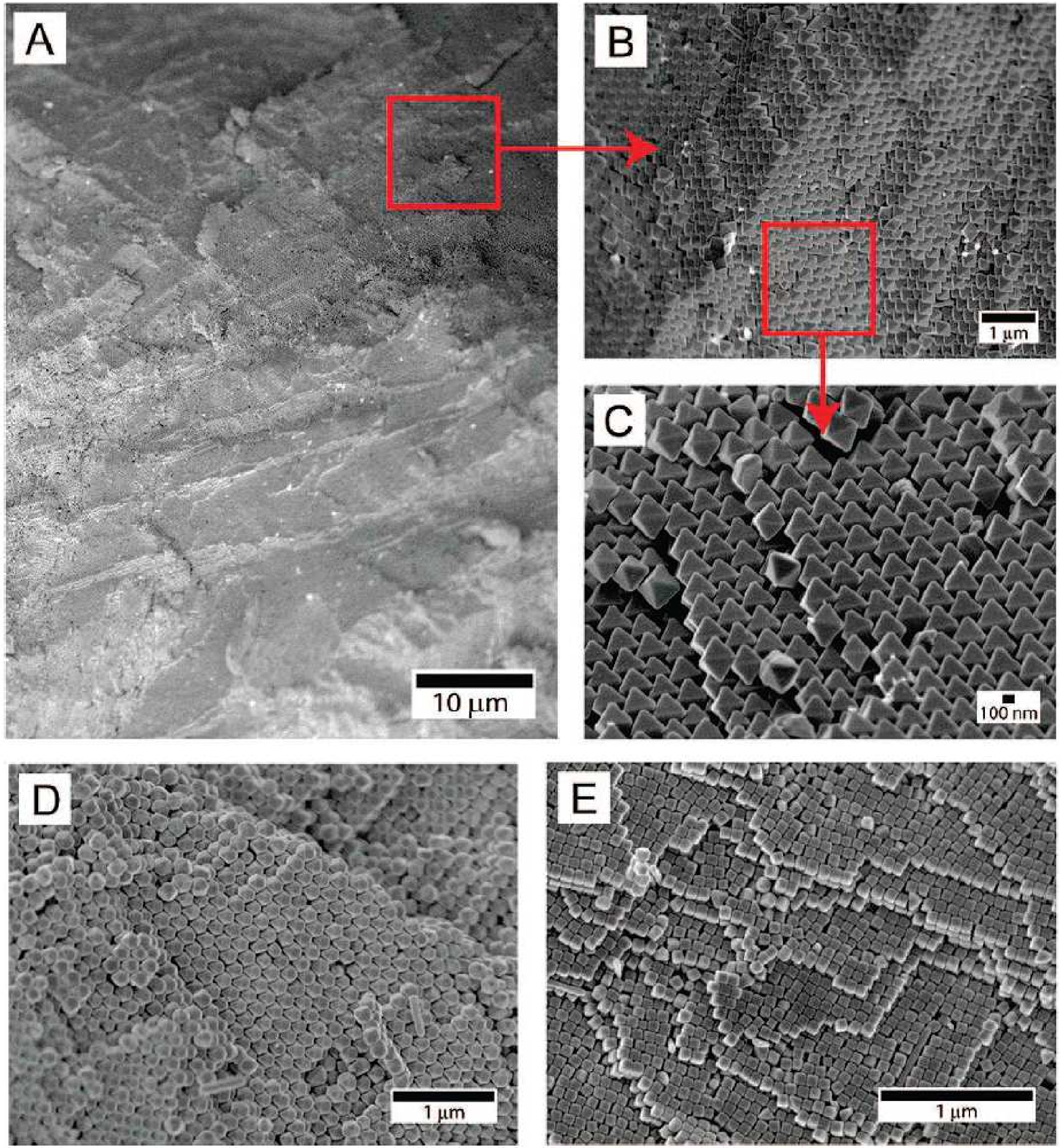


Dense close-packed structure with excellent ordering after the nanocrystals sediment by gravity

Broadband optical response of plasmonic colloidal crystal



Nano Lett., 8, (2008), 4033, A. R. Tao et al.



A
10 µm
B
1 µm
C
100 nm
D
1 µm
E
1 µm

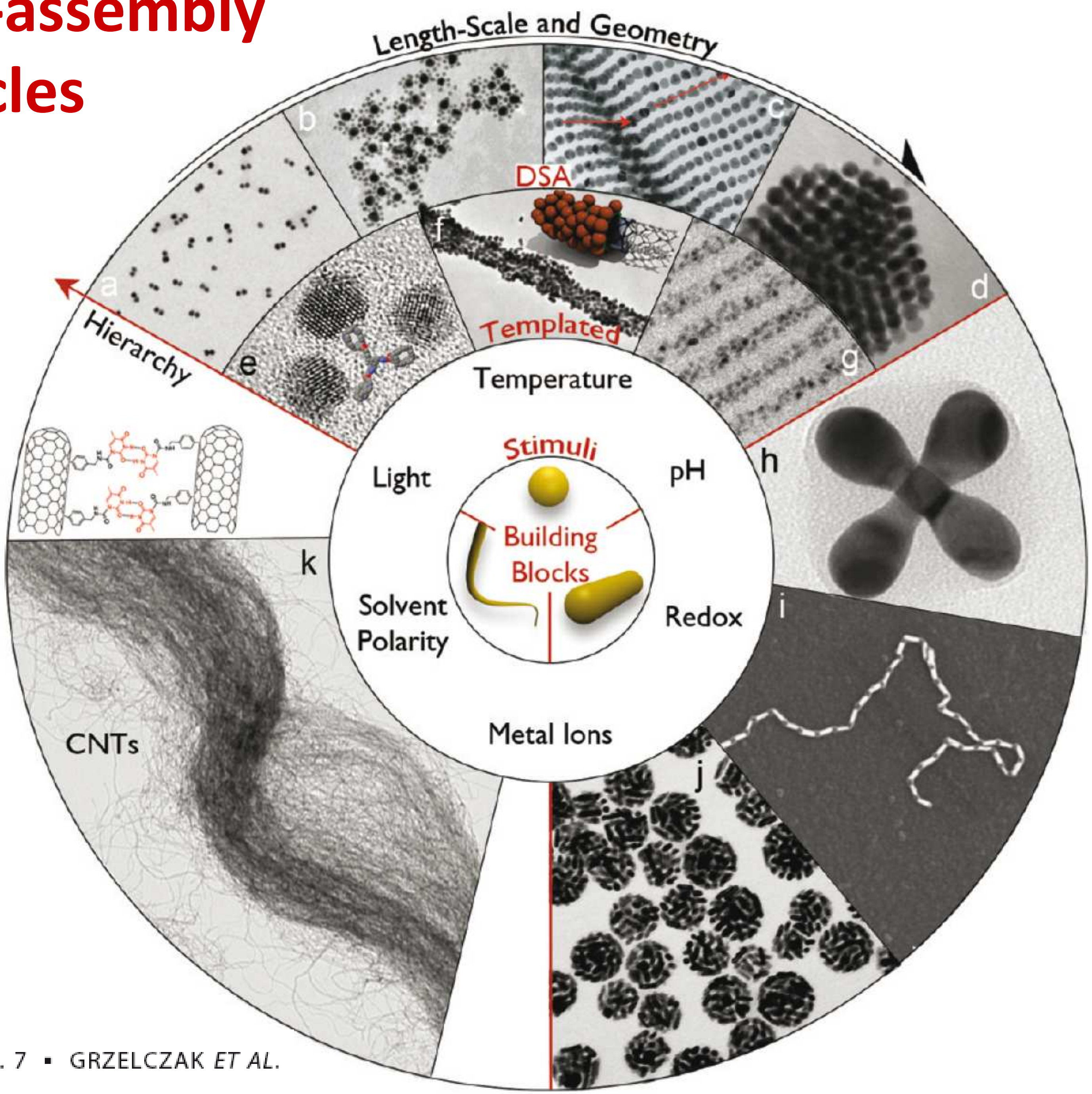
Directed self-assembly of nanoparticles

Available building blocks characterized via aspect ratio (AR):

AR=1 isotropic, mostly spheres

1<AR<15 rodlike

AR>15 wires



ACS NANO VOL. 4 ▪ NO. 7 ▪ GRZELCZAK *ET AL.*

Directed self-assembly of nanoparticles

Self-assembly - process by which nanoparticles or other discrete components spontaneously organize into ordered structures

Directed assembly – process whereby an intrinsically self-assembling system is aided or modulated using directing agents, external fields, or templates

Templates – any surface-modified object (1D, 2D, or 3D), which contains active sites, suitable for selective nanoparticle deposition

Directing fields – externally imposed fields (in a broad sense), such as electric, magnetic, and flow fields, or combinations thereof, that modulate or enhance the thermodynamic forces that drive self-assembly

Capillarity or capillary action – forces exerted by interfacial or surface tension effects that lead to a directed self-assembly at interfaces or in thin films

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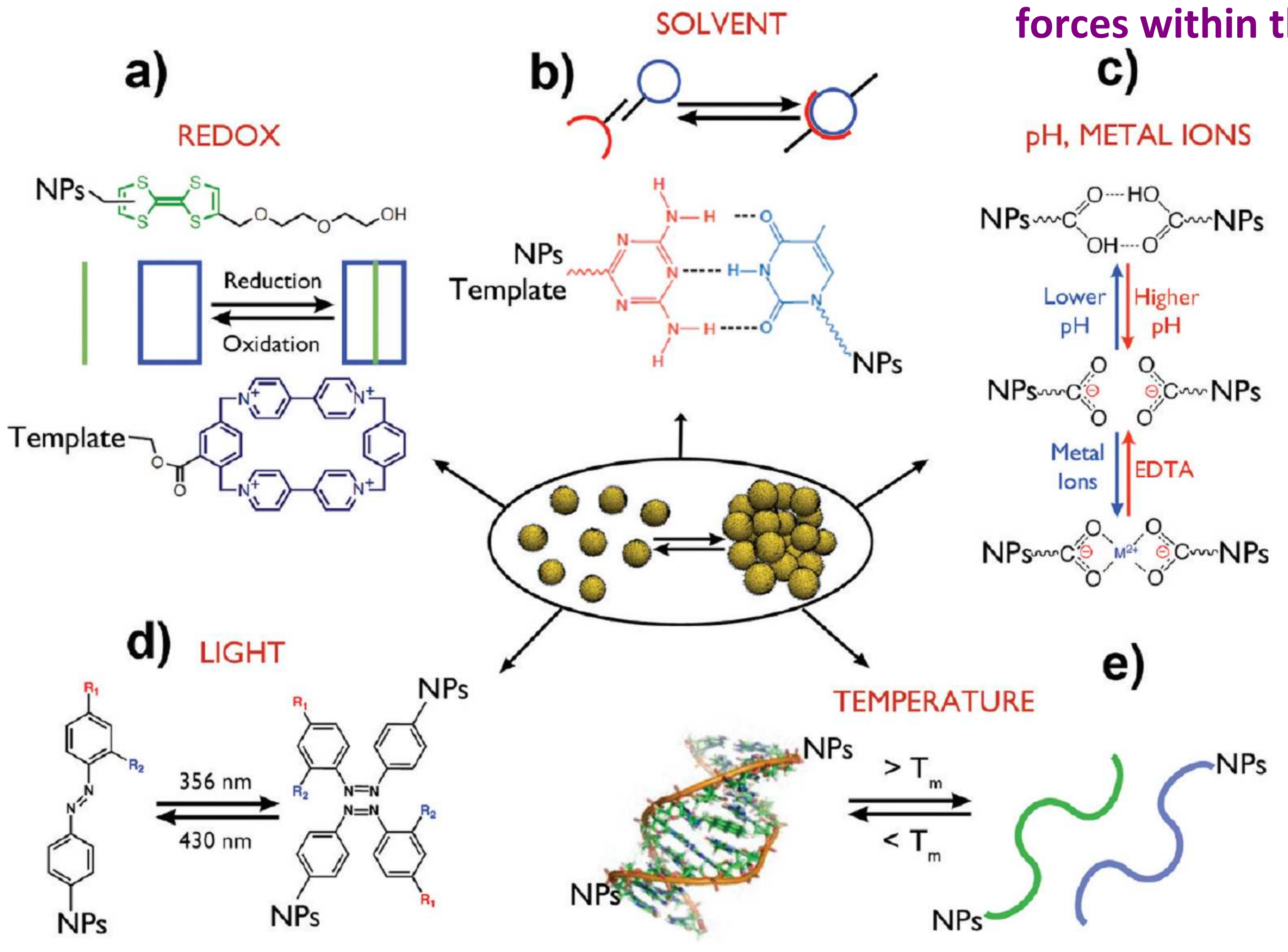
Directed self-assembly of nanoparticles
by molecular interactions

Mostly limited to 100 nm size particles due to limited length scale of molecular forces within the colloidal interface



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The most usual STIMULI employed to spatially distribute the particles:

- **temperature,**
- **electromagnetic radiation (e.g., light),**
- **pH,**
- **solvent polarity,**
- **redox activity**

Directed self-assembly of nanoparticles by molecular interactions

Template-free DSA

Templated DSA

Templates - surface-modified substrates (in 1D, 2D, or 3D), containing active sites, which can selectively induce nanoparticle deposition

Any object serving as a scaffold onto which different particles can be arranged into a structure with a morphology that is complementary to that of the template - single molecules , microstructures (e.g., carbon nanotubes), or block copolymers

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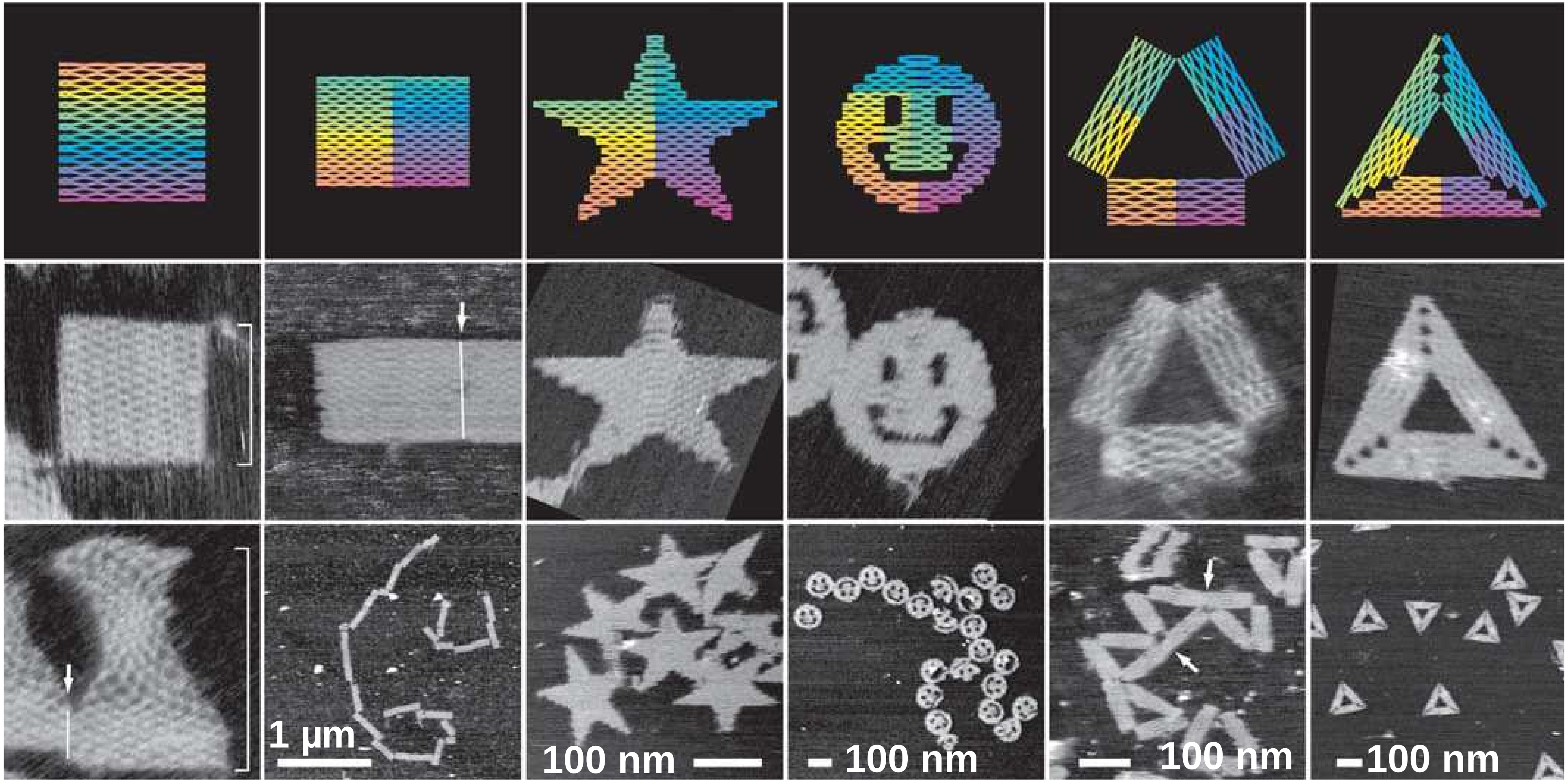
DNA origami



P. W. K. Rothemund, Nature 2006, 440, 297.

Concept of DNA controlled nanocrystal self-assembly

Mirkin, C. A.et al. Nature 1996, 382, 607–609.
A DNA-Based Method for Rationally Assembling Nanoparticles into Macroscopic Materials.
Alivisatos, A. P.et al. Nature 1996, 382, 609–611.
Organization of 'Nanocrystal Molecules' using DNA.

DNA-guided self-assembly

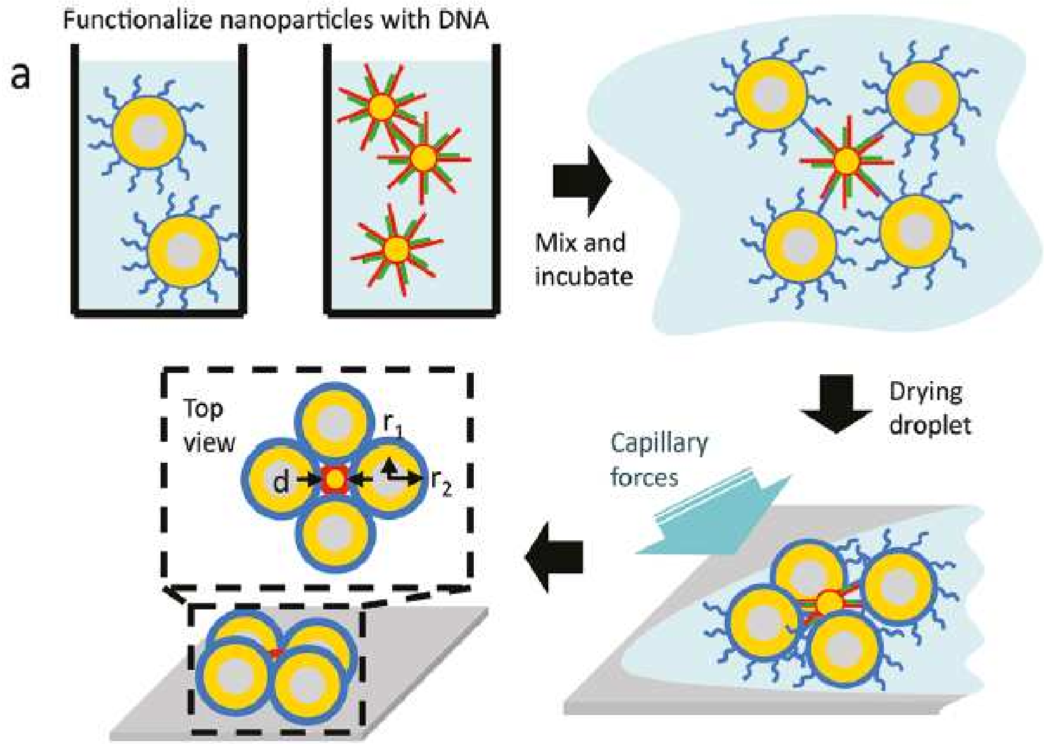
DNA – soft template

Soft templates possess a spatial distribution of specific reactive sites with affinity toward certain particles, resulting in a controlled periodicity of the assembled particles and eventual formation of hierarchical structures

Nanoparticles can be functionalized by:

