The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

2132-13

Winter College on Optics and Energy

8 - 19 February 2010

INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING

D. Comoretto
Universita' di Genova
Italy

INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING

DAVIDE COMORETTO

Dipartimento di Chimica e Chimica Industriale
Università di Genova

comorett@chimica.unige.it

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

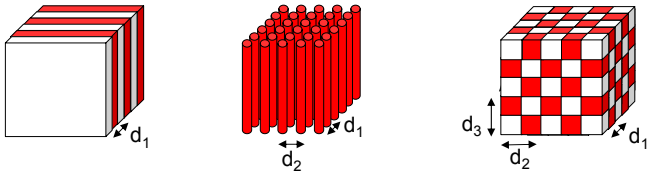
SUMMARY

INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING

- Photonic Crystals
- Natural Photonic Crystals
- Growth & Preparation of Photonic Crystals
- Photonic Crystals Theory
- Photonic Crystals Applications
- Photonic Crystal in Photovoltaic Devices

PHOTONIC CRYSTALS

1D 2D 3D



$d_j >> a_0$ (Bohr's radius)

$d_j \sim \lambda$ of visible light

→ The dielectric constant (ε) must be considered (dielectric lattice)

VOLUME 58, NUMBER 20 PHYSICAL REVIEW LETTERS 18 MAY 1987

Inhibited Spontaneous Emission in Solid-State Physics and Electronics

Eli Yablonovitch
Bell Communications Research, Navesink Research Center, Red Bank, New Jersey 07701
(Received 23 December 1986)

VOLUME 58, NUMBER 23 PHYSICAL REVIEW LETTERS 8 JUNE 1987

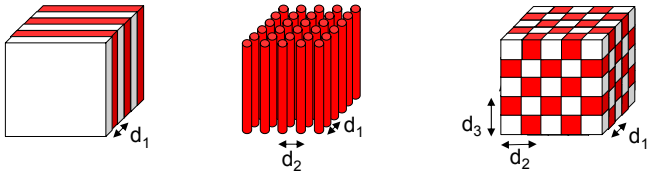
Strong Localization of Photons in Certain Disordered Dielectric Superlattices

Sajeev John
Department of Physics, Princeton University, Princeton, New Jersey 08544
(Received 5 March 1987)

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY, Trieste 8 – 19 February 2010

PHOTONIC CRYSTALS

1D 2D 3D

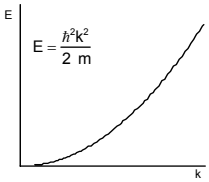


$d_j >> a_0$ (Bohr's radius)

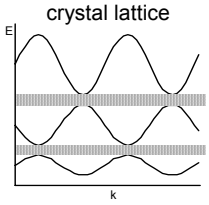
$d_j \sim \lambda$ of visible light

→ The dielectric constant (ε) must be considered (dielectric lattice)

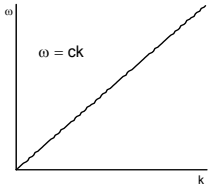
Free electron



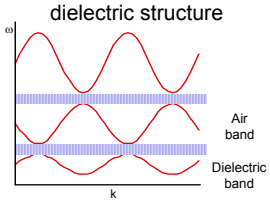
Electron in a crystal lattice



Photon in vacuum

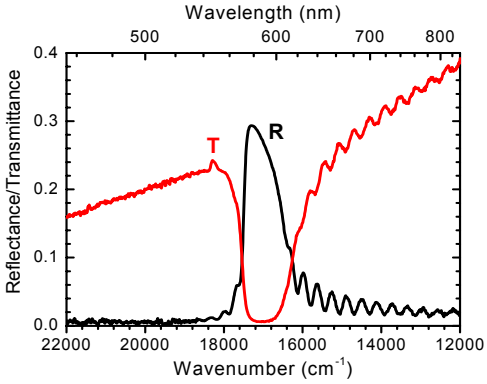


Photon in a periodic dielectric structure

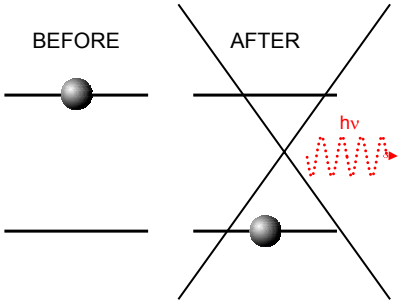


OPTICAL EFFECTS OF PHOTONIC BAND GAP

polystyrene opal film (Ø 260 nm)



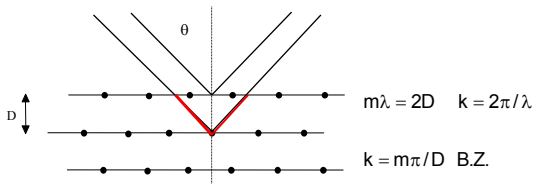
Photons having energy within the band gap cannot propagate inside the photonic crystals thus being backward diffracted