(i) large numbers of DNA strands, leading to network materials,

(ii) discrete numbers of DNA strands, forming discrete assemblies



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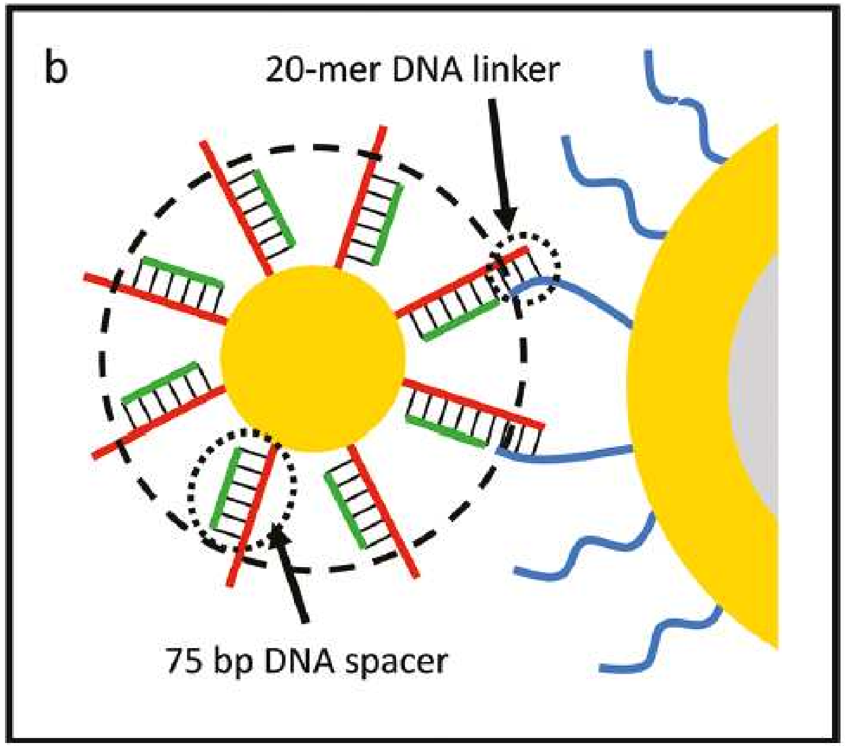
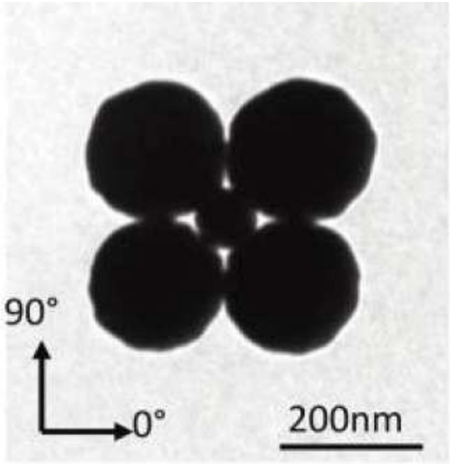
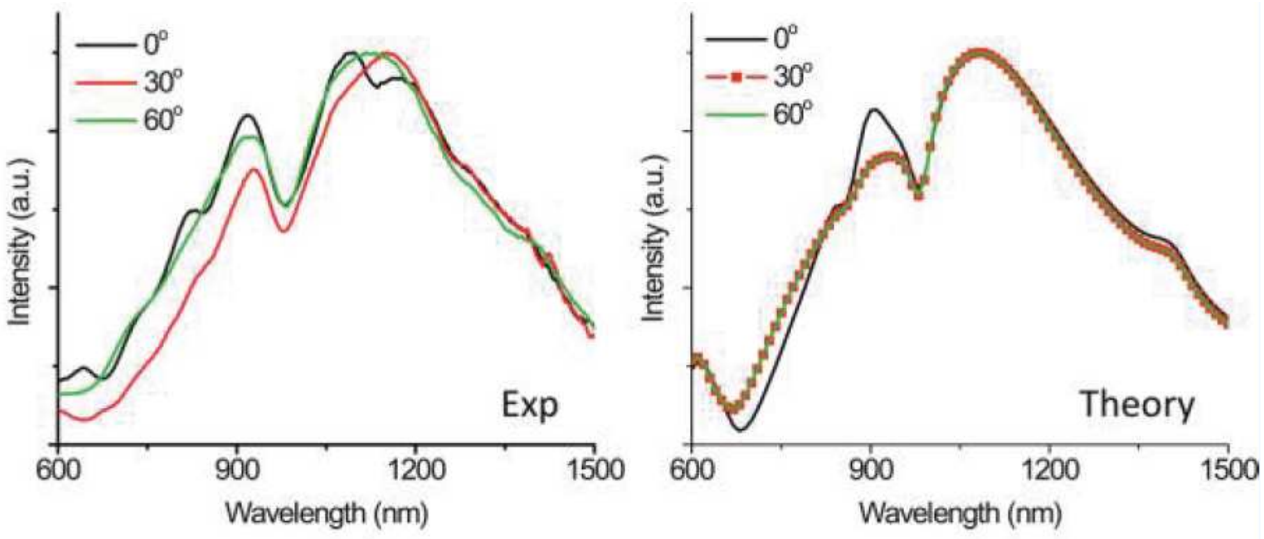
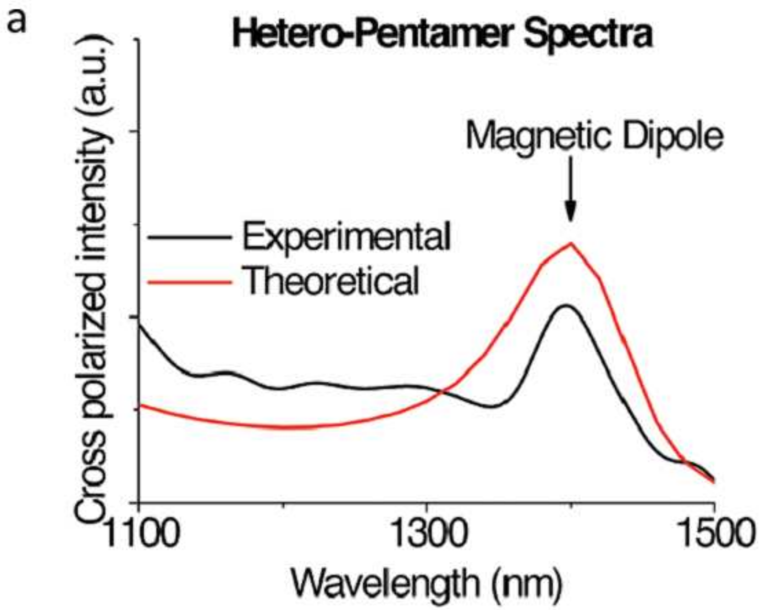


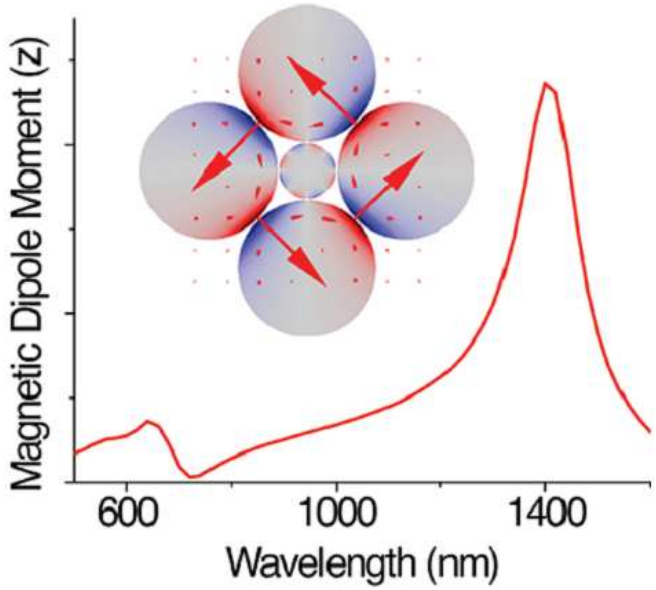
Jonathan A. Fan | *Nano Lett.* 2011, 11, 4859–4864

DNA-guided self-assembly



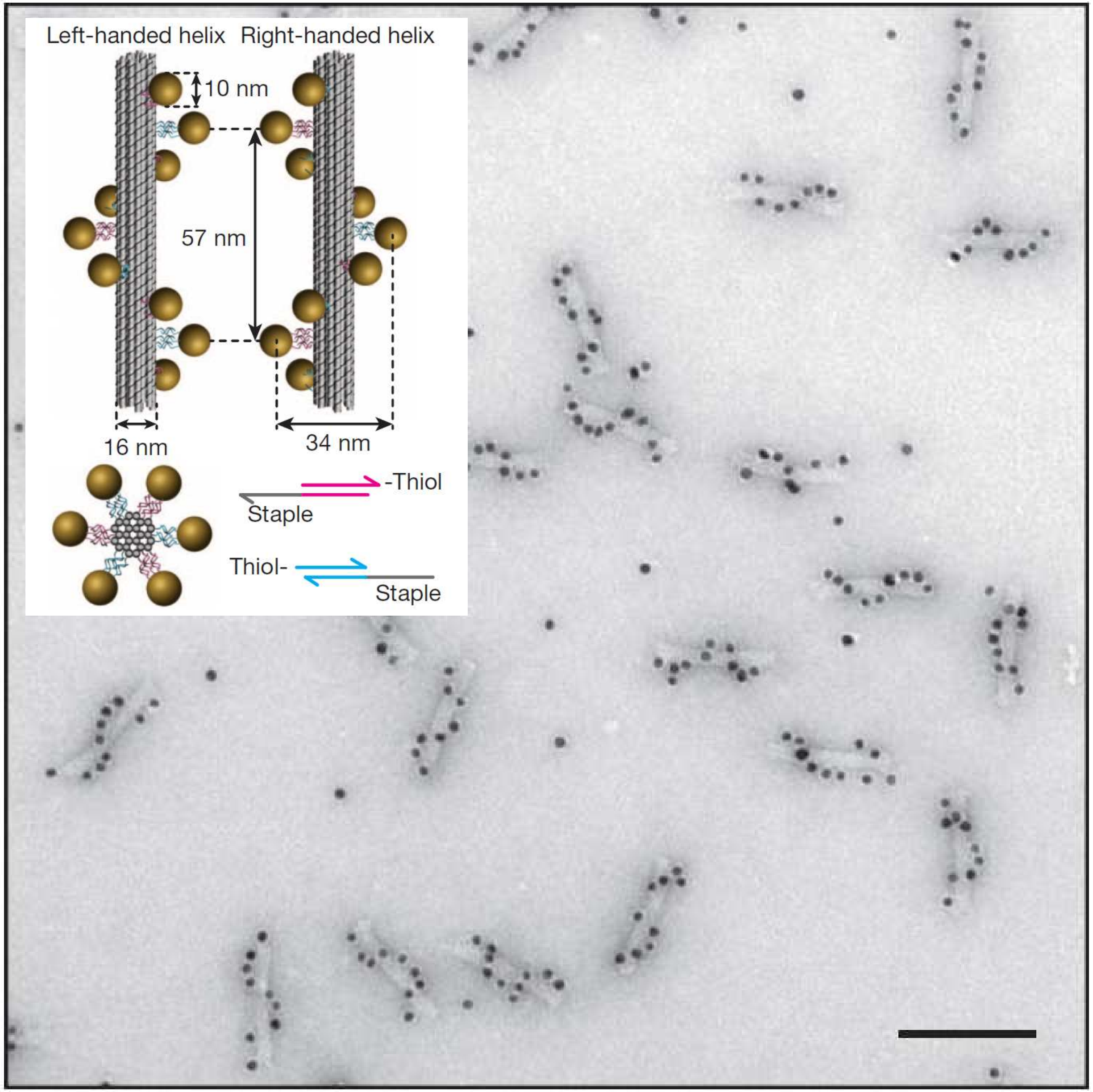


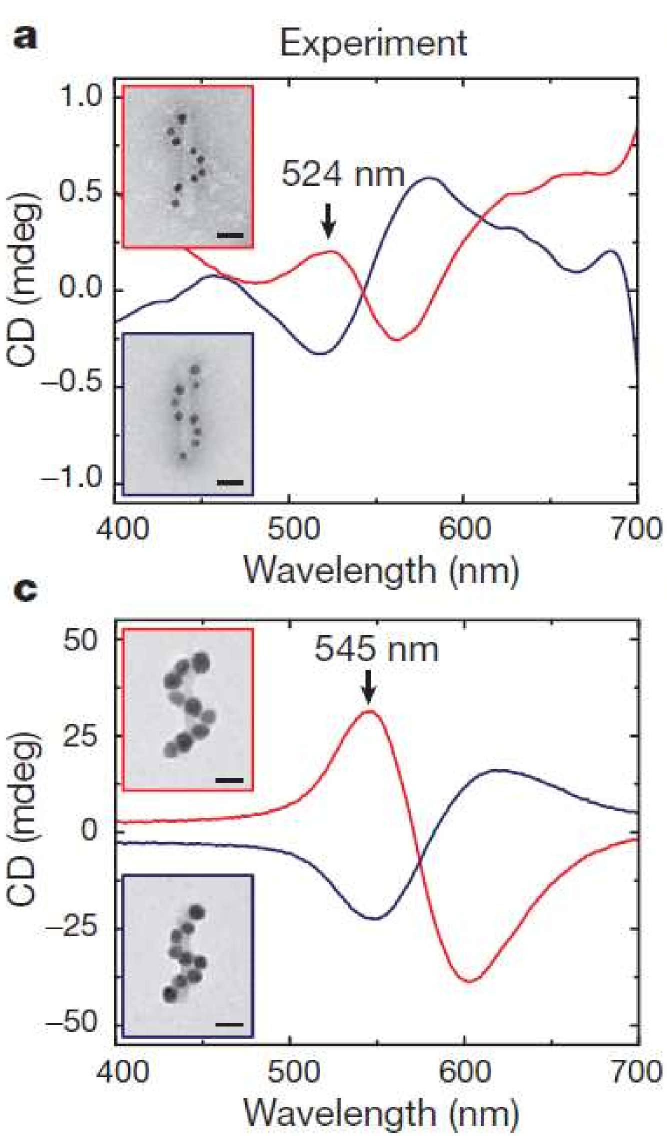




Nanoletters, J. A. Fan, …F. Capasso

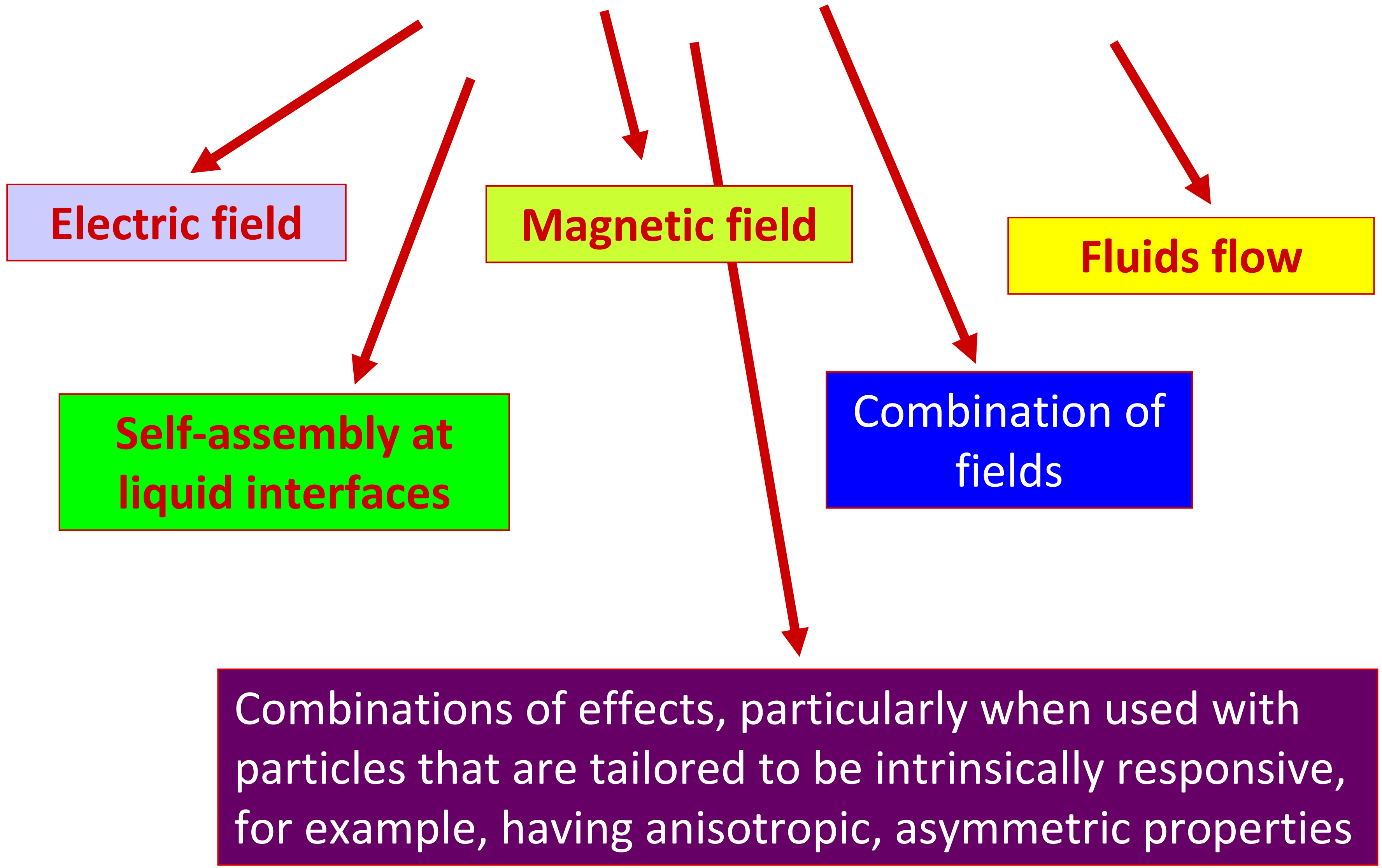
DNA-guided self-assembly



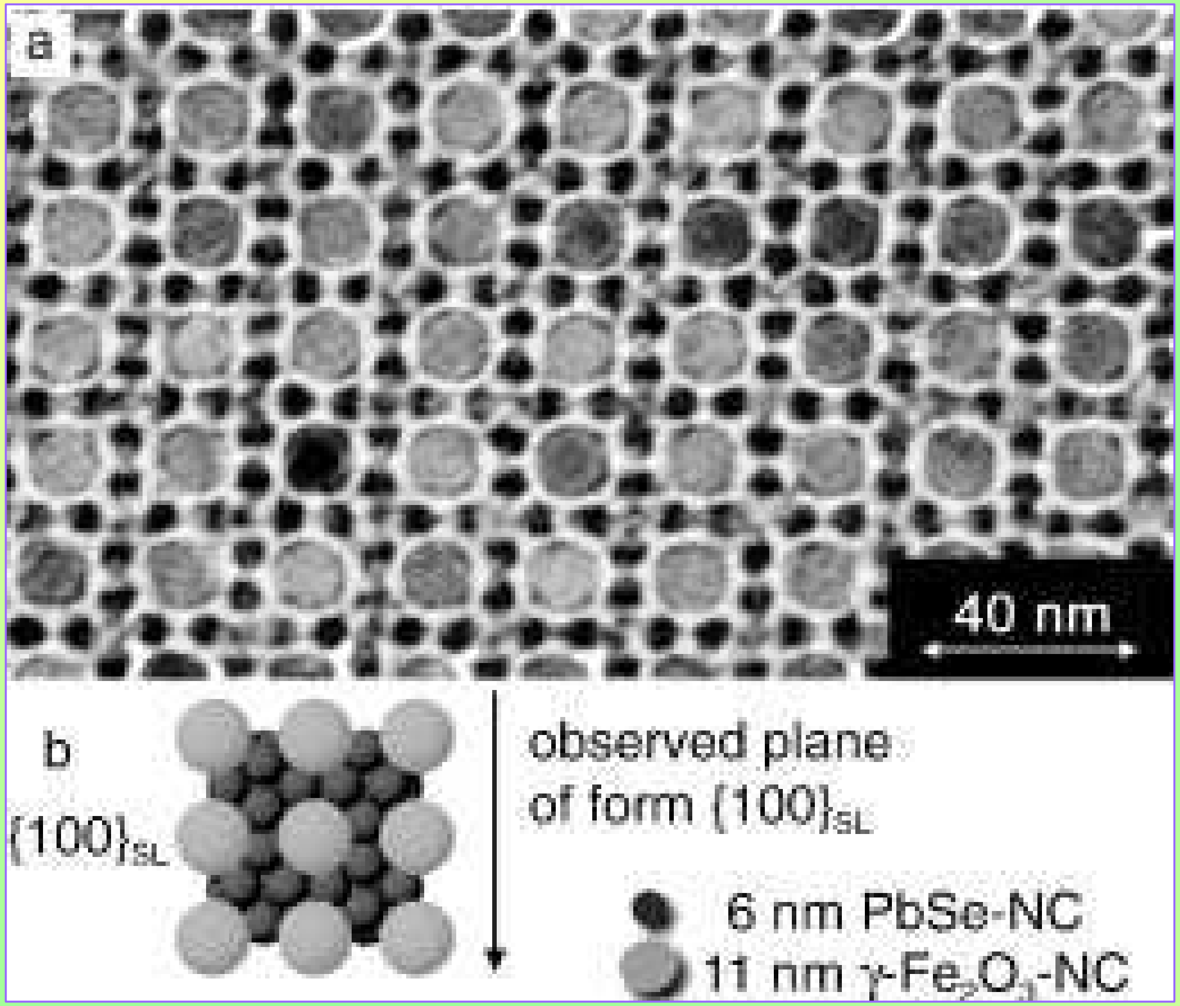


A. Kuzyk et al. Nature 2012, 483, 311

Externally directed self-assembly of nanoparticles



Binary superlattices of nanoparticles (BNSL)



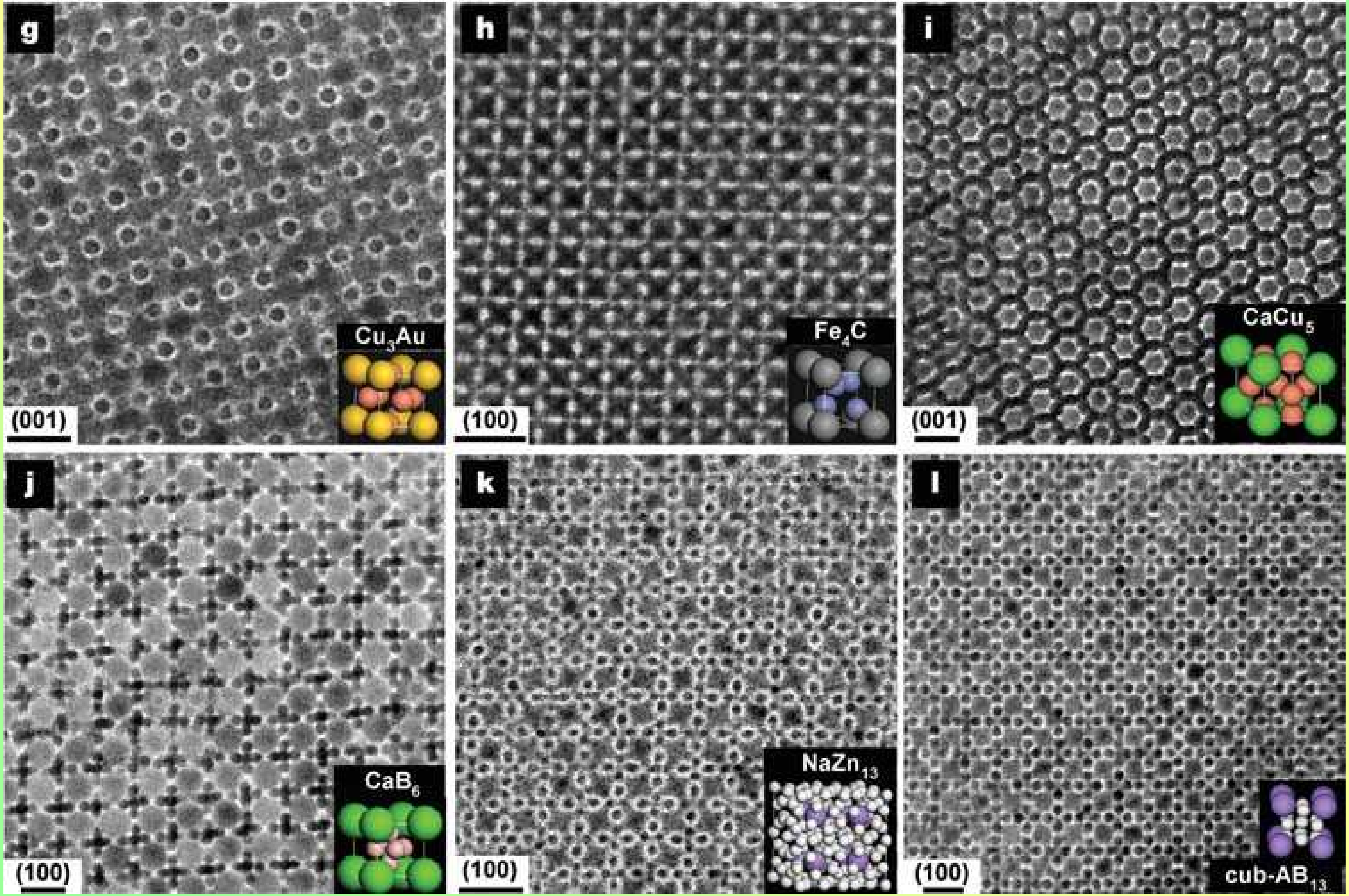
Applying oposite charges to the nanoparticles can stabilize binary lattices, while destabilizing single component lattices

The charges can be altered by adding surfactant molecules

TEM image of a 3D superstructure of γ-Fe_2O_3 (11 nm) and PbSe (6 nm)

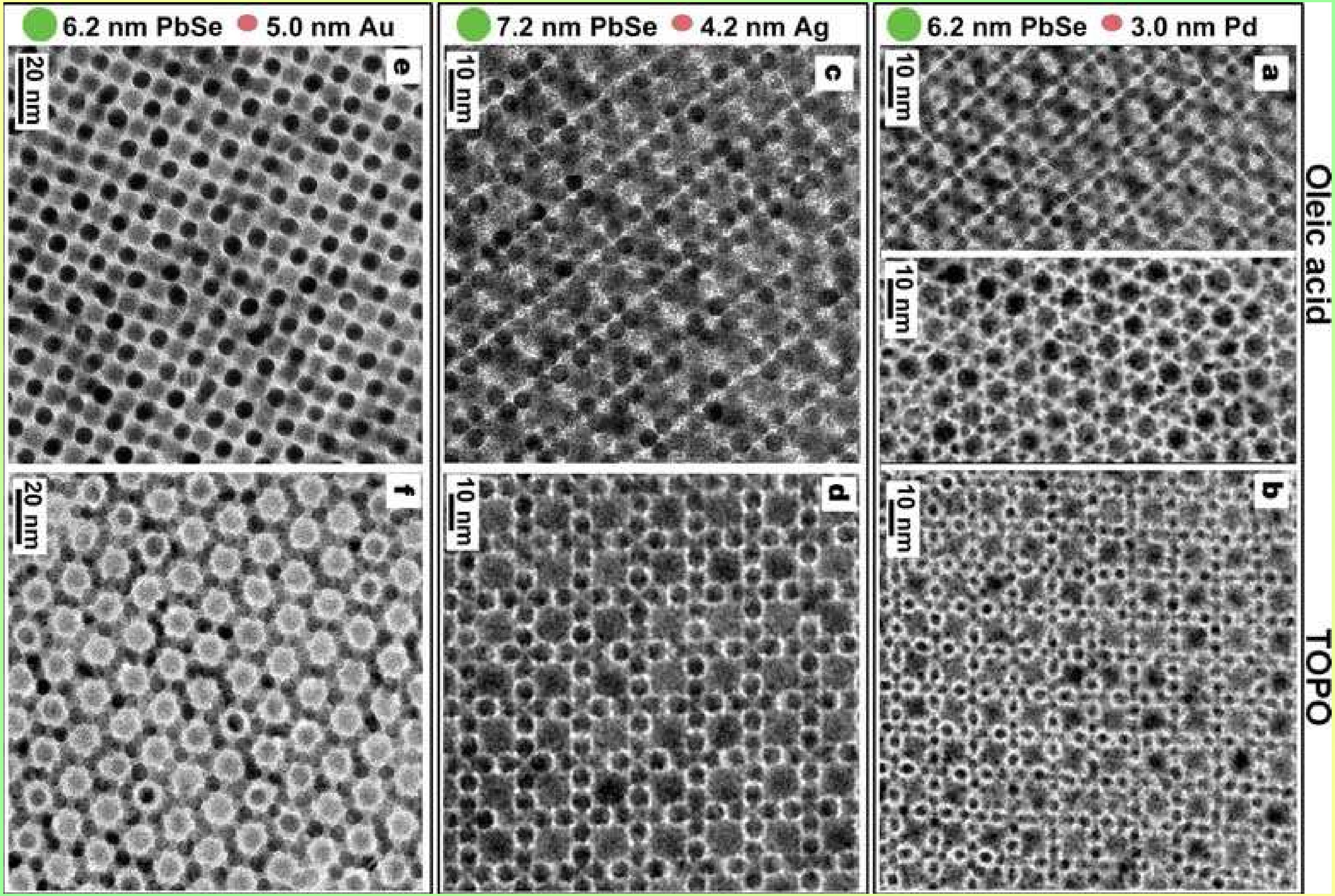
Nature, 439, (2006), 55, Shevchenko,..., Murray, Nature., 423, (2003), 968, F.X. Redl

Binary superlattices of nanoparticles (BNSL)



Nature, 439, (2006), 55, Shevchenko,..., Murray

Binary superlattices of nanoparticles (BNSL)



Nature, 439, (2006), 55, Shevchenko,..., Murray

Mimicking photosynthetic proteins to manipulate metal at nanoscale

Porphyrins – active part of photosynthetic proteins

\+

Platinum salt

\+

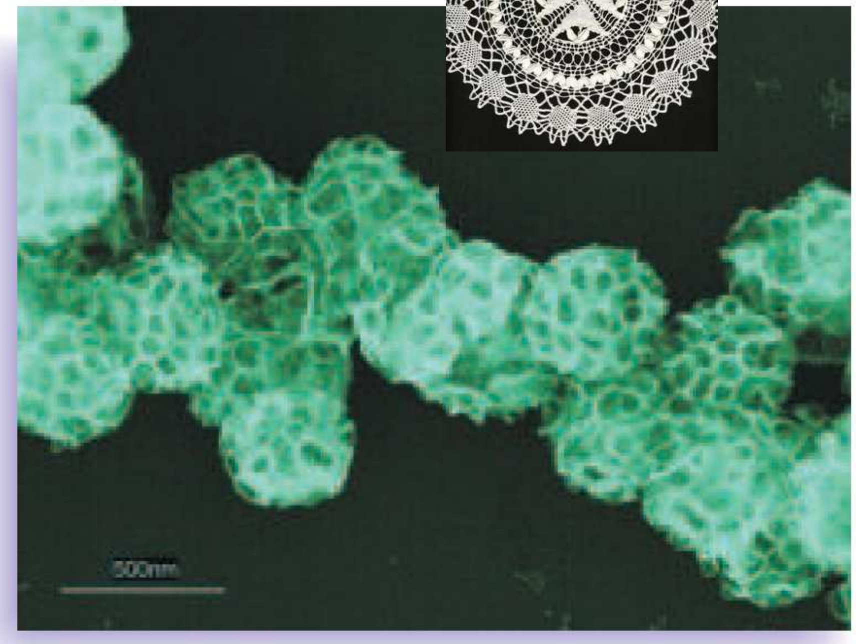
Aqueous solution of **ascorbic acid**

Porphyrins – exite and become catalyst for **platinum reduction and deposition**

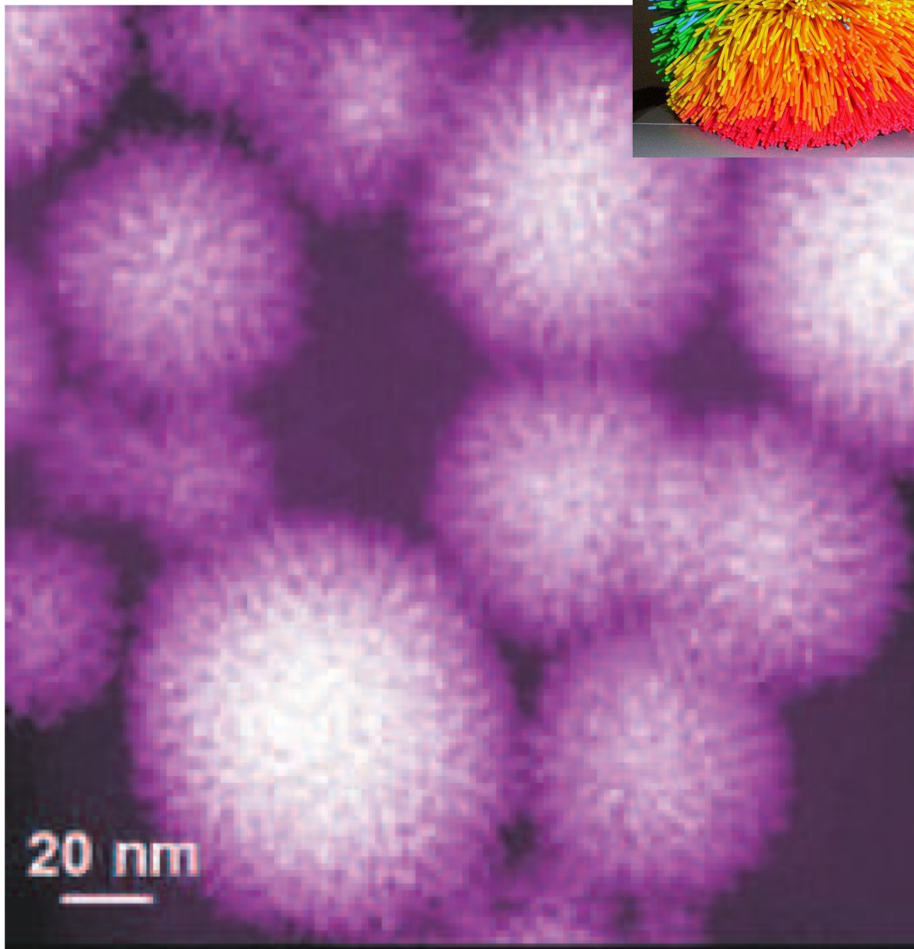
Platinum nanostructures – take different forms when prepared under different conditions

J. Failure Analysis and Prevention., 4, (2004), 7, Industry updates

Mimicking photosynthetic proteins to manipulate metal at nanoscale



Platinum lace-nanoballs
SEM image

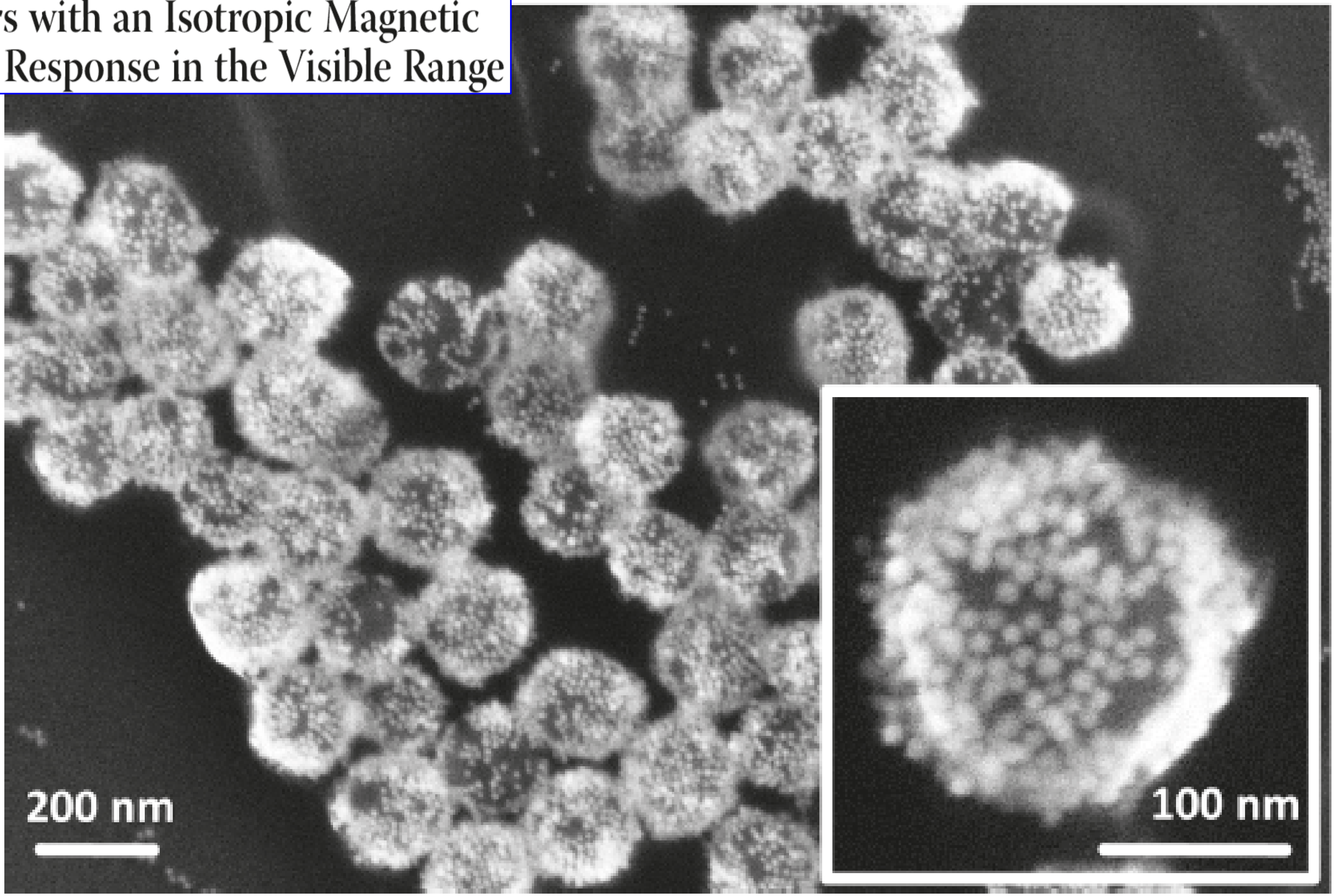


Platinum nano-Koosh balls *TEM image*

J. Failure Analysis and Prevention., 4, (2004), 7, Industry updates

Core-shell clusters

Clusters with an Isotropic Magnetic Dipole Response in the Visible Range

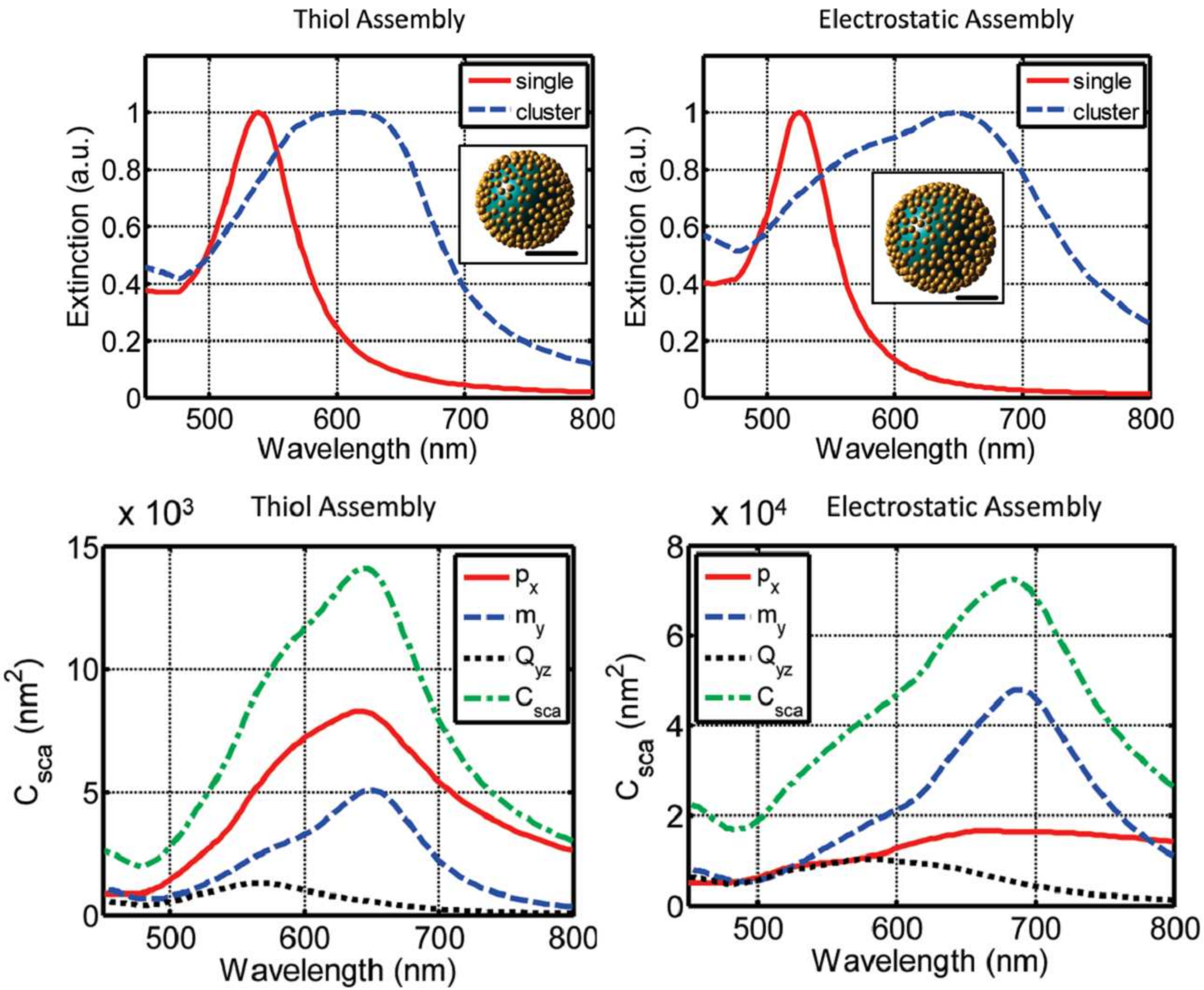


Thiol assembly

Stefan Mühlig,

VOL. 5 ▪ NO. 8 ▪ 6586–6592 ▪ 2011 ACS NANO

Core-shell clusters



Stefan Mühlig,

VOL. 5 ■ NO. 8 ■ 6586–6592 ■ 2011 ACSNANO

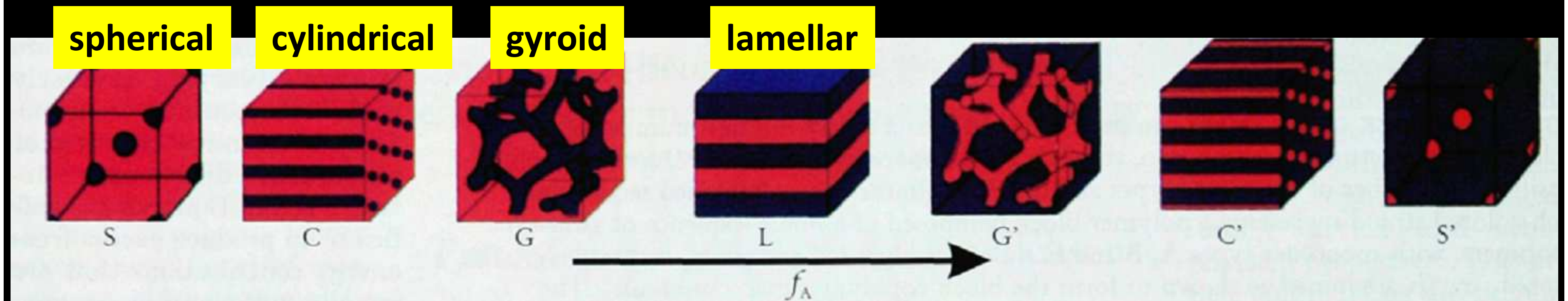
Self-assembly of block copolymers (BCPs)

- ✓ Block copolymer molecule contains 2 or more polymer chains attached at their ends. It can self-assemble to form a nanoscale structure with a domain spacing
- ✓ Typical periodicity is in the range 10-200 nm

Can be used to produce:

- ✓ highly ordered nanostructures over large surface areas
- ✓ ordered metal nanoparticles
- ✓ structured metal surfaces

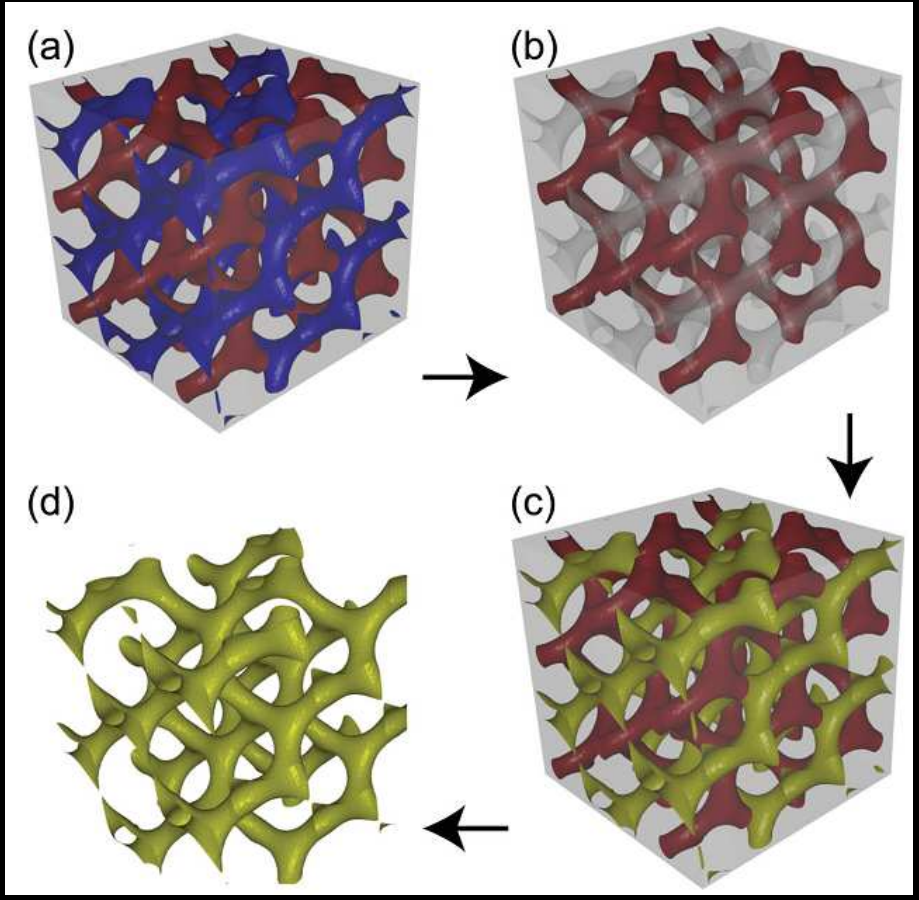
Multiblock copolymer constructs:
- exhibit very regular self-assembled nanostructures,
- are intrinsically chemically selective due to the differing solubility and coordination properties of the blocks