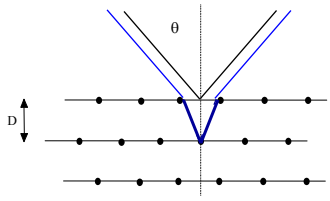


Inhibition of spontaneous emission (Purcell's effect)

BAND GAP FORMATION

$$E = \frac{\hbar^2 K^2}{2m} \quad \Leftarrow \quad \psi_K = e^{iKx} \quad \Rightarrow \quad \omega = K\frac{c}{n}$$





$$m\lambda = 2D\cos(\vartheta) = 2D\sqrt{1-\sin^2(\vartheta)}$$

$$m\lambda = 2D\sqrt{n_{eff}^2 - \sin^2(\vartheta)}$$

$$\psi_\pm = e^{iKx} \pm e^{-iKx}$$

The **electronic** band gap formation is due to the **electron waves** coherently scattered from **different potential regions**

The **photonic** band gap formation is due to the **electromagnetic fields** coherently scattered at **the interfaces between different dielectric regions**

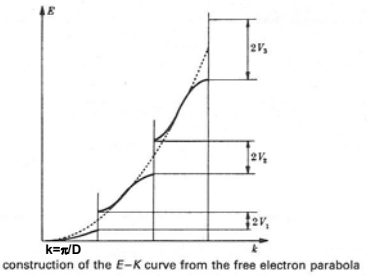
BAND GAP FORMATION

$$\psi_{\pm} = e^{iKx} \pm e^{-iKx}$$

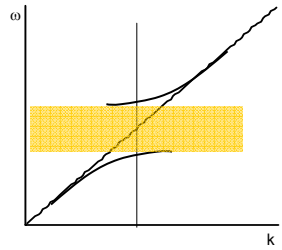
$$V_{\pm} = \frac{1}{L}\int \left|\psi_{\pm}\right|^2 V(x)\,dx = \pm V_n$$

Potential energy for the two waves is different (V(x) Kronig-Penney potential), while kinetic one is unchanged

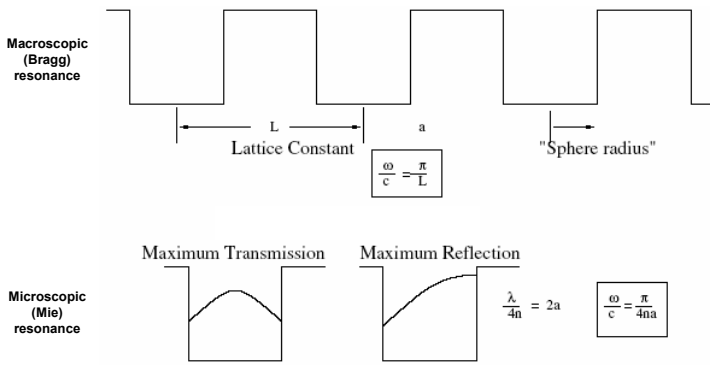
$$E_{\pm} = \frac{\hbar^2 K^2}{2m} \pm V_n$$



construction of the *E*–*K* curve from the free electron parabola

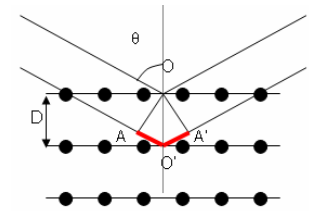


BAND GAP FORMATION



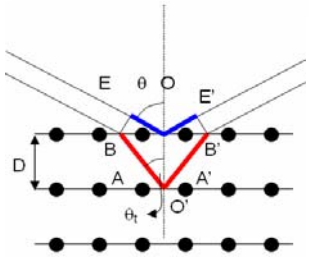
- A different way to explain the origin of the band gap concerns the role of Mie and Bragg scattering. The former is a microscopic process at the single repetition unit, while the latter involve the array.
- A photonic band gap appears when **the density of dielectric scatterers is such that the microscopic (Mie) scattering resonance of a single unit cell of the PC occurs at the same frequency as the macroscopic (Bragg) resonance of the periodic array.**
- The **Bragg** scattering condition is $\lambda = 2L$, where λ is the vacuum wavelength of light.
- **Mie** resonance in one dimension occurs when a quarter wavelength fits into a single well $\lambda/(4n) = 2a$.
- Combining these two conditions yields the optimal volume filling fraction $f \equiv 2a/L = 1/(2n)$.

BAND GAP: BRAGG-SNELL LAW



$$m\lambda = 2D\cos\theta = 2D\sqrt{1-\sin^2\vartheta}$$ Bragg's law

$$n_i \sin\theta_i = n_t \sin\theta_t$$ Snell's law



$$m\lambda = 2D\sqrt{n_{eff}^2 - \sin^2\theta}$$ Bragg-Snell law

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY, Trieste 8 – 19 February 2010

SUMMARY

INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING

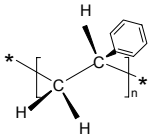
- Photonic Crystals
- Natural Photonic Crystals
- Growth & Preparation of Photonic Crystals
- Photonic Crystals Theory
- Photonic Crystals Applications
- Photonic Crystal in Photovoltaic Devices

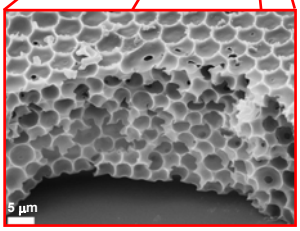
NATURAL PHOTONIC CRYSTALS

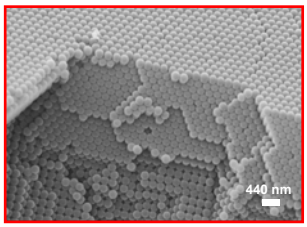
- Natural photonic crystals are mainly due to self-organization: suitable building blocks self-assemble in mesomorphic structures.
- Such structures might have different degree of order and this affects both the optical response of the system as well as the associated biological function.

EFFECT OF NANOSTRUCTURE ON THE TRANSPARENCY OF POLYSTYRENE

Transparent amorphous polystyrene





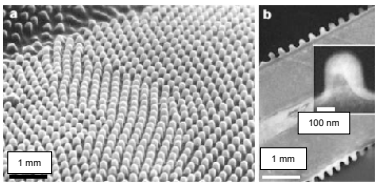


M. Civardi et al., Langmuir 21, 3480 (05)

Highly diffusing (white) microstructured polystyrene film cast from CS_2 solutions in a wet environment

Colloidal opal photonic crystal (iridescent) grown by vertical deposition of monodisperse polystyrene microspheres

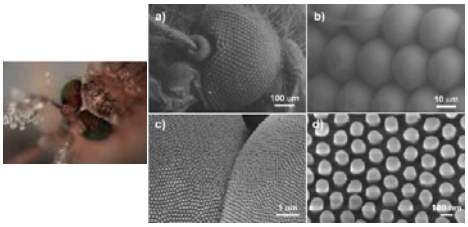
NANOSTRUCTURED MEDIA IN NATURE



Anti-reflecting ripple arrays on (a) arthropoda ommatidia and (b) transparent wings of a diurnal moth.

Nanostructures allow to tune the refractive index from bulk to air in a continuous way thus reducing dielectric contrast and then reflection

P. Vukusic and J.R. Sambles, Nature 424, 852 (2003)

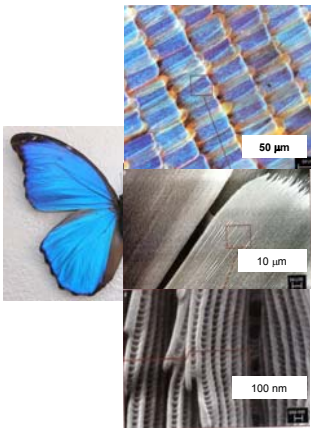


Compound eyes of the mosquito *C. pipiens* possess ideal superhydrophobic properties that provide an effective protective mechanism for maintaining clear vision in a humid habitat. This unique property is attributed to elaborate micro- and nano-structures:

- hexagonally close-packed (hcp) ommatidia at the **microscale** efficiently **prevent fog droplets trapping** in the voids between the ommatidia.
- hexagonally non-close-packed (ncp) nipples at the **nanoscale prevent microscale fog droplets condensation** on the ommatidia surface

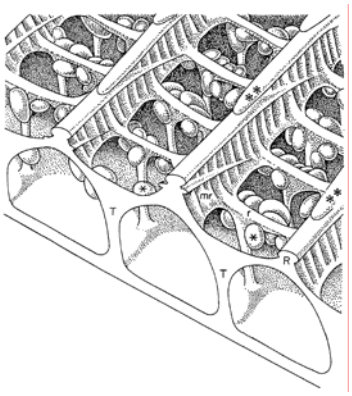
X. Gao et al. Adv. Mater. 19, 2213 (2007)

NATURAL PHOTONIC CRYSTALS

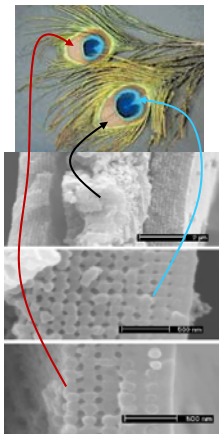


Butterfly wings
"Morpho"

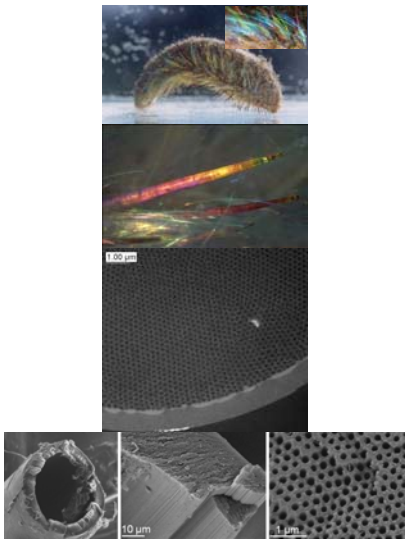
Fig. 3. Diagrammatic representation of part of a fractured scale showing the relationship between the lower lamina, trabeculae (T), ridges (R), lamellae (**), ribs (r), and microribs (mr). This view also shows pigment granules (*), not present in all scales.