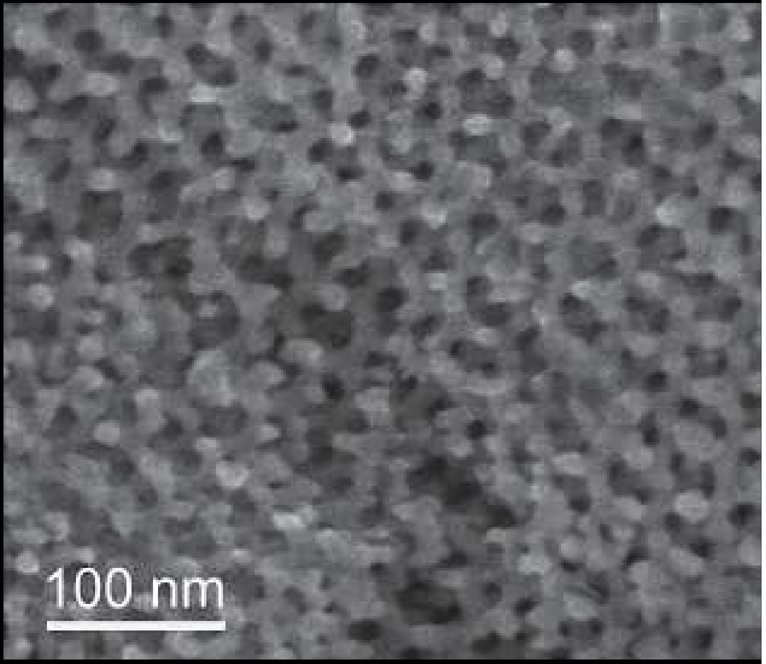
F. S. Bates and G. H. Fredrickson Phys. Today 52(2), 32 (1999)

Self-assembly of block copolymers (BCPs)

(a) isoprene-block-styrene-block-ethylene triblock copolymer with double gyroid nanostructure



First self-assembled chiral optical metamaterials with 3 D structure



grey matrix – styrene
blue – isoprene
red - ethylene oxide

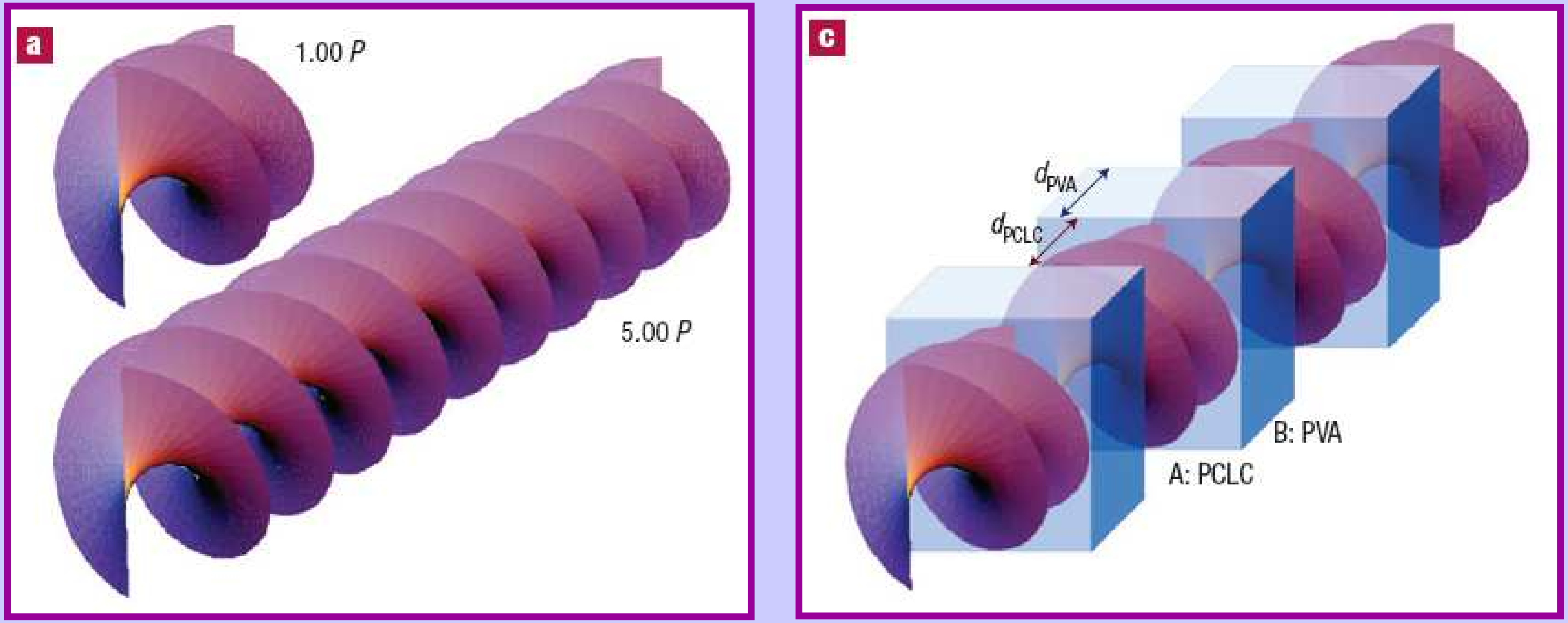
(b) isoprene removing
(c) gold filling
(d) etyhlene oxide and styrene removing

S. Vignolini et al. Adv. Mater. 24, 23 (2012)

J. Pendry, *A Chiral route to negative refraction*, Science, 306, 1353, 2004

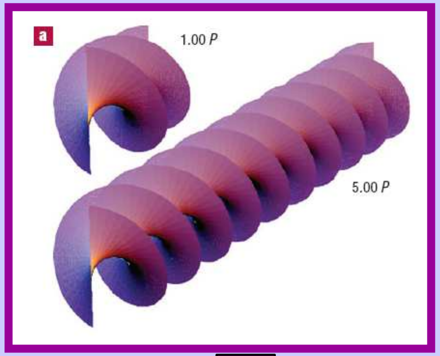
Chiral particles/molecules

A cholesteric liquid crystal (CLC) is a self-assembled photonic crystal formed by rodlike molecules, including chiral molecules, that arrange themselves in a helical fashion.

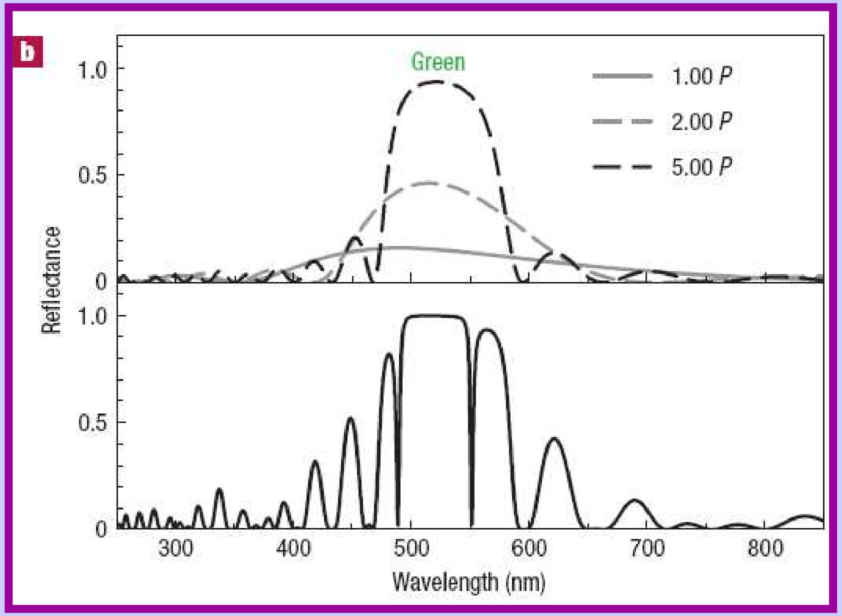


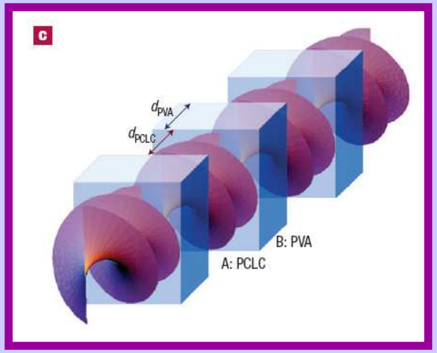
Nature , 7, (2008), 43, Na Young Ha, et al.

Chiral particles/molecules



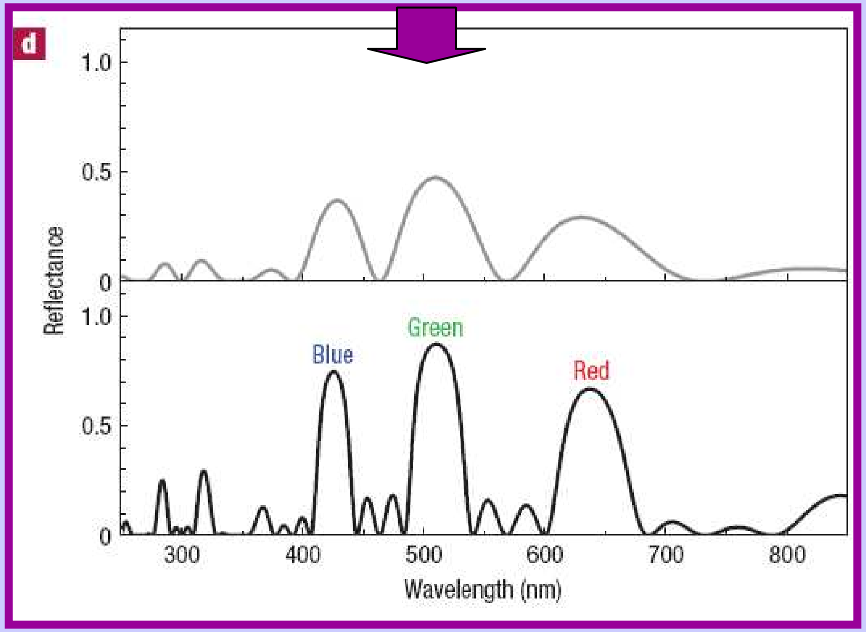
Single photonic bandgap for circularly polarized light with the same handedness as the CLC helix (selective reflection)





CLC system consisting of thin isotropic films and of polymeric CLC films

Simultaneous red, green and blue reflections (multiple photonic bandgaps)



Electrically conducting organic crystals and polymers

Electrically conducting organic crystals and polymers → **Potential optoelectronic materials**

If exhibiting sufficiently high charge carrier mobilities and easy to make and process

Organic single crystals

High charge carrier mobilities but impractical

Polymers

Good processability but low mobilities

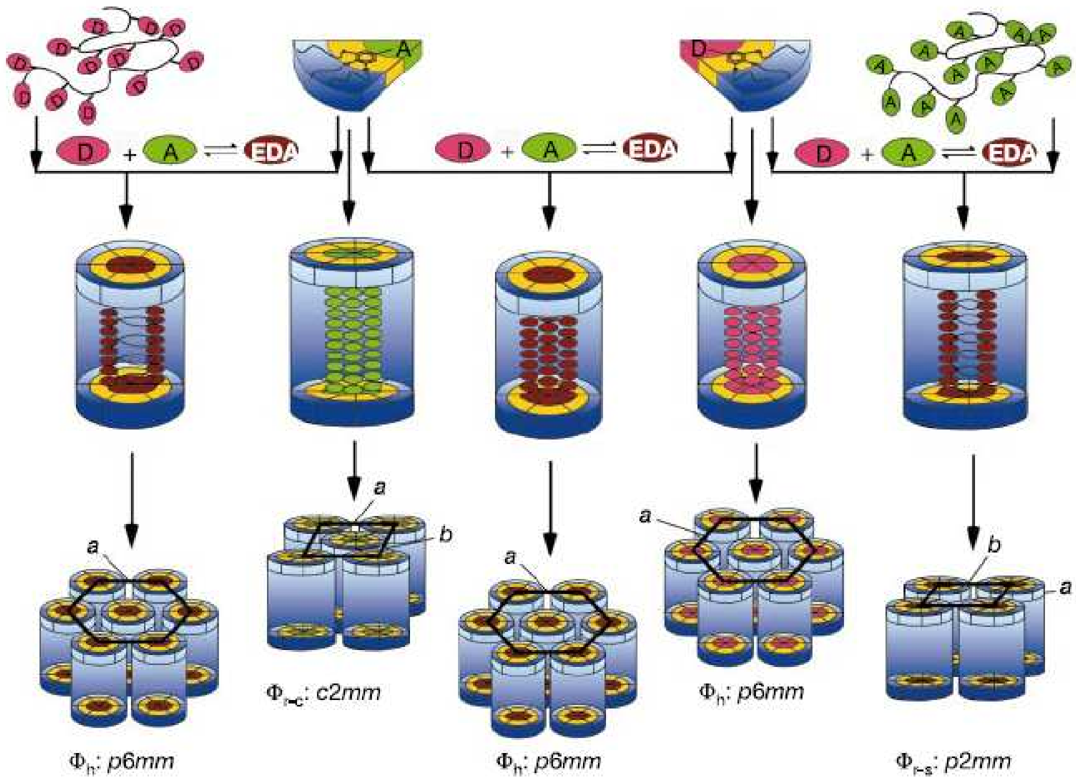
Liquid crystals

Mobilities approaching those of single crystals and are suitable for applications

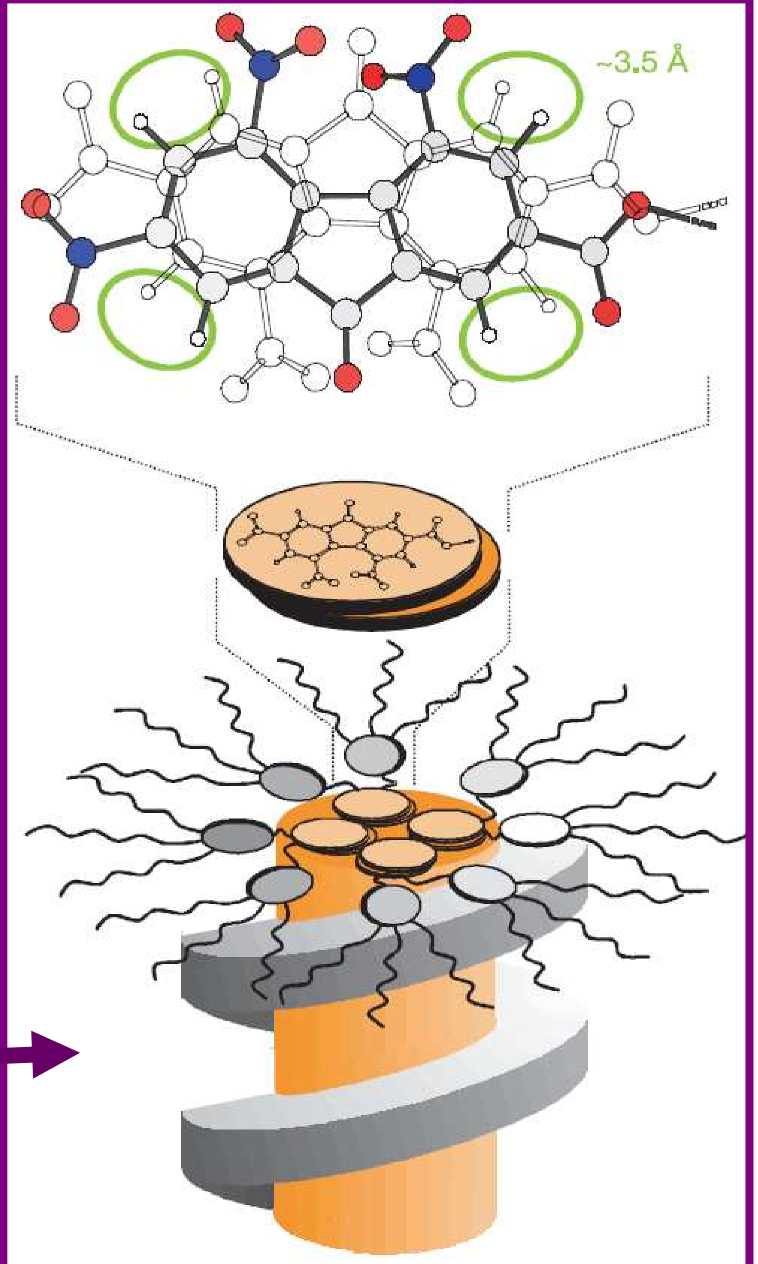
Optics Express 15, (2007), 5730, A. Baev, et al.

Nature, 419, (2002), 384, V. Percec et al.

Self-organization of supramolecular helical dendrimers into complex electronic materials



Nanometer scale columns
(enhanced charge carrier mobilities)

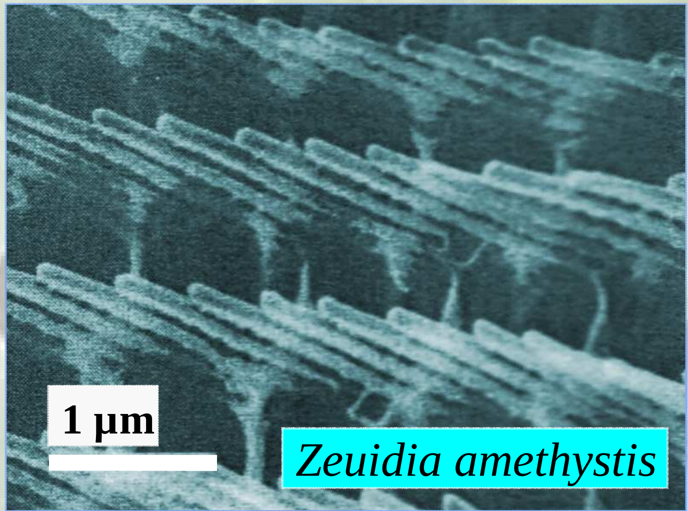


Optics Express 15, (2007), 5730, A. Baev, et al.

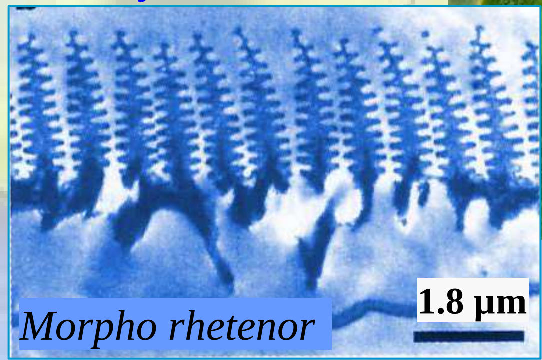
Nature, 419, (2002), 384, V. Percec et al.