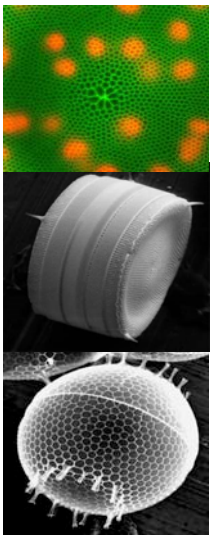
NATURAL PHOTONIC CRYSTALS



Peacock feathers



Sea mouse



Diatomee

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

A PHOTONIC CRYSTAL FISH

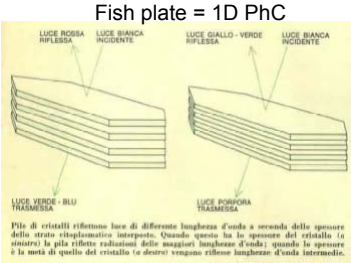
I riflettori dei pesci

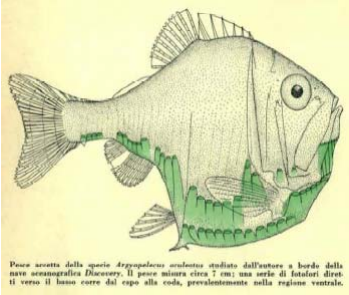
Molti pesci producono sostanze azotate che cristallizzano in strati riflettenti speculari. Nelle squame e sulla pelle questi strati hanno funzione ornamentale e mimetica; in altri casi migliorano la visione

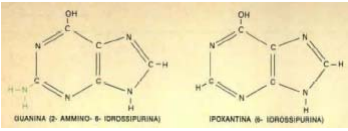
Le Scienze 32, 92 (1971)

di Eric Denton

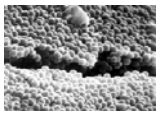
Fish plate = 1D PhC



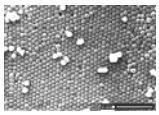


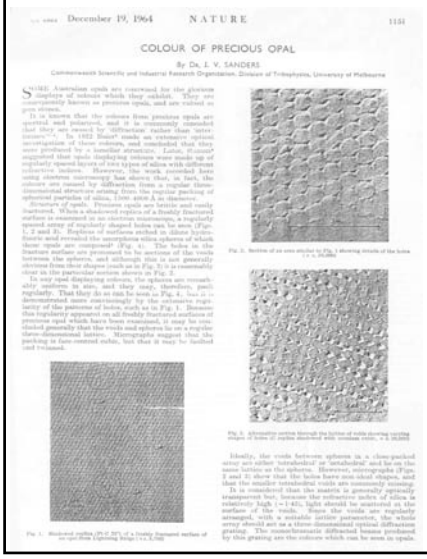


- 1D PhC: multilayer composed of molecular crystals layers (n_1=1.8) alternate to cytoplasma (n_2=1.33).
- High reflectance is observed since $\lambda/4$ condition is achieved ($\lambda/4=n_1d_1=n_2d_2$).



OPAL STRUCTURE AND PHOTONIC CRYSTALS



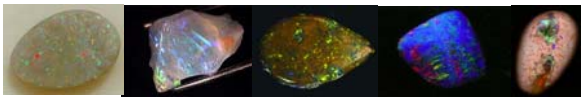


December 19, 1964 NATURE 1151

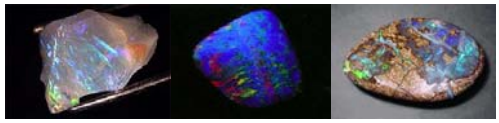
COLOUR OF PRECIOUS OPAL

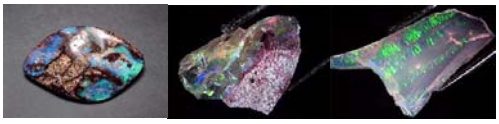
By Dr. J. V. SANDERS

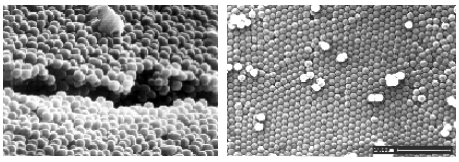
- Name of the products derived from natural ageing of silica hydrogels under high pressure and temperature.
- Sanders, showed the structure of opals and provided a rough explanation for their colors.
- From the Old Greek υπαλλος "To see the changing of the color".
- From the Latin **OPALLUS**, derived from the Sanskrit "Gem stone".

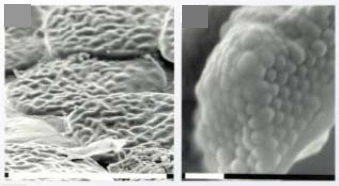


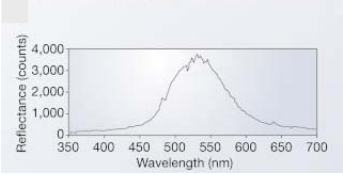
NATURAL AND ARTIFICIAL OPALS











SUMMARY

INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING

- Photonic Crystals
- Natural Photonic Crystals
- Growth & Preparation of Photonic Crystals
- Photonic Crystals Theory
- Photonic Crystals Applications
- Photonic Crystal in Photovoltaic Devices

PHOTONIC CRYSTALS GROWTH

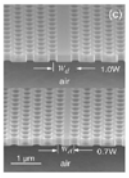
TOP-DOWN

Bulk materials are carved to obtain the periodic dielectric constant nano-structure.

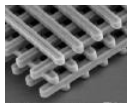
- Selective etching of the substrate below a mask. → 2D
- Electron beam or X-ray lithographic techniques. → 3D
- Two-photon polymerization

1D

2D

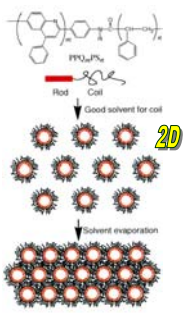


3D

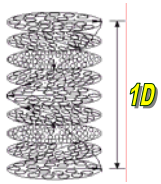


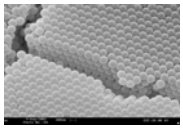
BOTTOM-UP

The photonic crystal is grown by self-assembly of both nano-units (e.g. spheres) or supramolecular aggregates (cholesteric liquid crystals, multi-block copolymers).



Science 283, 372 (99)





3D

TWO-PHOTON POLYMERIZATION FOR 3D-MICROFABRICATION AND DEFECT-WRITING

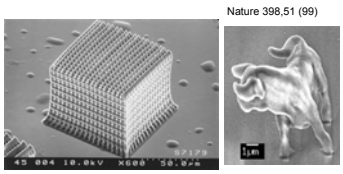
Two-photon excitation provides a means of activating chemical or physical processes with high spatial resolution in 3D and has made possible the development of

- 3D Fuorescence imaging
- Optical data storage
- Lithographic microfabrication.

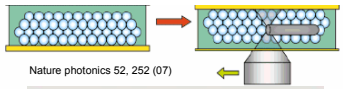
$$TPA \div I^2_{laser}$$

$$TPA_{volume} \div \lambda^3_{laser}$$

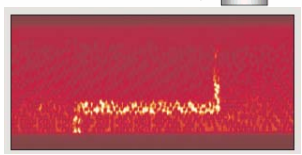
Photo-chemical reaction are confined to TPA_{volume} small volumes

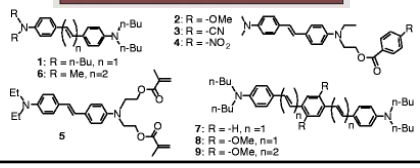


Nature 398,51 (99)

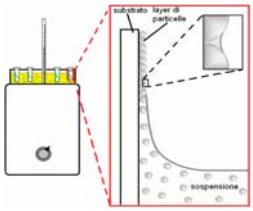


Nature photonics 52, 252 (07)



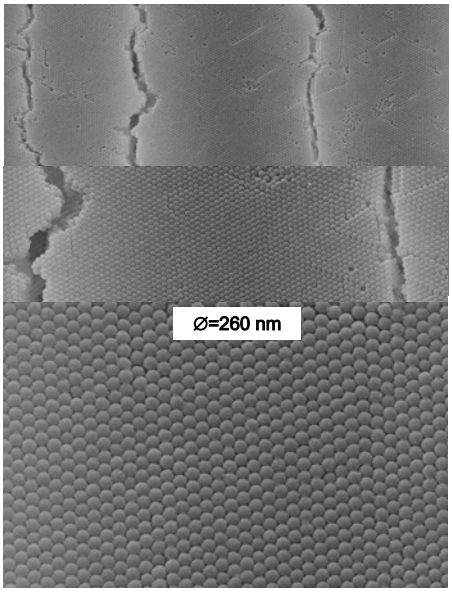


ARTIFICIAL OPALS



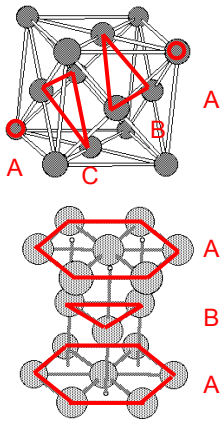
- T=**55°C**
- μ-sphere concentration **0,05%**

- T=**45°C**
- μ-sphere concentration 0,**025%**



HARD SPHERES PACKING

- Freezing of hard spheres is one of the most dramatic illustrations that crystalline order can be entropy driven.
- the FCC (ABCABC…) phase is more stable than HCP (ABABAB…) one by 9±2 10^{-4} $K_B T$ per particle.
- As the free-energy difference between the two phases is very small, the spontaneous generation of stacking faults is quite common (randomly stacked hexagonal close-packed, RHCP, crystallites).