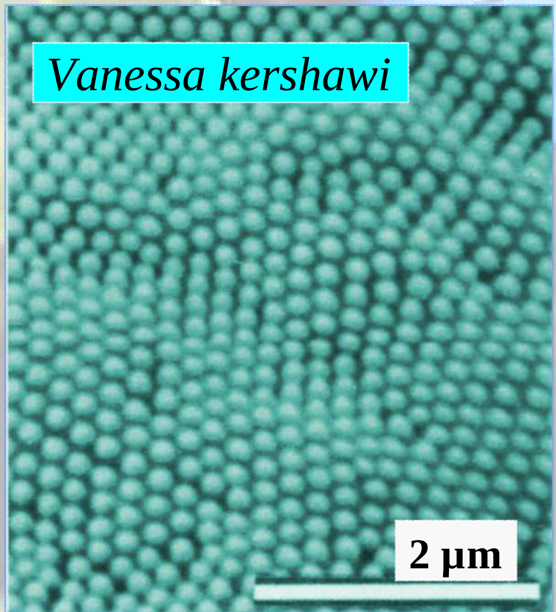

Wonders of nature –
optical effects in nature

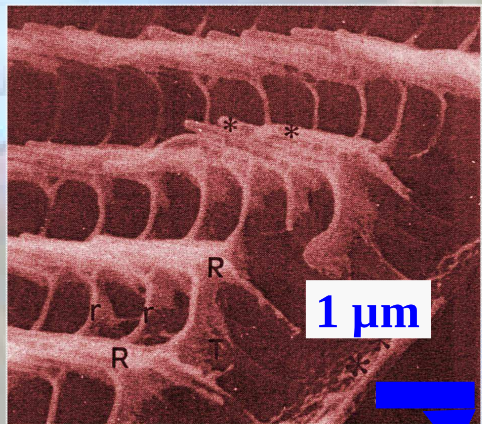
Structural colours

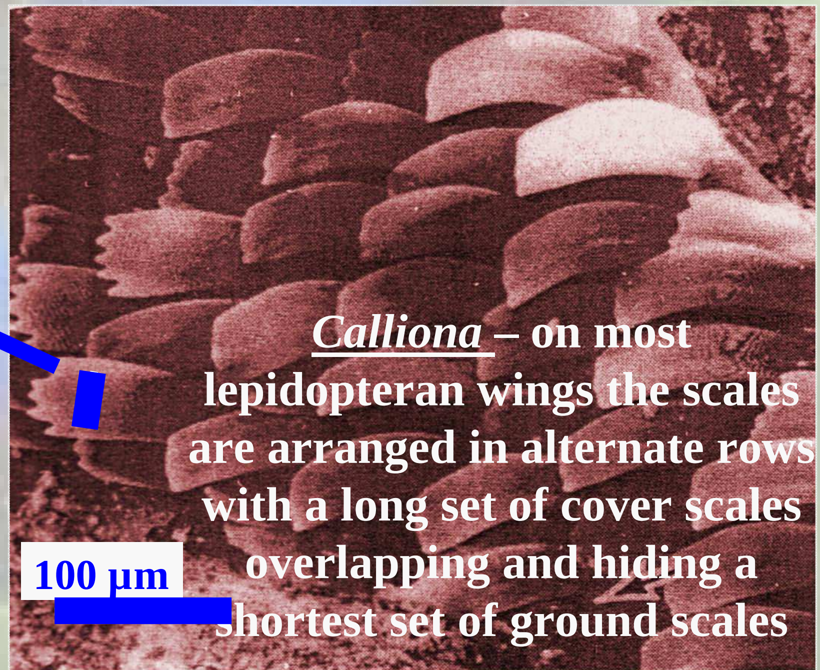


Visibility – half a mile





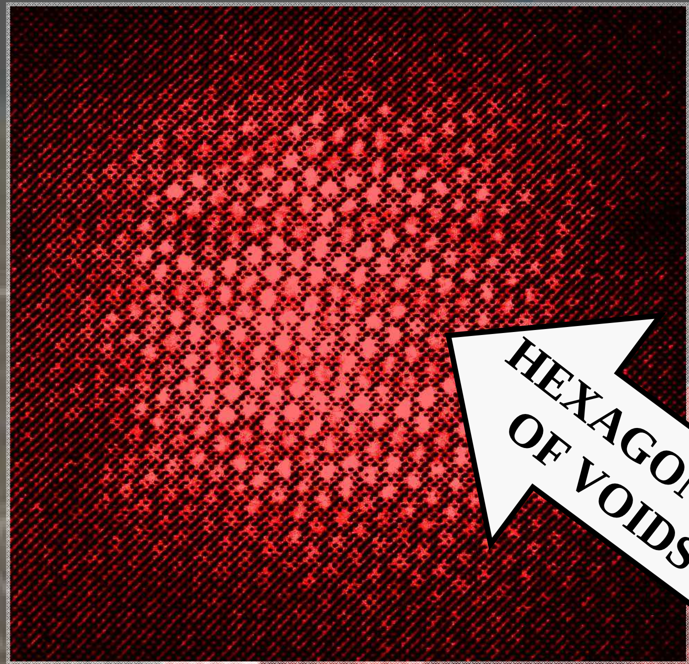




Calliona **– on most lepidopteran wings the scales are arranged in alternate rows with a long set of cover scales overlapping and hiding a shortest set of ground scales**

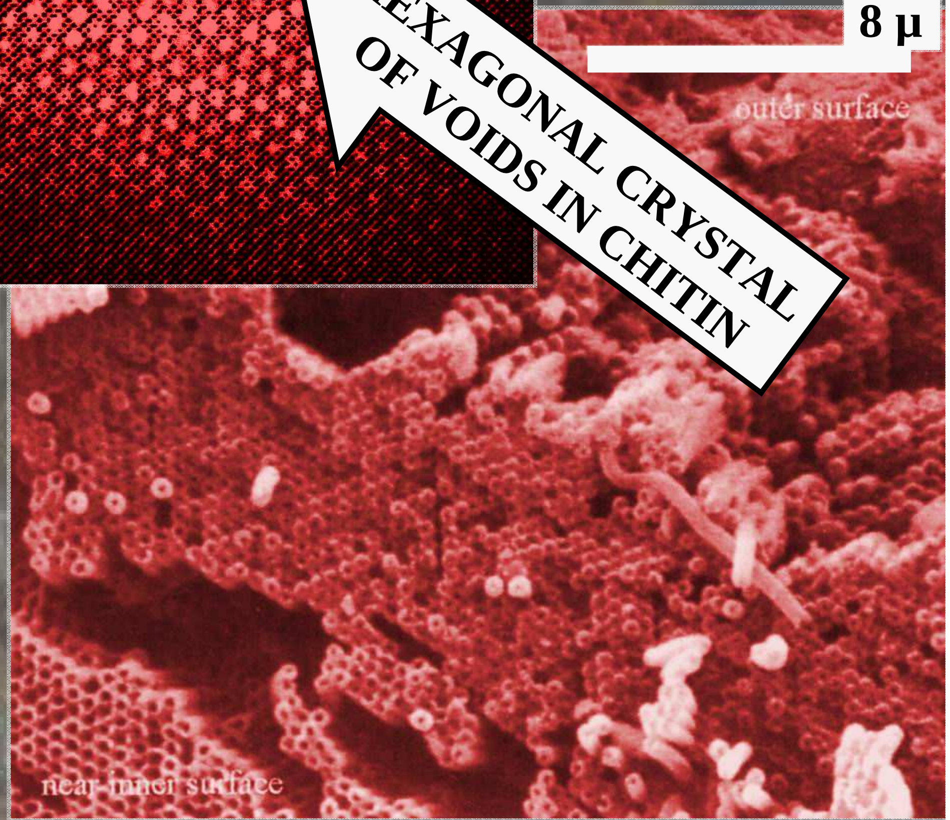
H. Ghiradella, Applied Optics, 30 (1991) 3492.
A. R. Parker, Materials Today, Sept 2002.
P. Vukusic et al., Nature, 424 (2003) 852.

Aphrodite's iridescence

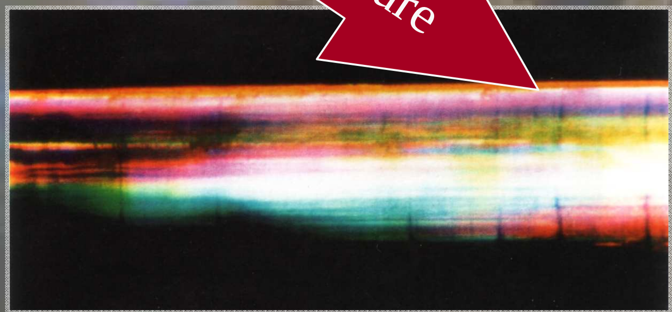


Chitin, n ≅ 1.56

Water, n ≅ 1.33

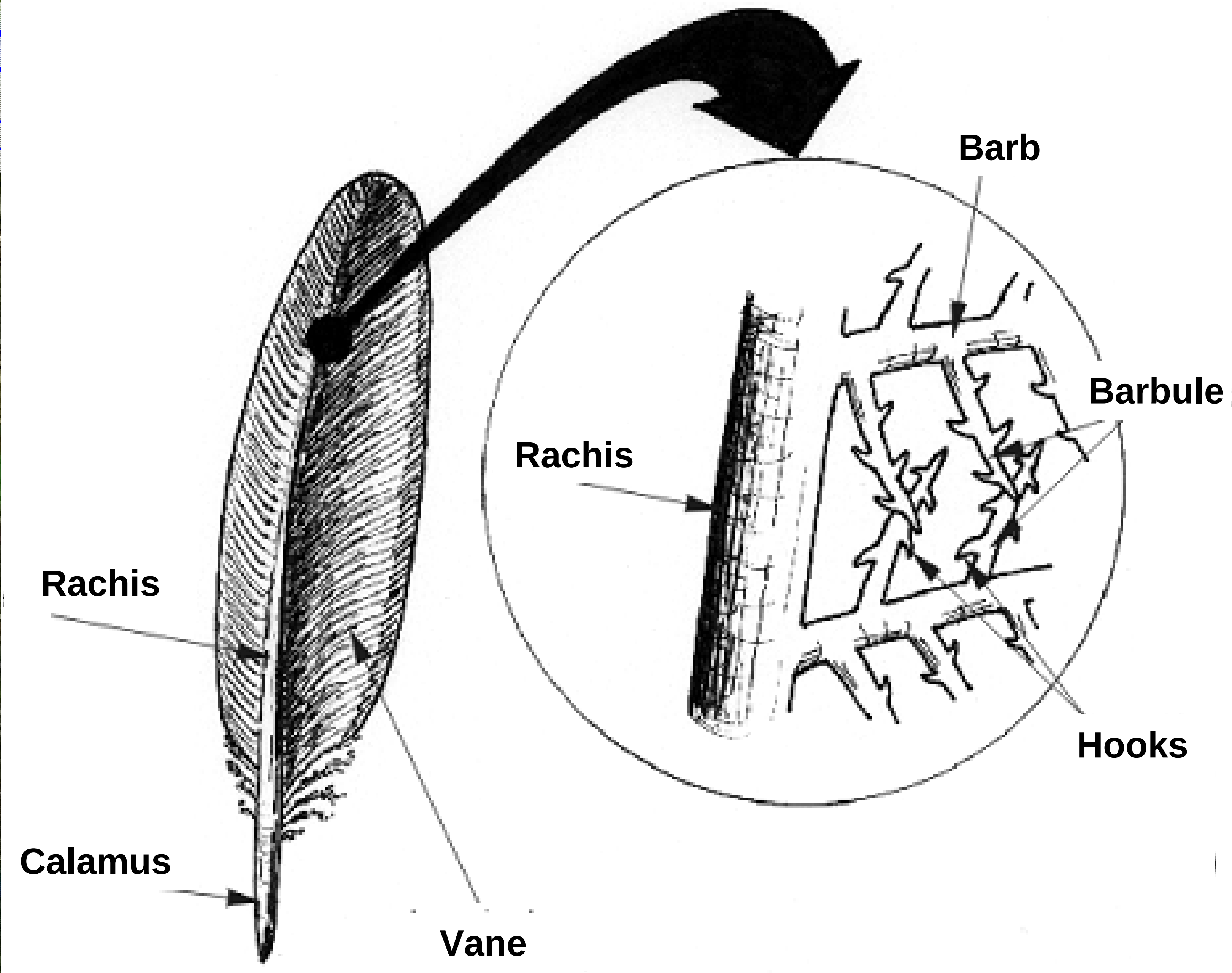


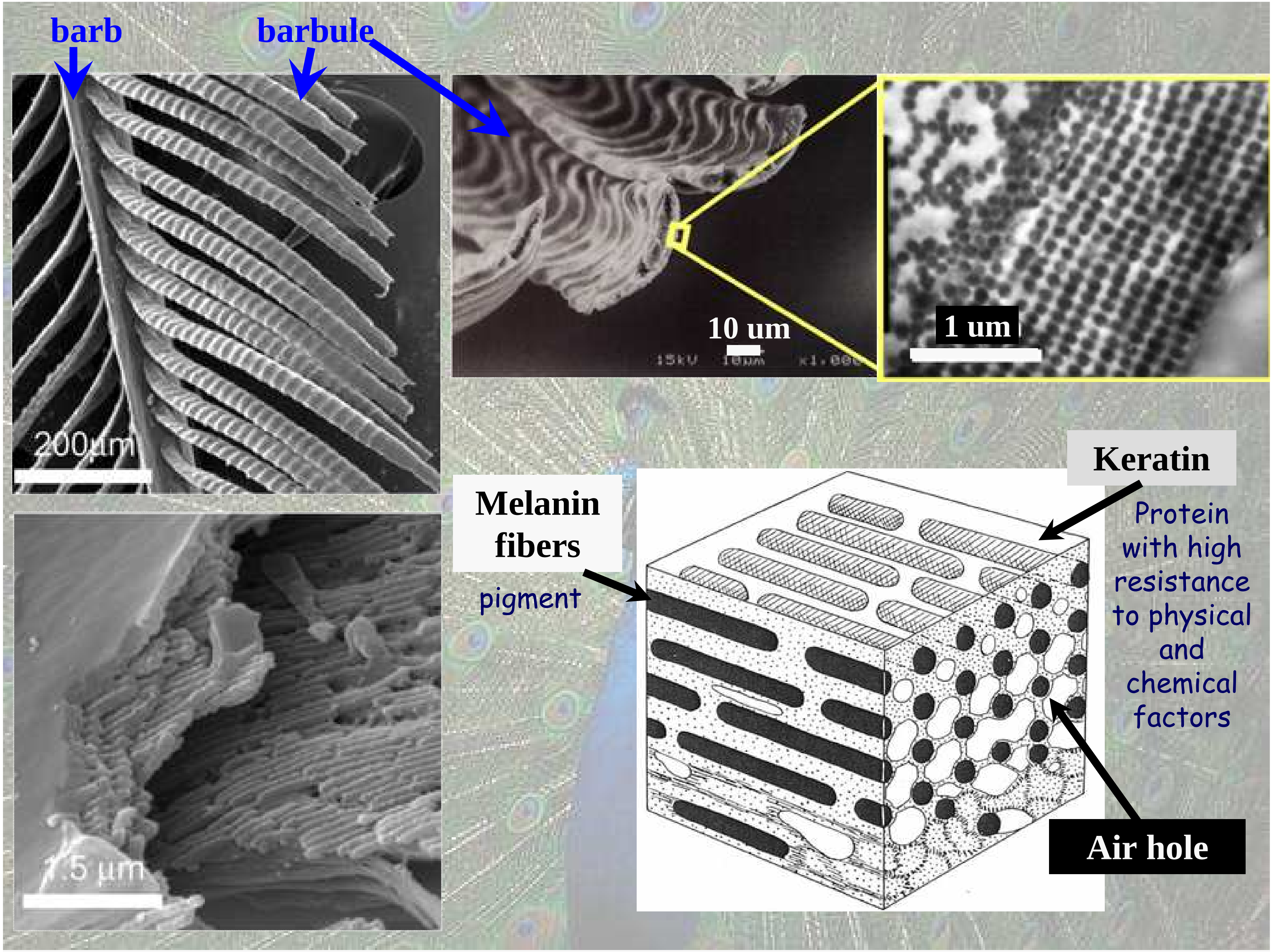
First PCF discovered in nature



A. R. Parker et al., NATURE, 409 (2001) 36.

A. R. Parker, Materials Today, Sept 2002


Barb
Barbule
Rachis
Hooks
Rachis
Calamus
Vane

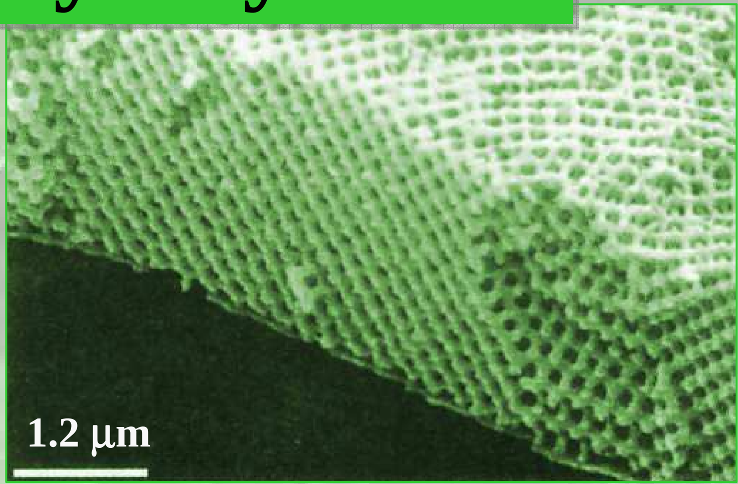


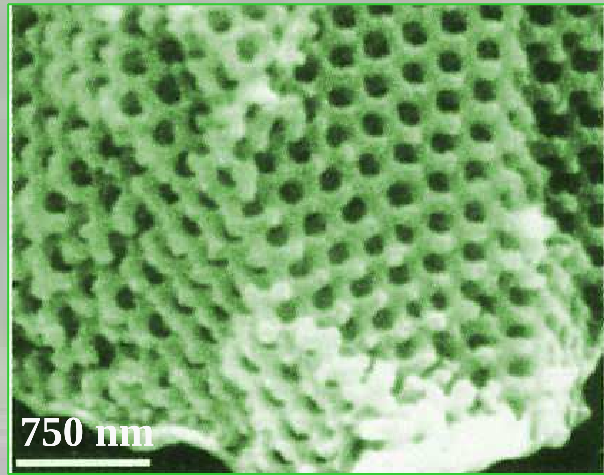
barb
barbule
200µm
10 um
15kV 10µm x1,000
1 um
1.5 µm
Melanin fibers
pigment
Keratin
Protein with high resistance to physical and chemical factors
Air hole


3 D structure
Parides sesostris

An easy way to 3D

Parides sesostris

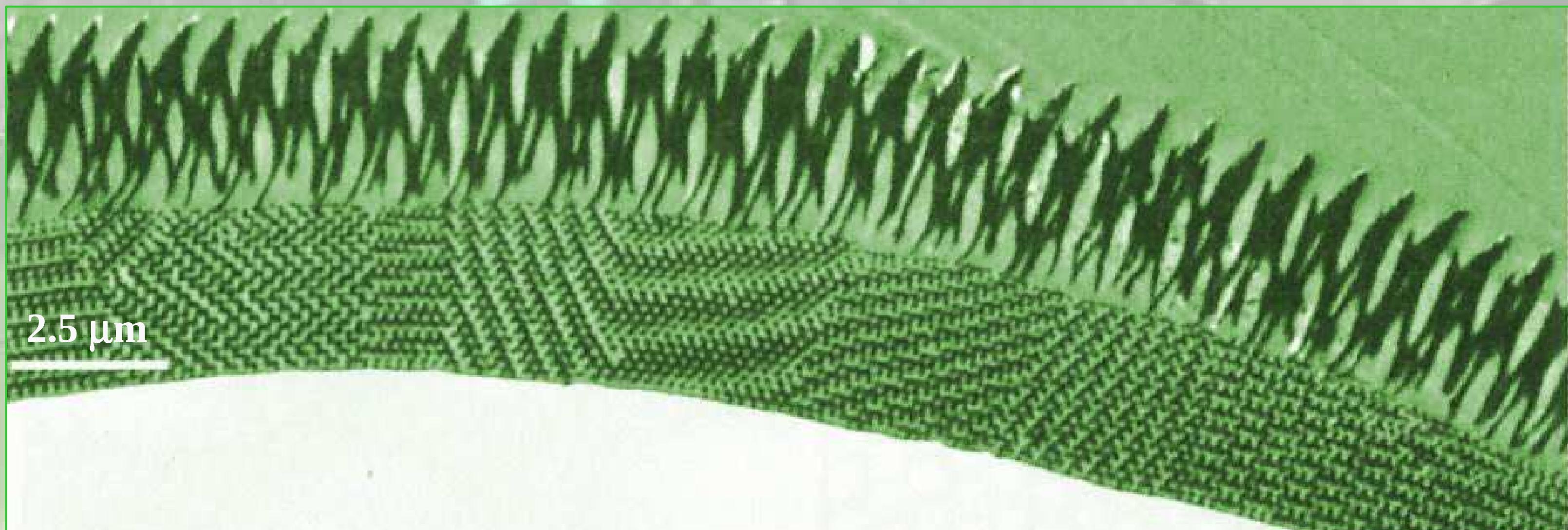




Neigbouring, but differently oriented, identical 3D structures

Green colour

Independent on the angle

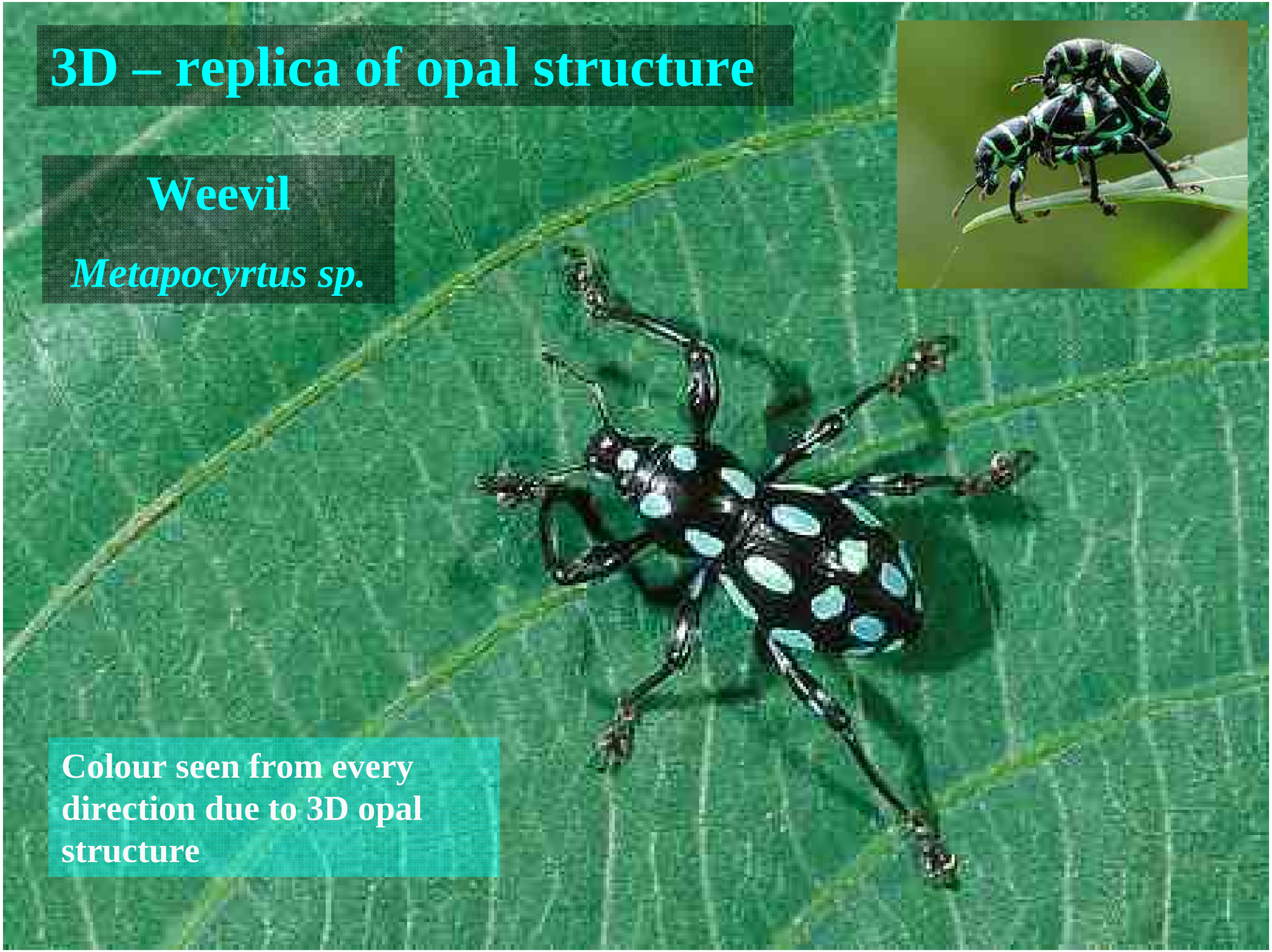


P. Vukusic, *Optical Interference Coatings*, Springer, New York, 2003.

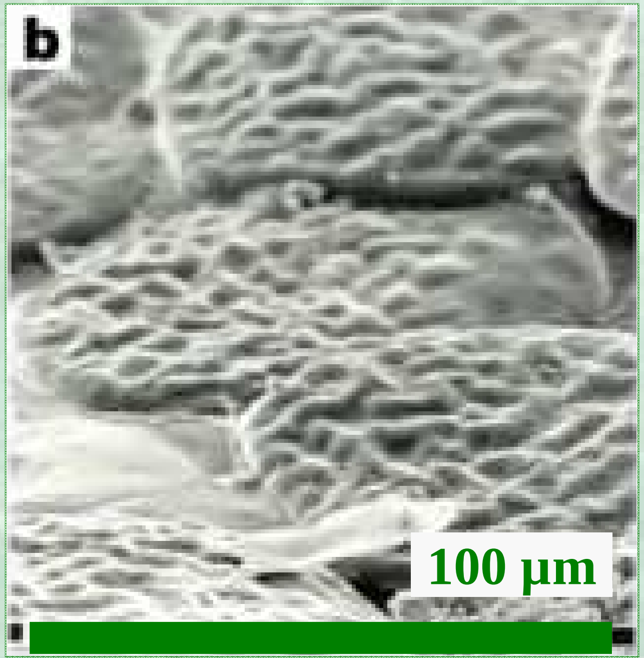
3D – replica of opal structure

Weevil

Metapocyrtus sp.



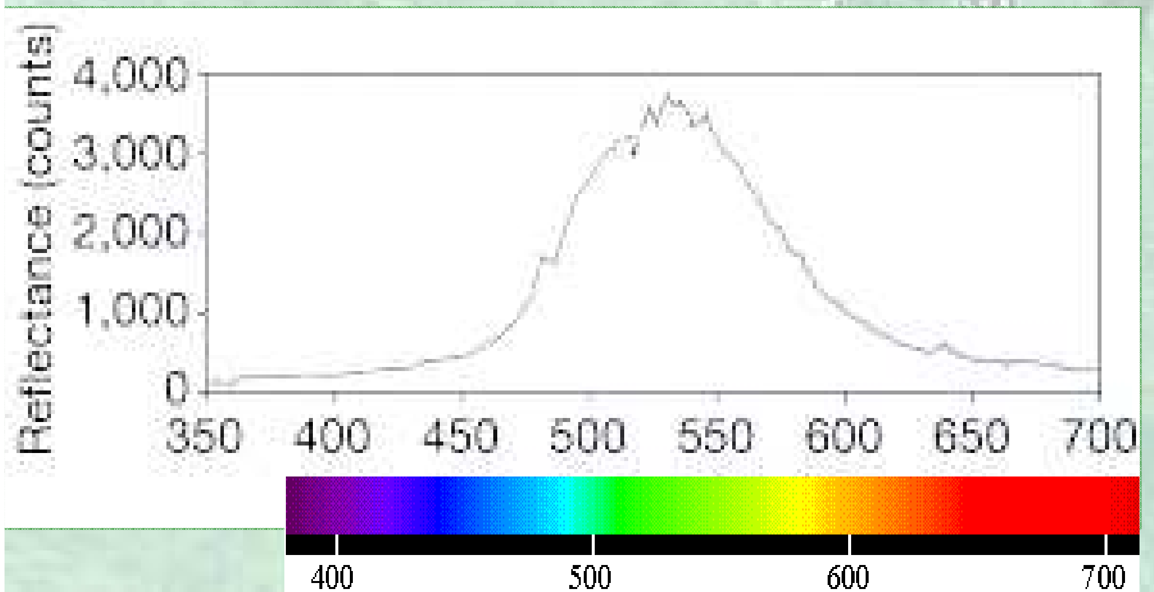
Colour seen from every direction due to 3D opal structure



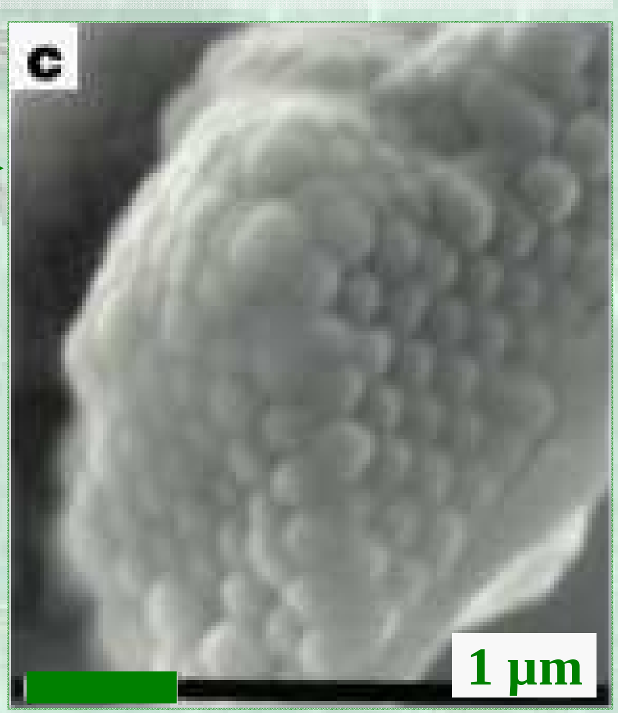
Scales placed parallel to the semicircular body

SCALE – Net of transparent spheres around 250 nm in diameter

Hexagonal close-packed structure

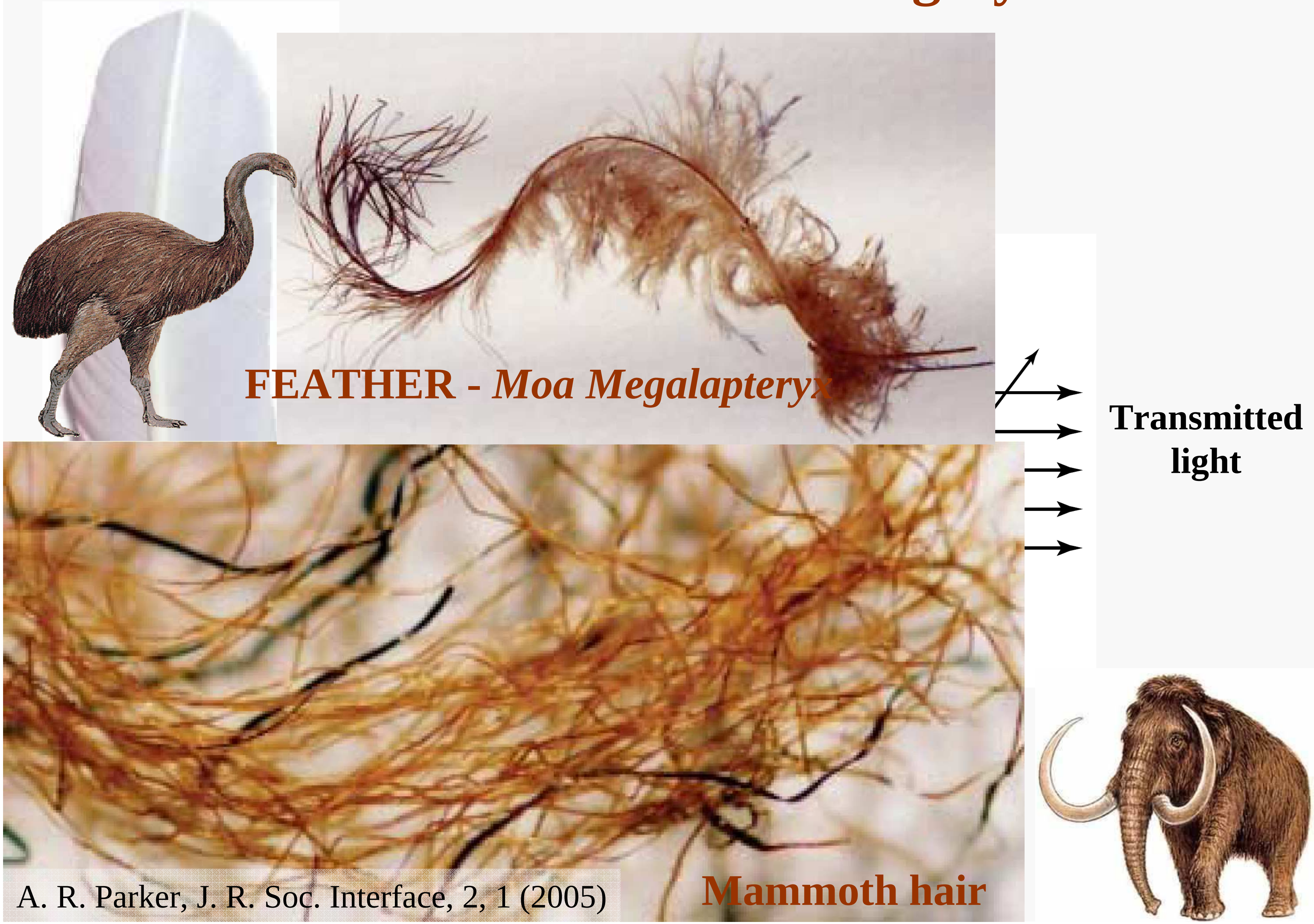


nm



A.R. Parker, Nature, 426, 786 (2003)

White colour → Brown/grey colour

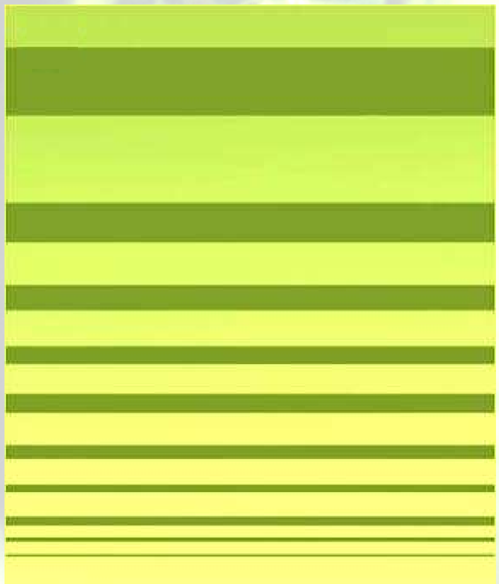


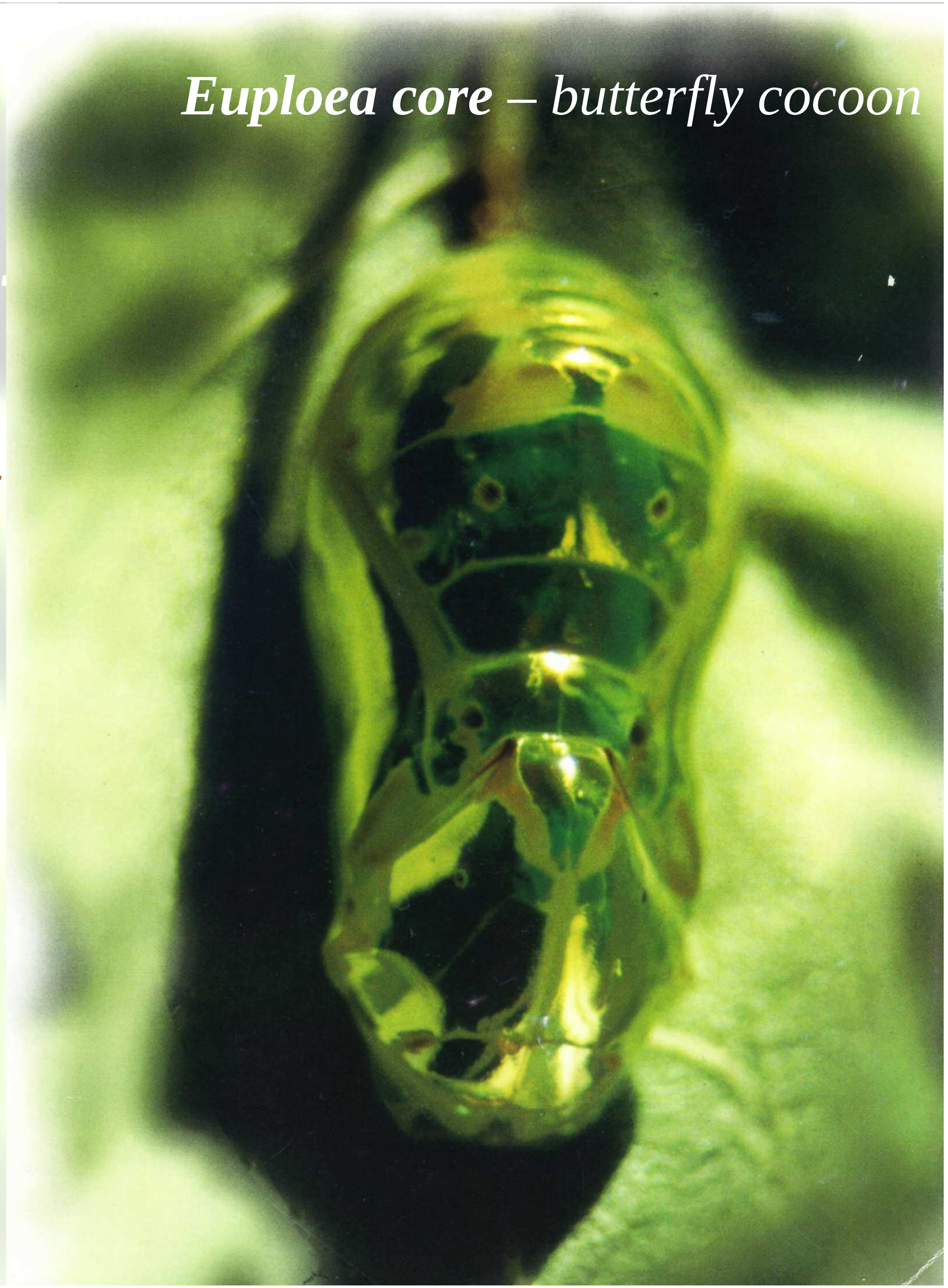
A. R. Parker, J. R. Soc. Interface, 2, 1 (2005)

Broadband reflection metallic lustre

Hangs in the environment with diffused light – reflects light – efficient camouflage

Metal lustre originates in many layers of chitin with different densities
The size of the layers decreases with depth



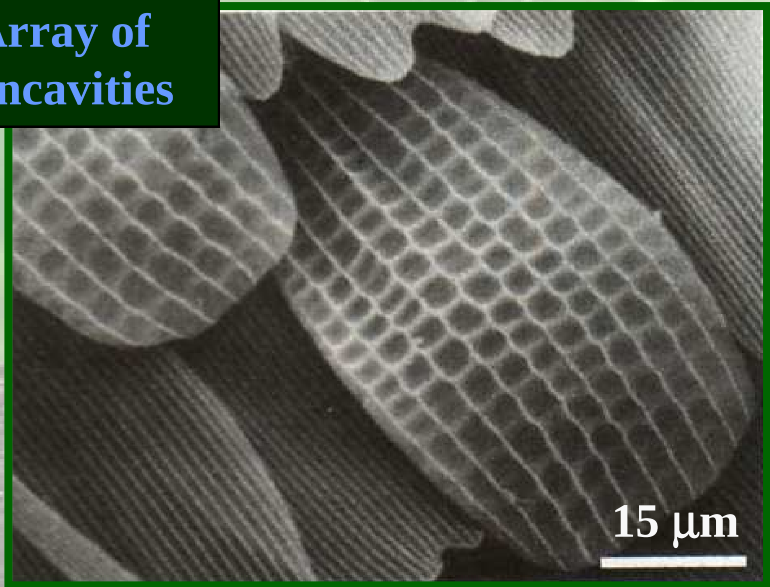


Pointillism in nature – additive colouring systems

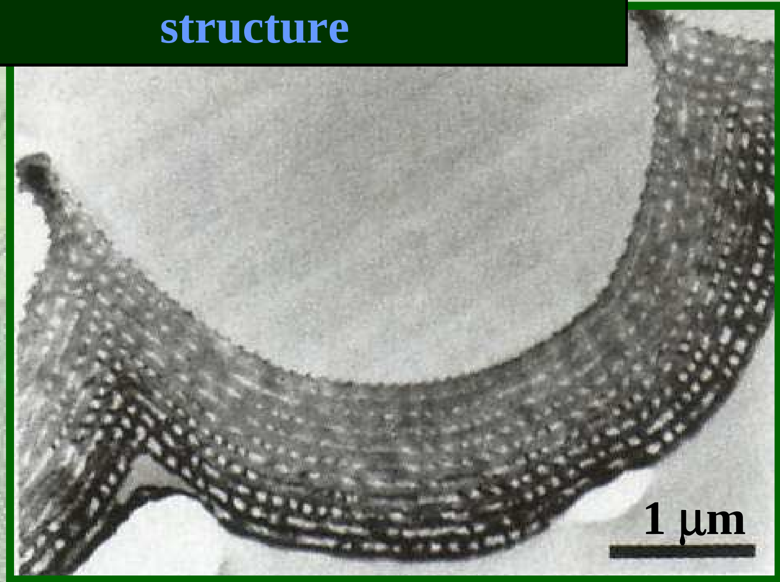
Papilo palinurus

***Pointillism** (z fr. pointiller) – neoimpresionistic technique of creating the paintings

Array of concavities

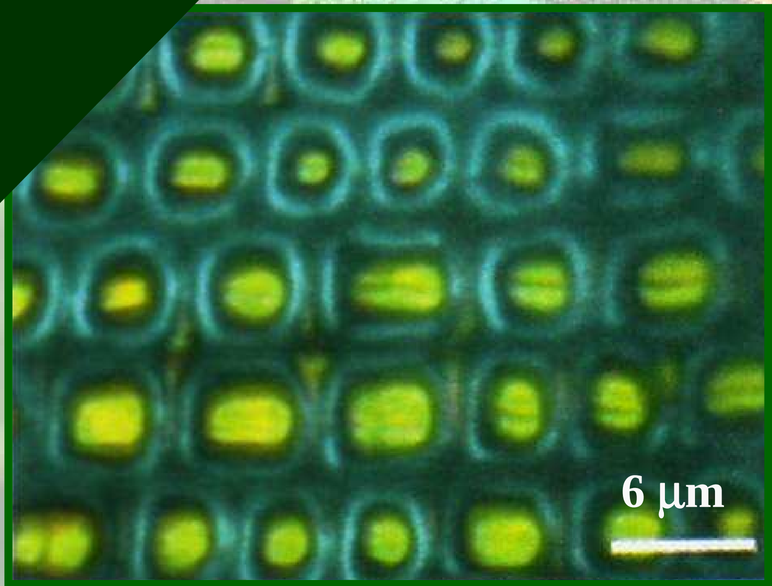


Curved multilayer structure

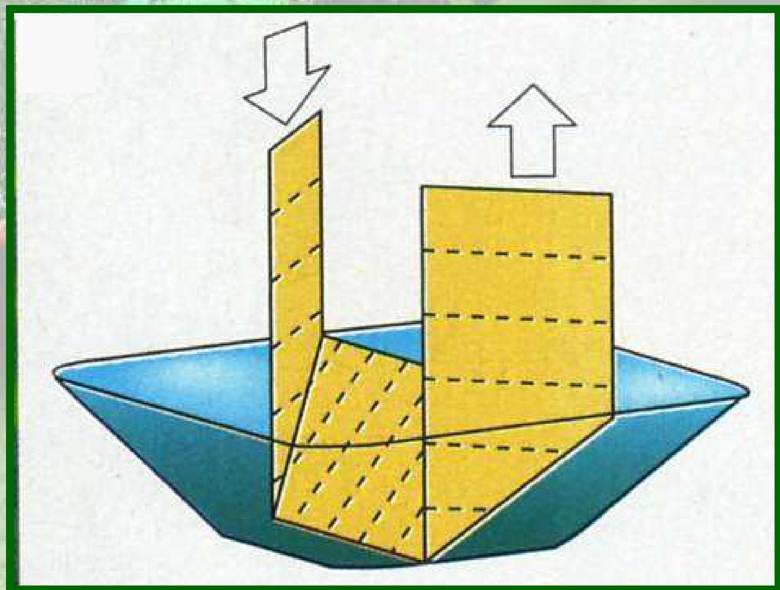


Structure produces two structural colours:

blue
and
yelow



BLUE – double reflection



P. Vukusic et al. Nature, 404 (2000) 457

Papilo palinurus

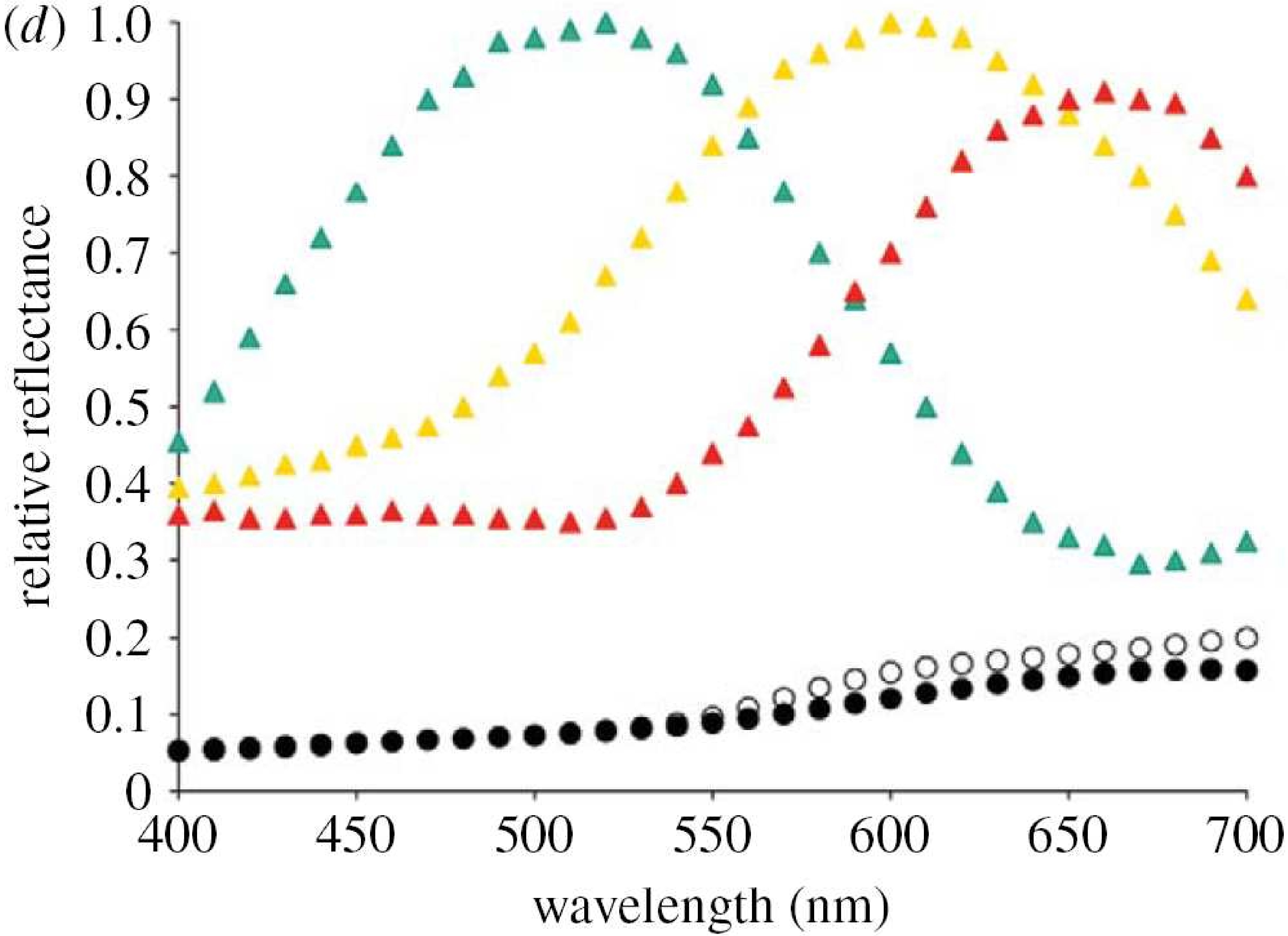
Cincidelinae

Cincindela hybrida

Cincidelinae are the quickest runners among insects in the world. If we take into account the human size, people would have to run 1200 km/h to be as quick as them