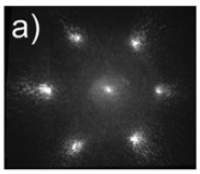
To estimate the rate at which the FCC phase grows from the RHCP phase, we need to estimate the relative free energy:

1. The difference in bulk free energies per particle of the pure FCC and HCP phases, $\Delta f = f_{HCP} - f_{FCC}$.
2. The interfacial free energy $\gamma_{HCP\text{-}FCC}$, which is the measure of the additional free-energy cost to create an FCC-HCP interface.
3. The stacking entropy of the RHCP phase (K_B ln 2 per plane).

Phys. Rev. Lett. 63, 2753 (89)
Phts. Rev. Lett. 79, 3002 (97)

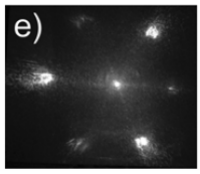
D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

LIGHT DIFFRACTION TO PROBE ORDER



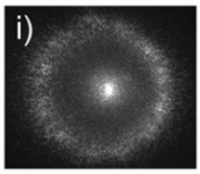
1 layers

All spots have same intensity (H)



6 layers

2 different set of spot intensity (FCC)



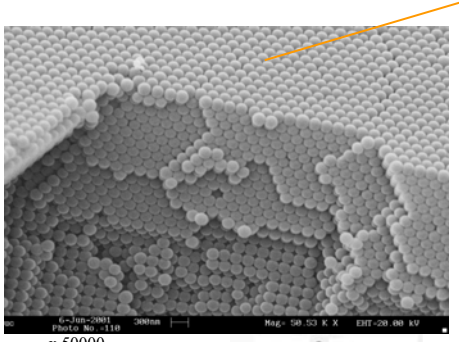
Disordered

Powder-like diffraction

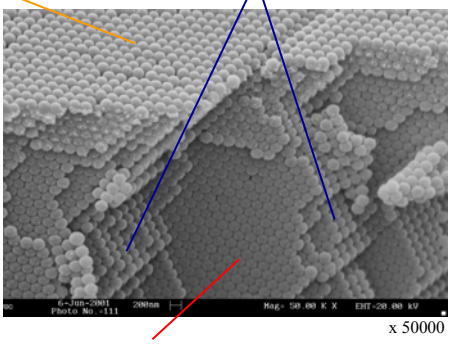
J. Galisteo-Lopez and C. Lopez, Photonics Europe 2004

SEM OF POLYSTYRENE BULK OPALS

(111) (010)

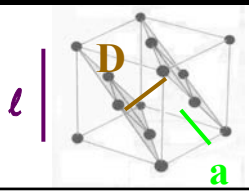


x 50000



x 50000

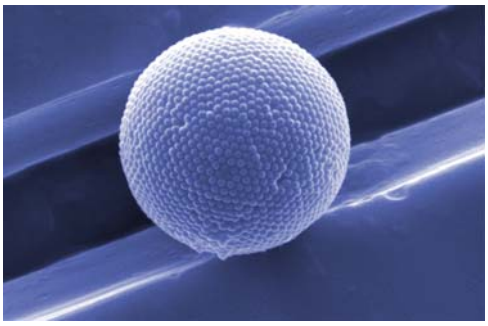
(111)

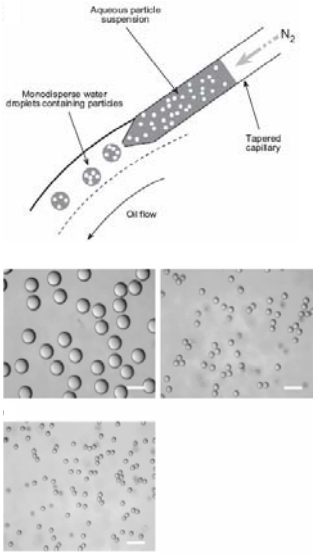


FCC packing structure of the spheres

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

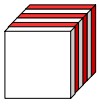
SPHERICAL OPALS: PHOTONIC BALLS

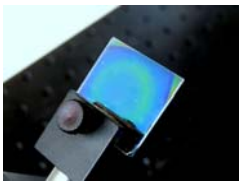




Adv. Mater. **2002**, *14*, No. 16, August 16
Synthetic Metals 139 (2003) 803–806

POLYMER MULTILAYERS





Polymeric multilayer films have been manufactured via three main methods:
co-extrusion, spin coating, and self-assembly.

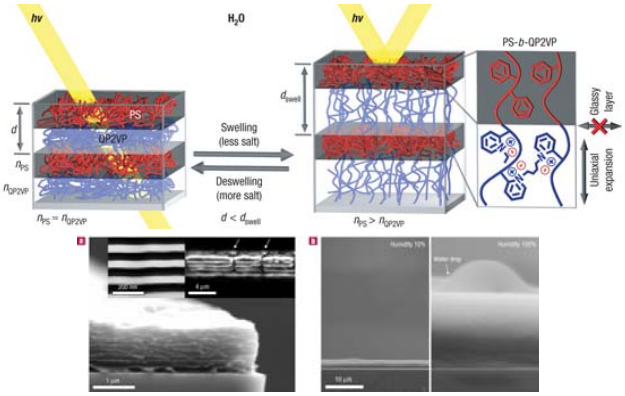
Co-extruded films containing large numbers of alternating layers of different refractive indices were produced over 30 years ago at Dow, with first order reflectivities approaching 100 %.

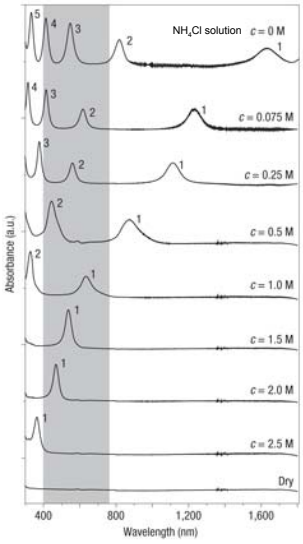
A fundamental problem encountered with co-extruded films is the occurrence of undesired thickness variations, which result in a broadening of the reflection spectrum and also unwanted higher order reflections.

Spin-coating deposition technique is also used for the preparation of multilayers.

SELF- ASSEMBLED POLYMERIC MULTILAYERS

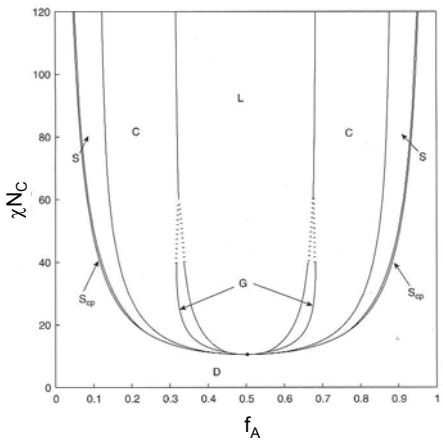
- Hydrophobic–hydrophilic polyelectrolyte block-copolymers form a simple one-dimensional periodic lamellar structure.
- This results in a responsive photonic crystal that can be tuned via swelling of the hydrophilic layers by contact with a fluid reservoir.





Nature Materials 6, 957 - 960 (2007)

SELF- ASSEMBLED STRUCTURES for DIBLOCK COPOLYMERS



D = DISORDERED PHASE
L = LAMELLAE
G = GYROIDS
C = CILINDERS IN HEXAGONAL LATTICE
S = SPHERESE IN BCC LATTICE
S_{CP} = CLOSE PACKED SPHERES

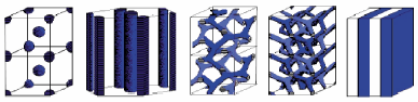
- AB diblock copolymer
- Total degree of polymerization, N_C
- Flory A-B interaction parameter, χ
- Block "A" volume fraction, f_A

Microphase diagram for conformationally symmetric diblock copolymers

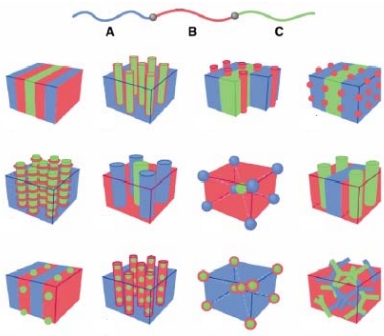
D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

SELF- ASSEMBLED POLYMERIC STRUCTURES

DI-BLOCK

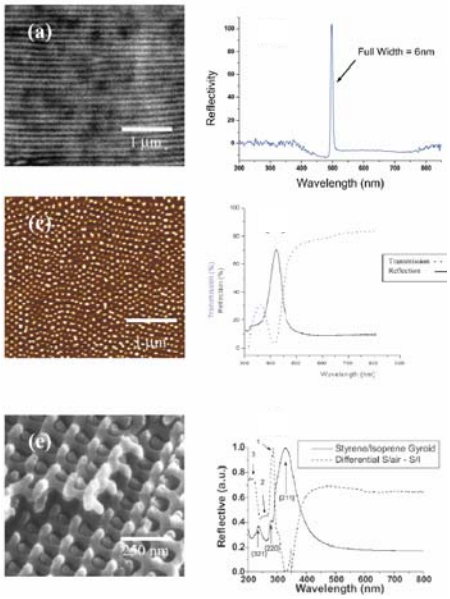
Nature of patterns	Spheres (SPH) (3D)	Cylinders (CYL) (2D)	Double gyroid (DG) (3D)	Double diamond (DD) (3D)	Lamellae (LAM) (1D)
Space group	$Im\bar{3}m$	p6mm	$Ia\bar{3}d$	$Pn\bar{3}m$	pm
Blue domains: A block					
Volume fraction of A block	0-21%	21-33%	33-37%		37-50%