A. E. Seago et al. J. R. Soc. Interface, 6 (2009) S165

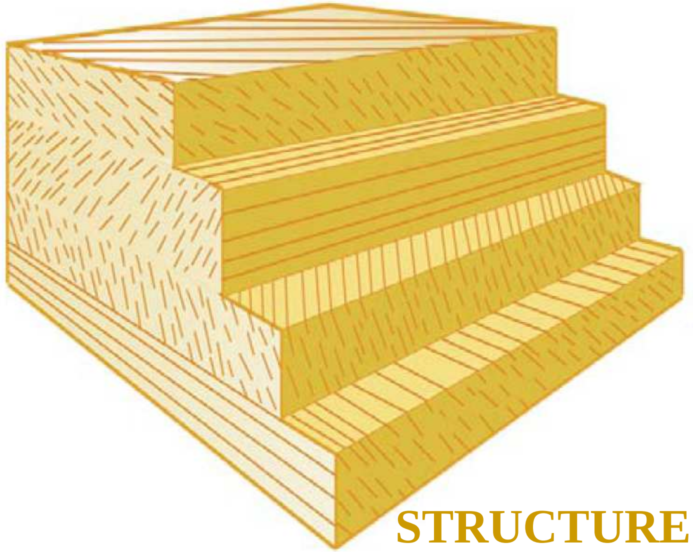

A. E. Seago et al. J. R. Soc. Interface, 6 (2009) S165.



A. E. Seago et al. J. R. Soc. Interface, 6 (2009) S165

Circularly polarized multilayer reflector

Beetle - Chrysina boucardi



← Birefringent chitin layers made of fibers arranged as helices

← Lattice period (the turn of a helice) = length of visible light

Beetle

Chrysina boucardi

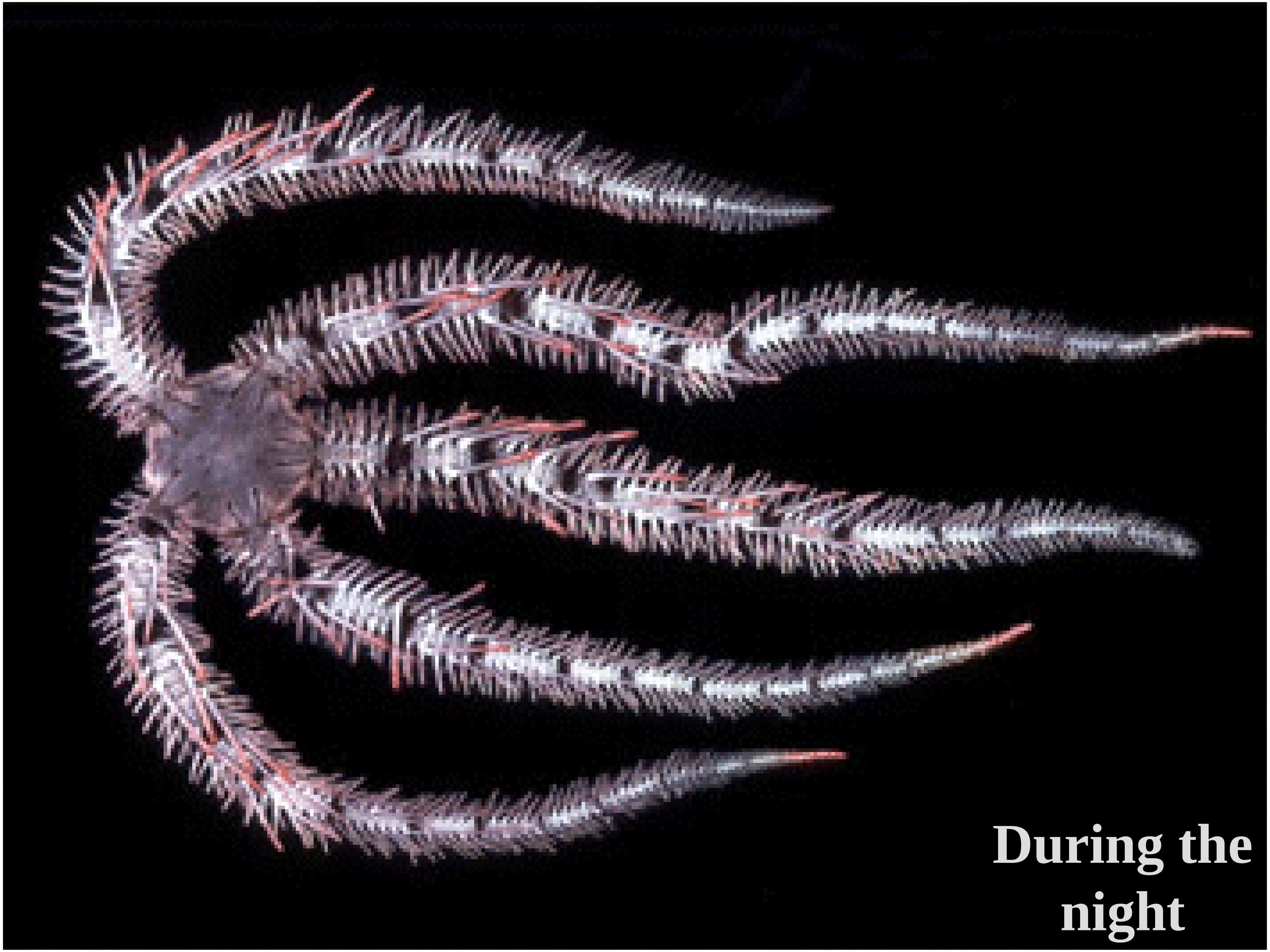
Observed through quarter wave plate rotated 0 deg.

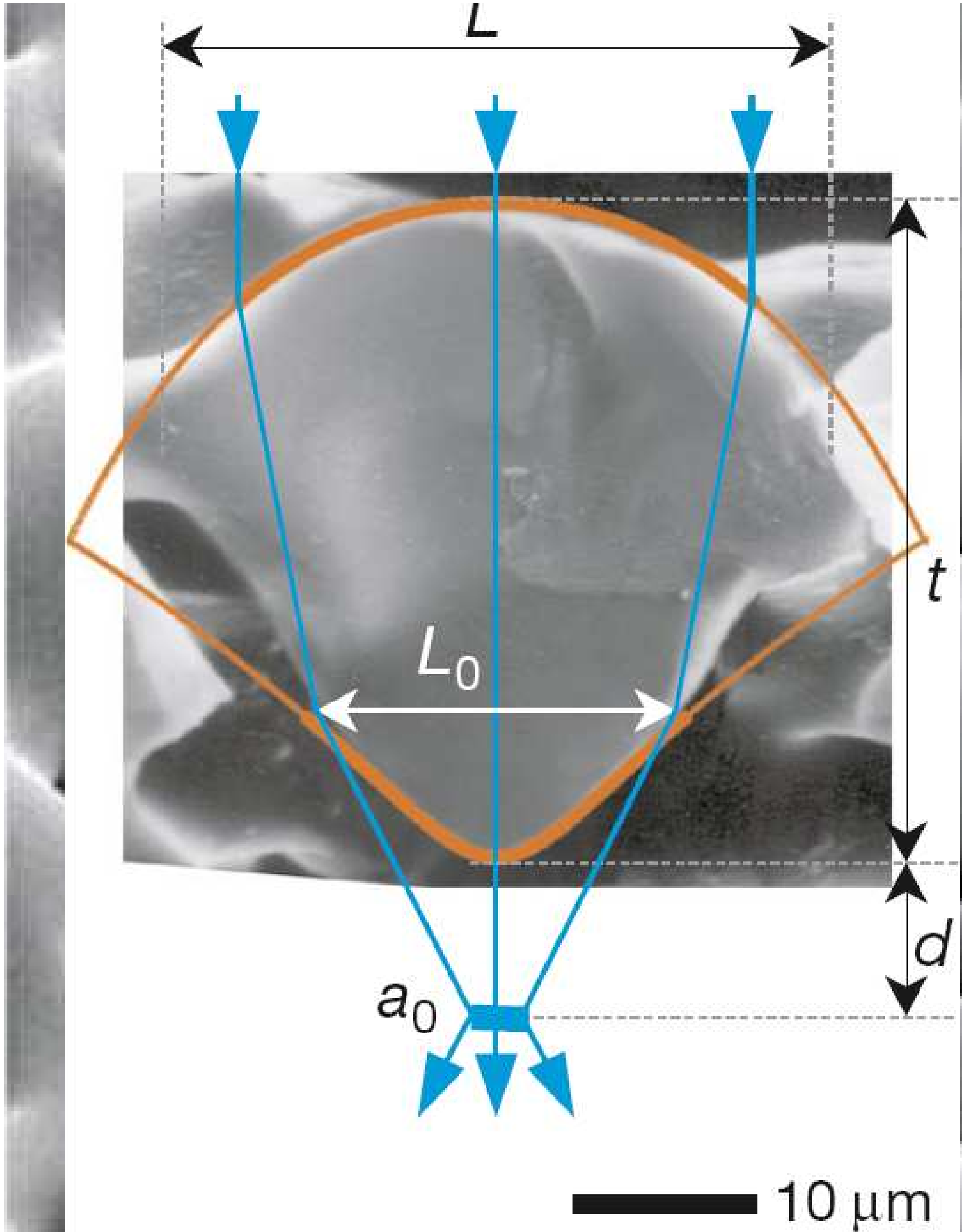
Beetle

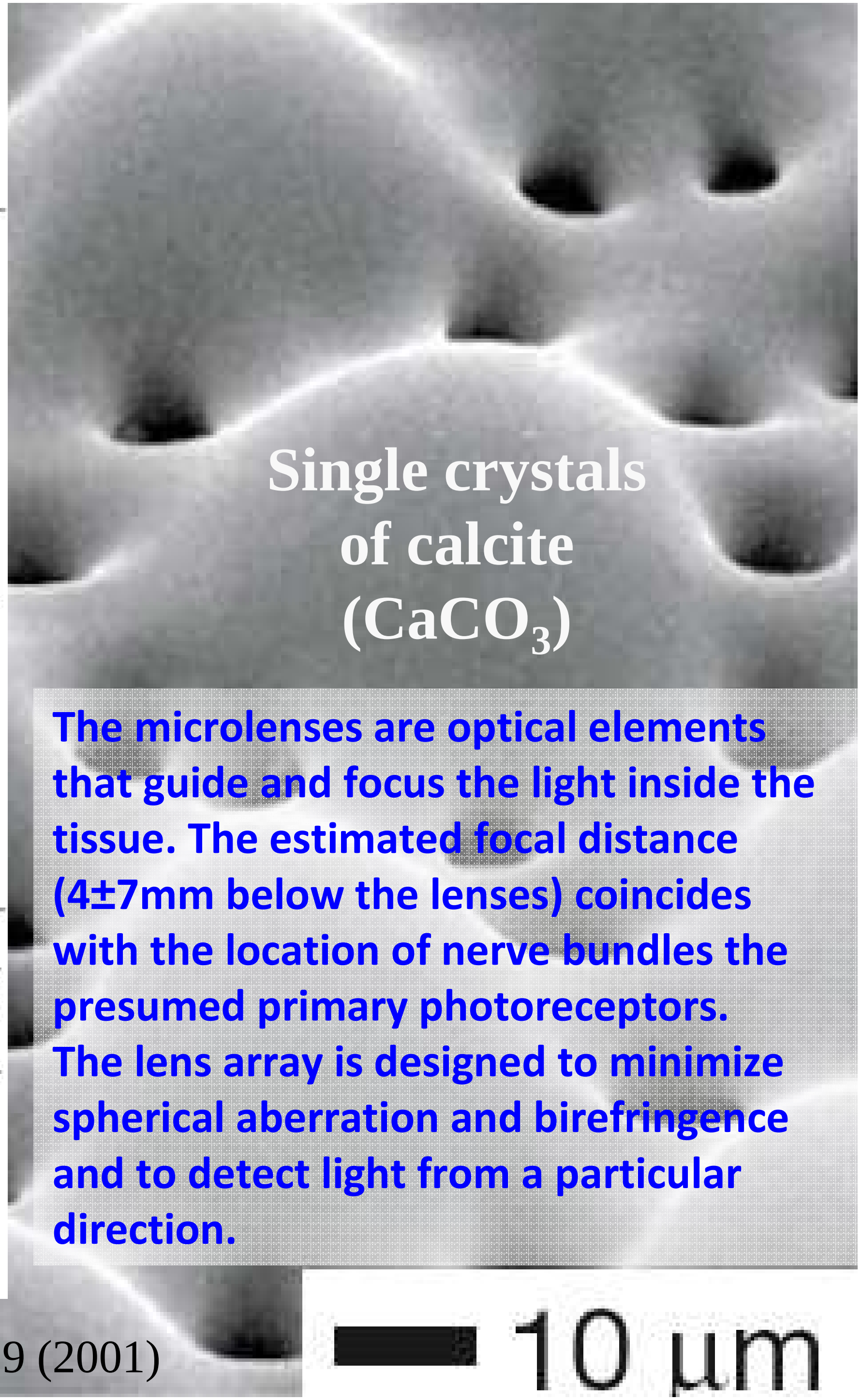
Chrysina boucardi

Observed through quarter wave plate rotated 90 deg. clockwise

A. E. Seago, J. R. Soc. Interface, 6, S165 (2009)


During the
night



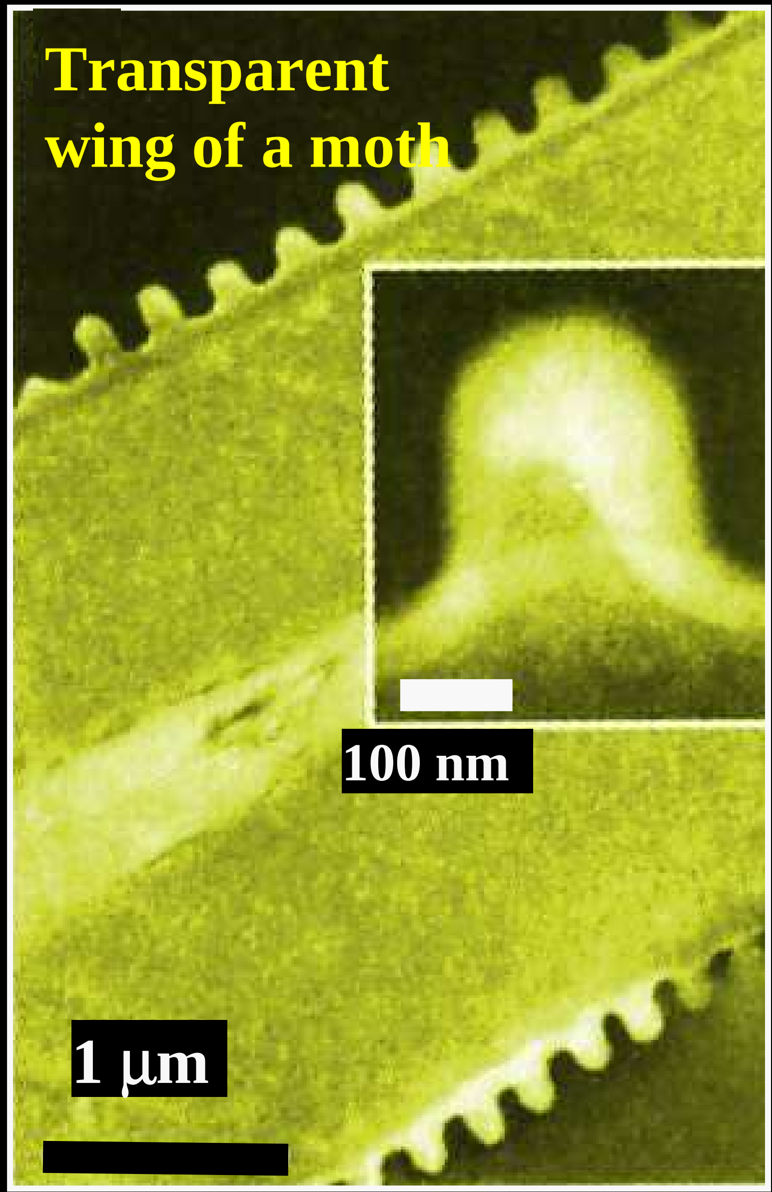


Single crystals of calcite ($CaCO_3$)

The microlenses are optical elements that guide and focus the light inside the tissue. The estimated focal distance (4±7mm below the lenses) coincides with the location of nerve bundles the presumed primary photoreceptors. The lens array is designed to minimize spherical aberration and birefringence and to detect light from a particular direction.

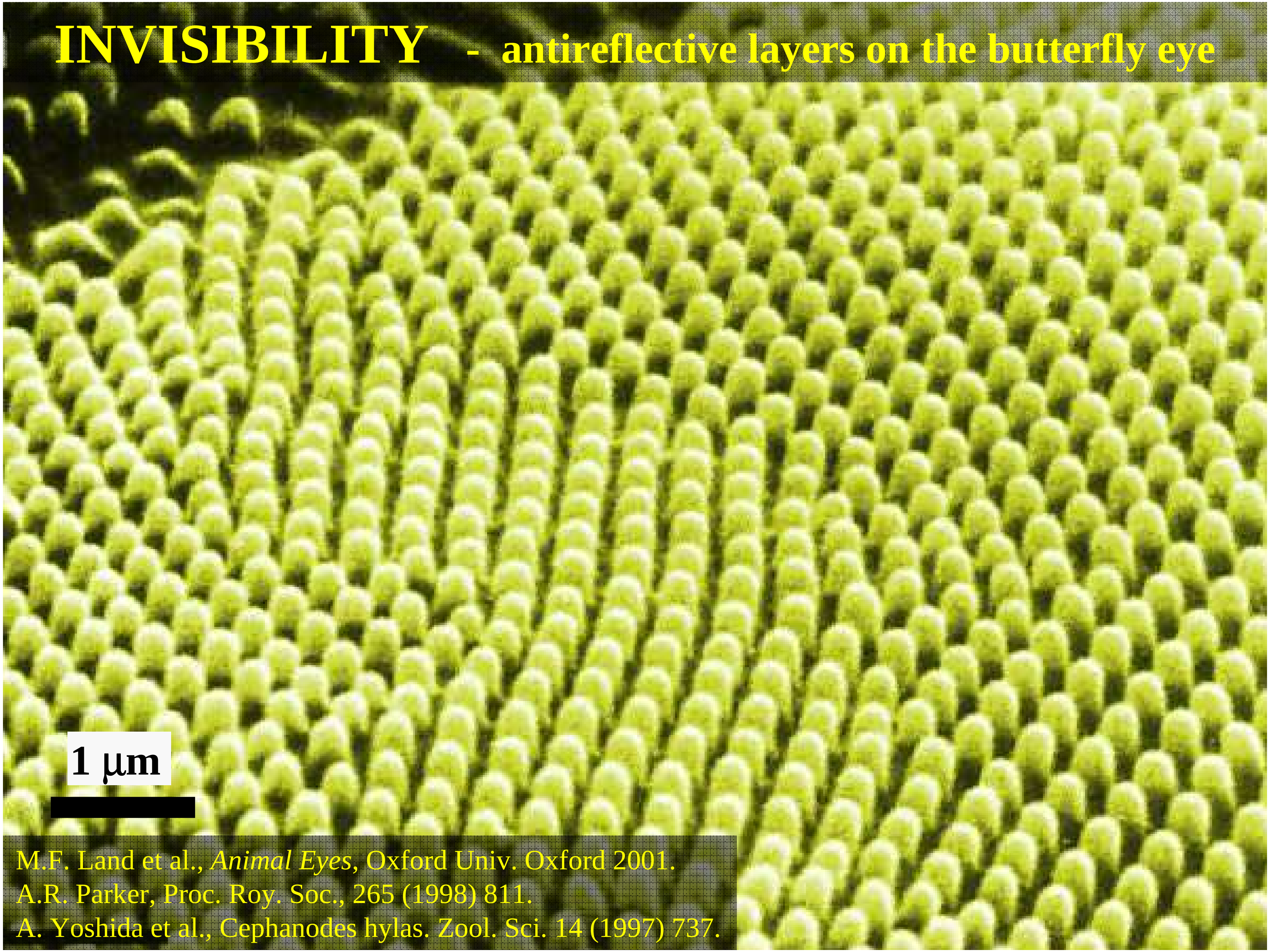
J. Aizenberg, Nature, 412, 819 (2001)

INVISIBILITY - antireflecting coating



M.F. Land et al., *Animal Eyes*, Oxford Univ. Oxford 2001.
A.R. Parker, Proc. Roy. Soc., 265 (1998) 811.
A. Yoshida et al., Cephanodes hylas. Zool. Sci. 14 (1997) 737.

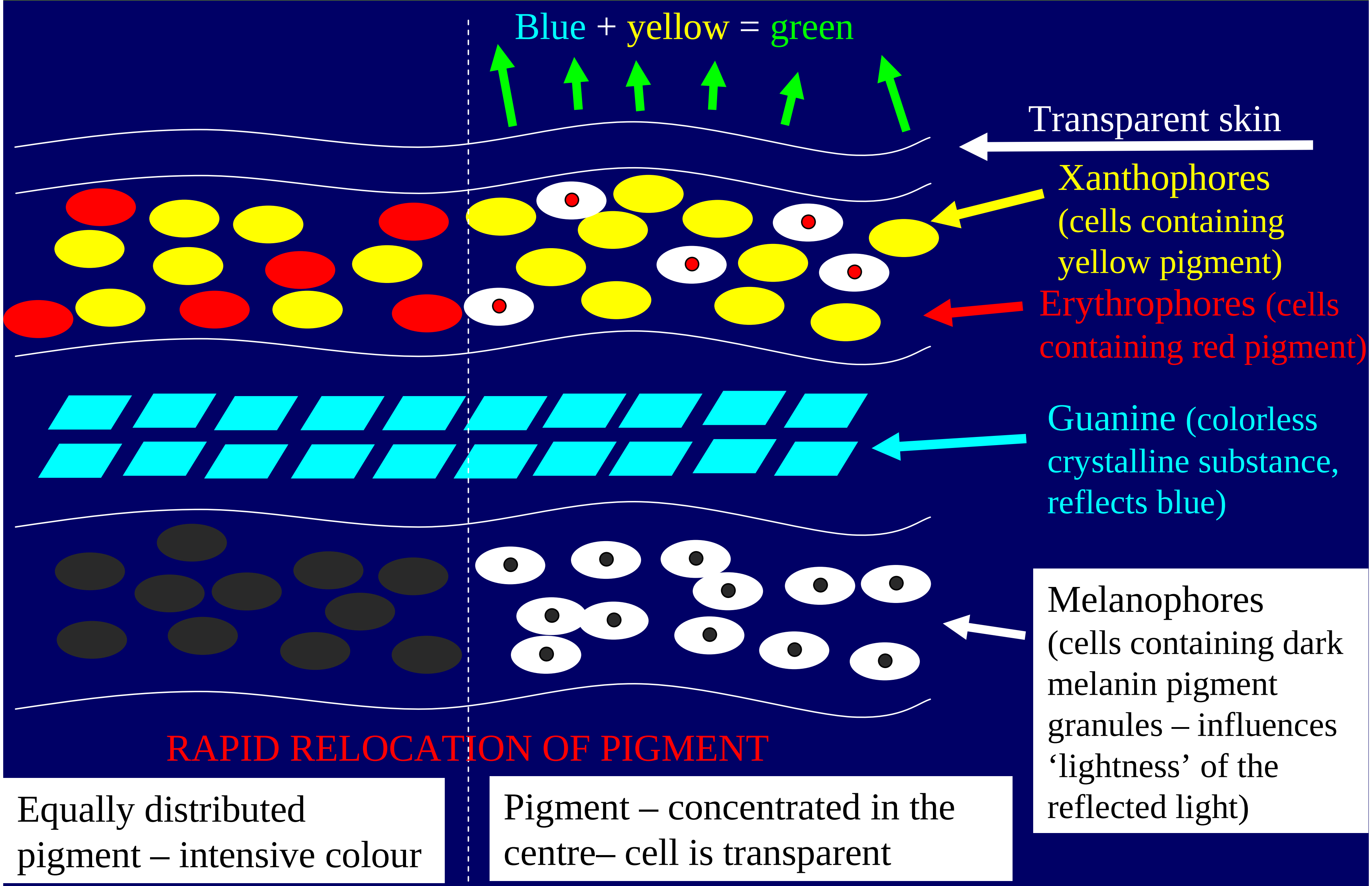
INVISIBILITY - antireflective layers on the butterfly eye



M.F. Land et al., *Animal Eyes*, Oxford Univ. Oxford 2001.
A.R. Parker, Proc. Roy. Soc., 265 (1998) 811.
A. Yoshida et al., Cephanodes hylas. Zool. Sci. 14 (1997) 737.

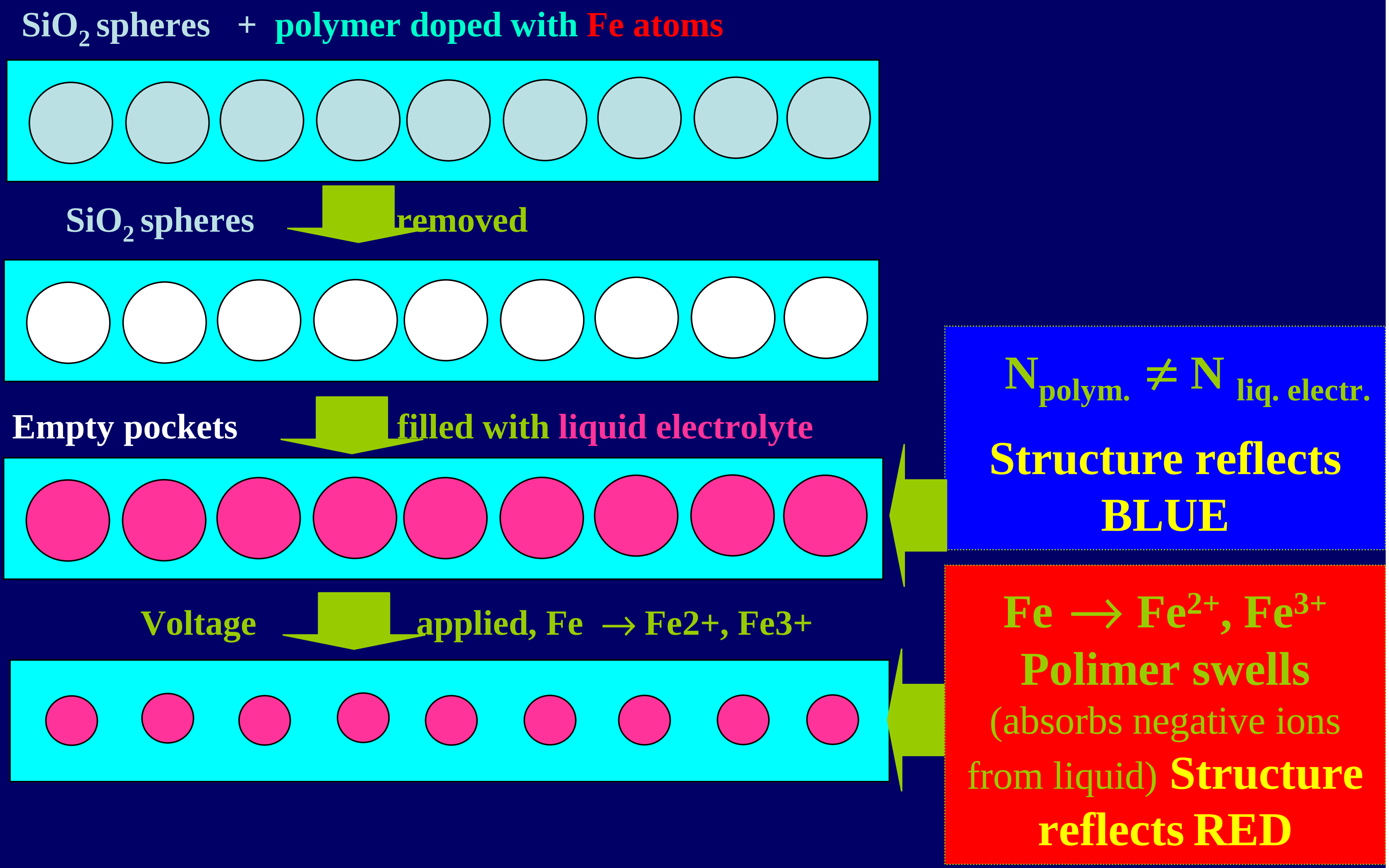
INVISIBILITY – dynamic camouflage of chameleon

CHAMELEON – dynamic stealth technology



Stuart-Fox, Moussalli, 2008. Selection for social signalling drives the evolution of chameleon colour change

Chameleon-like ‘opal’ can take on any colour



Angew. Chem. 2009, I. Manners, A. Arsenault et al.

Chameleon-like ‘opal’ can take on any colour

SHIFTING COLOUR ▶▶▶ pulse of voltage

CHANGING TIME
from blue to red ▶▶▶ < 1 sec

Mantaining COLOUR
in a given state ▶▶▶ no energy

APPLICATION ▶▶▶ Full-colour electronic paper

Angew. Chem. 2009, I. Manners, A. Arsenault et al.

Changing red from anger

dynamic change of colour in stress

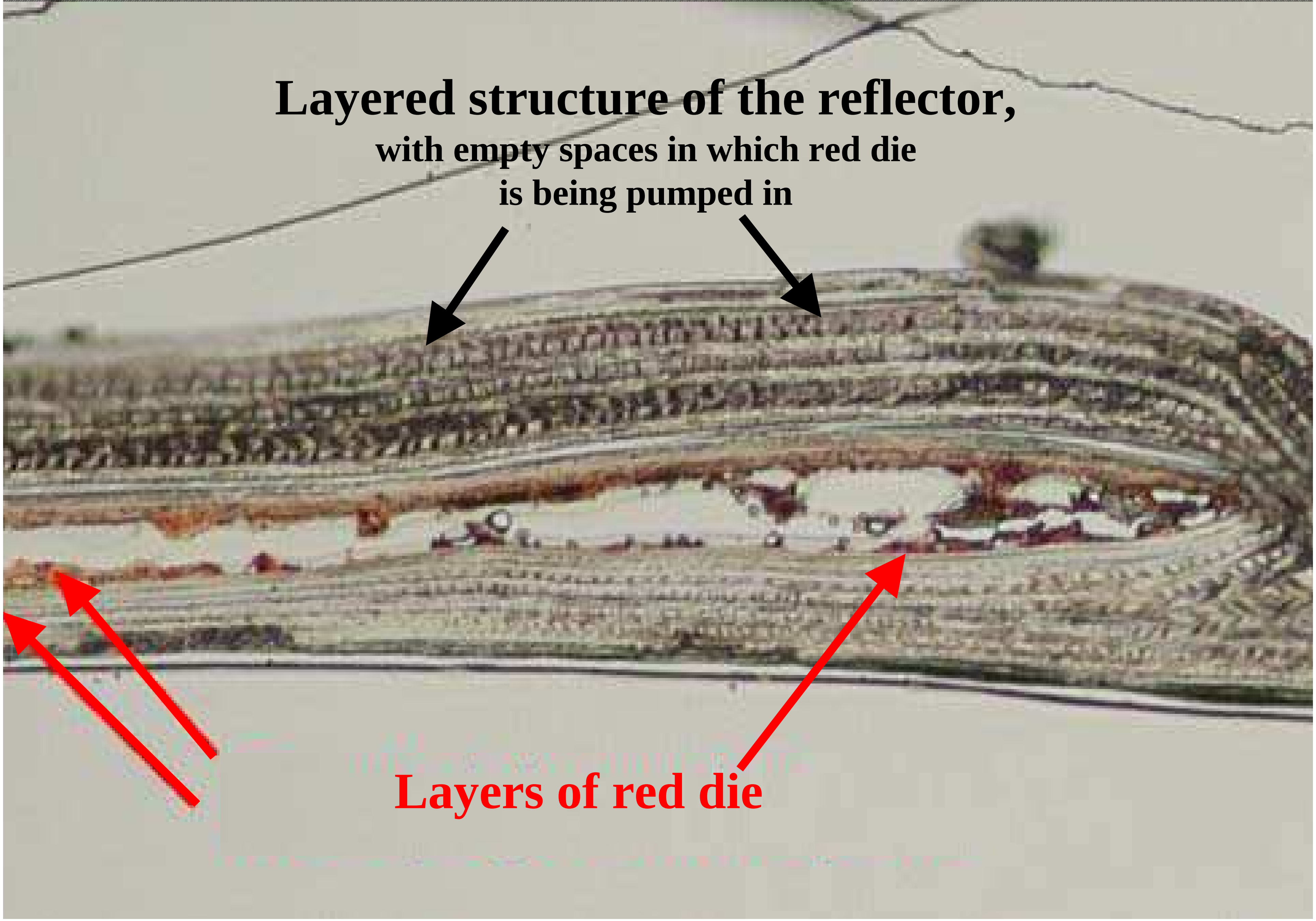
Tortoise beetles have broad, hard and strong armour, which goes well beyond borders of their body

Tortoise beetle

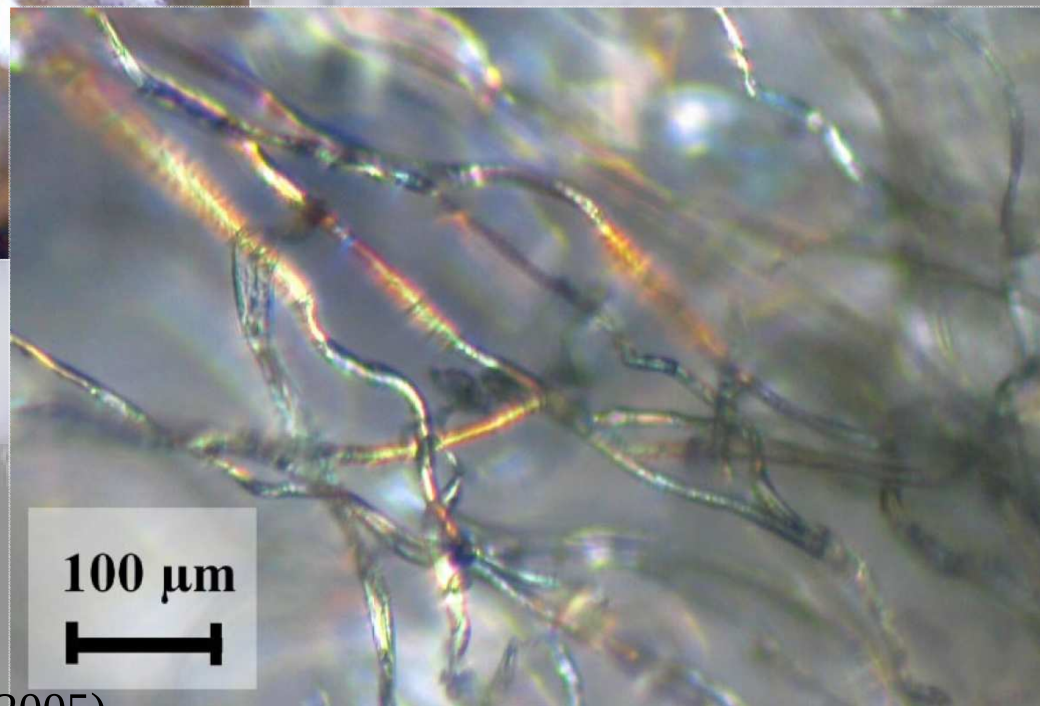
Charidotella egregia

J. P. Vigneron, Phys. Rev. B, 76, 031907 (2007)

Charidotella egregia - section through the lid



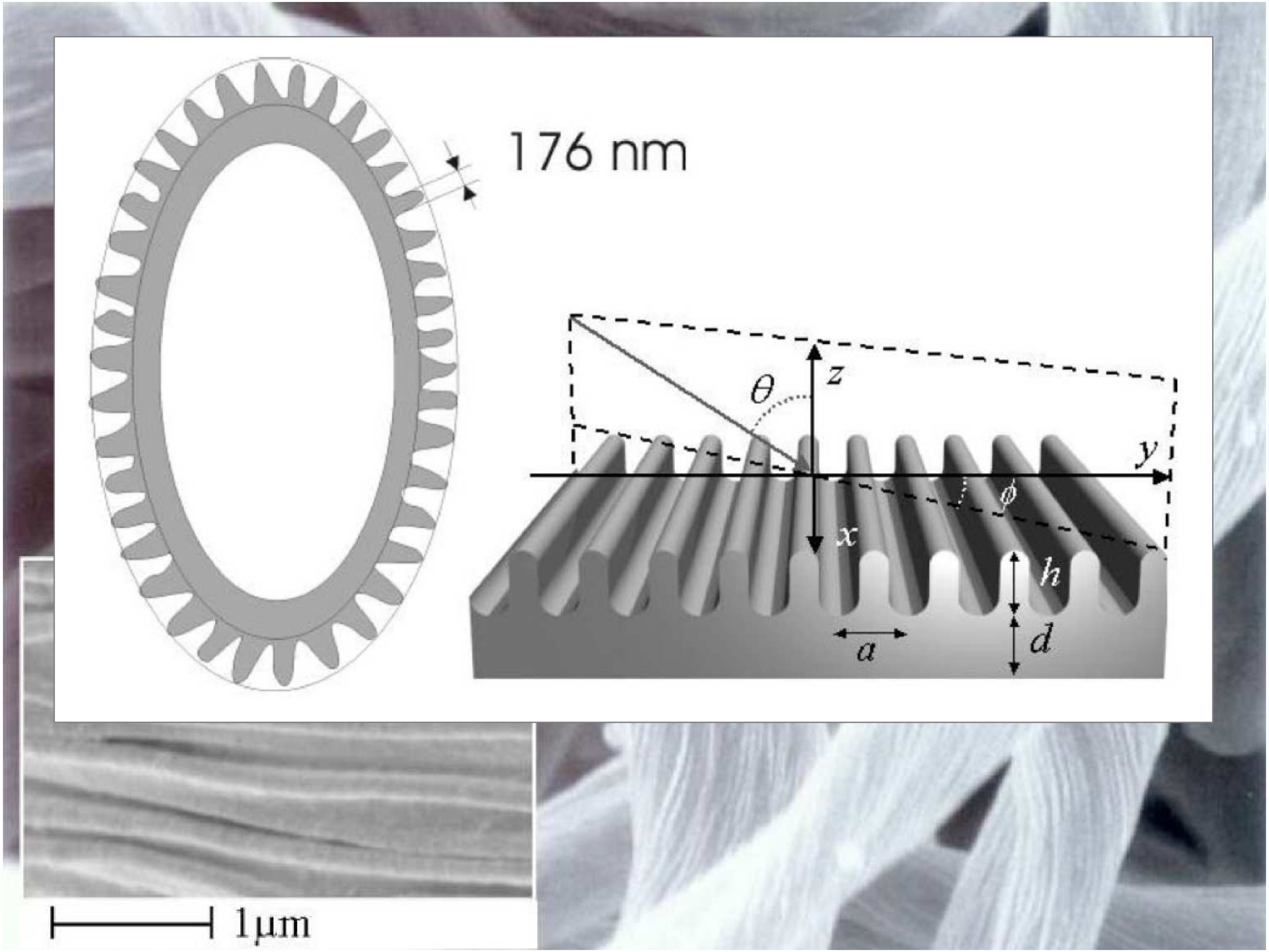
Multifunctional ‘wool’

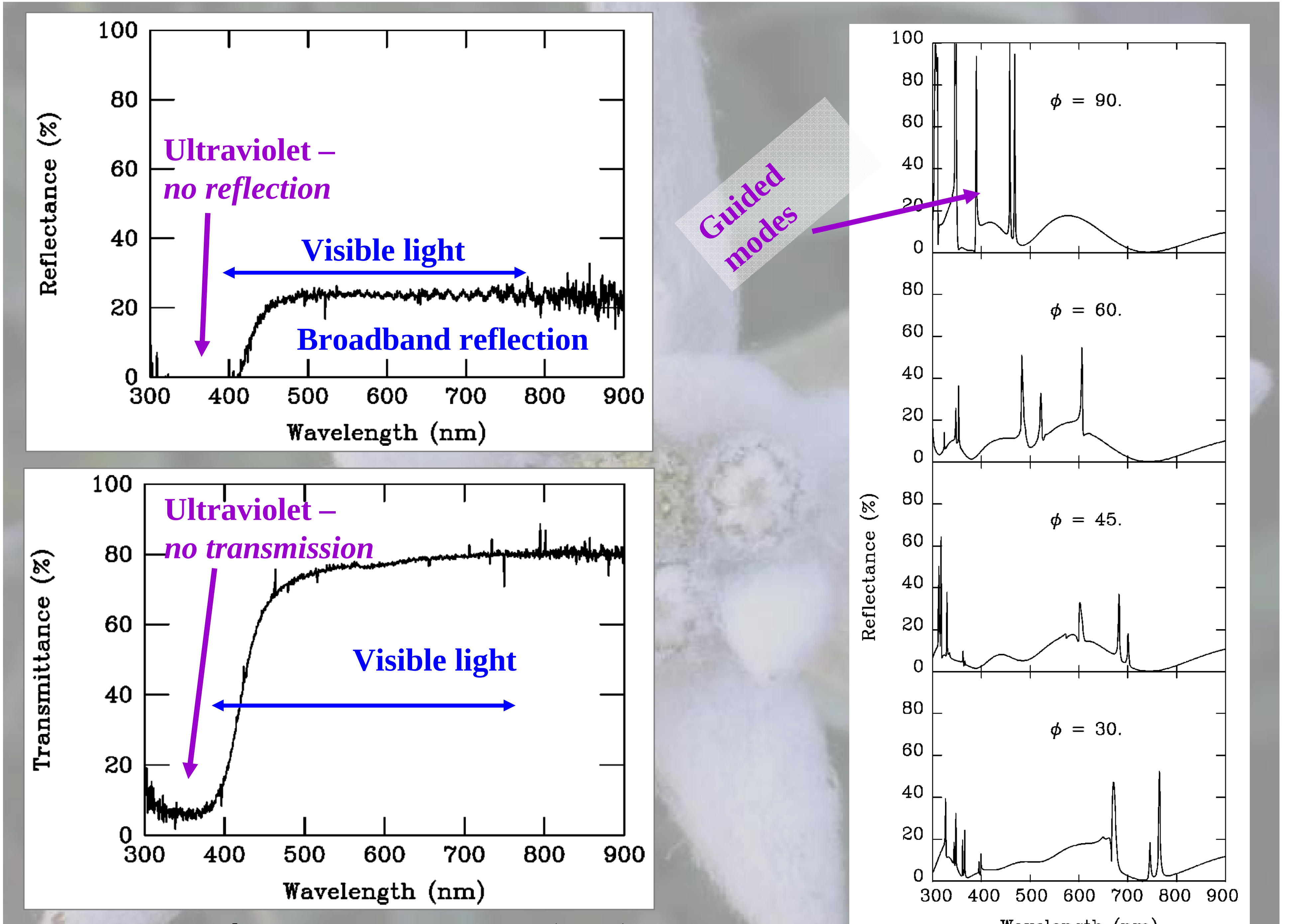


Edelweiss

Leontopodium nivale subsp. alpinum

J. P. Vigneron, Phys. Rev. E, 71, 011906 (2005)


176 nm
θ
z
y
ϕ
x
h
a
d
1μm



J. P. Vigneron, Phys. Rev. E, 71, 011906 (2005)


Thank you for your attention!