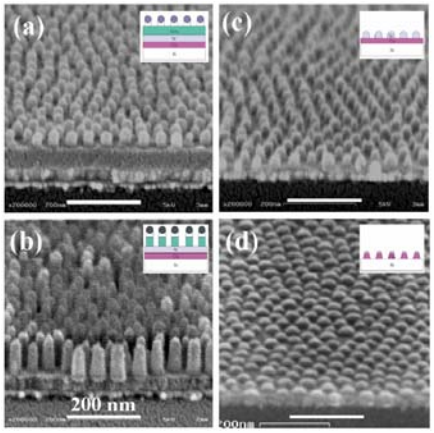
TRI-BLOCK



Schematic phase diagram showing the different classical block copolymers morphologies adopted by non crystalline di- and tri-block polymers

SELF- ASSEMBLED POLYMERIC STRUCTURES





Polymer 44 (2003) 6725

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

SUMMARY

INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING

- Photonic Crystals
- Natural Photonic Crystals
- Growth & Preparation of Photonic Crystals
- Photonic Crystals Theory
- Photonic Crystals Applications
- Photonic Crystal in Photovoltaic Devices

PHOTONIC CRYSTALS: MAXWELL'S EQUATIONS

$$\nabla\cdot B=0 \qquad \nabla\cdot D=4\pi\rho$$

$$\nabla\times E+\frac{1}{c}\frac{\partial B}{\partial t}=0 \qquad \nabla\times H-\frac{1}{c}\frac{\partial D}{\partial t}=\frac{4\pi}{c}j$$

ρ =0, **J**=0, **B=H, D=** ε**E**

$$\nabla\cdot H(r,t)=0 \qquad \nabla\cdot[\varepsilon(r)E(r,t)]=0$$

$$\nabla\times E(r,t)+\frac{1}{c}\frac{\partial H(r,t)}{\partial t}=0$$

$$\nabla\times H(r,t)-\frac{\varepsilon(r)}{c}\frac{\partial E(r,t)}{\partial t}=0$$

$\varepsilon(\mathbf{r})=\varepsilon(\mathbf{r}+\mathbf{R})$ Dielectric lattice

ε_a, ε_b Dielectric contrast

} are key parameters

$$\tilde{\varepsilon}=\varepsilon+\cancel{i\varepsilon_2}$$

$$\varepsilon(\omega)=\varepsilon$$

We assume non absorbing and non dispersive media

$$H(r,t)=H(r)e^{i\omega t}$$

$$E(r,t)=E(r)e^{i\omega t}$$

Plane wave expansion

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY, Trieste 8 – 19 February 2010

PHOTONIC CRYSTALS: MAXWELL'S EQUATIONS

$$\nabla\times H(r,t)-\frac{\varepsilon(r)}{c}\frac{\partial E(r,t)}{\partial t}=0$$

$$H(r,t)=H(r)e^{i\omega t}$$

$$\nabla\times E(r,t)+\frac{1}{c}\frac{\partial H(r,t)}{\partial t}=0$$

$$E(r,t)=E(r)e^{i\omega t}$$

Eigenfunction

Eigenvalues (optical modes)

non Hermitian operator

Hermitian operator

$$\hat{\Xi}\mathbf{D}(\mathbf{r})\equiv\nabla\times\left(\nabla\times\frac{1}{\varepsilon(\mathbf{r})}\mathbf{D}(\mathbf{r})\right)=\left(\frac{\omega}{c}\right)^2\mathbf{D}(\mathbf{r})$$

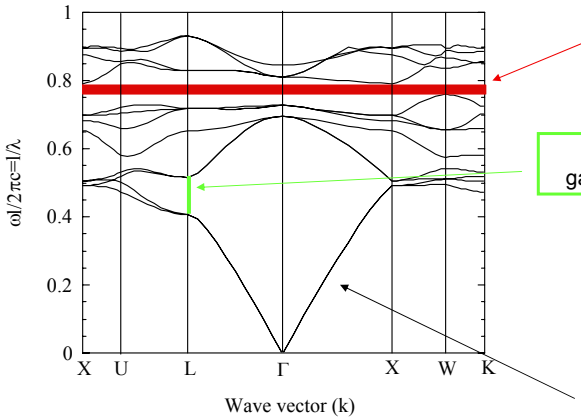
$$\hat{\Theta}\mathbf{H}(\mathbf{r})\equiv\nabla\times\left(\frac{1}{\varepsilon(\mathbf{r})}\nabla\times\mathbf{H}(\mathbf{r})\right)=\left(\frac{\omega}{c}\right)^2\mathbf{H}(\mathbf{r})$$

$$\nabla\cdot D(r)=0 \longrightarrow H(r)=\frac{i\omega}{c}\nabla\times D(r)$$

$$\nabla\cdot H(r)=0 \longrightarrow E(r)=\left(\frac{-ic}{\omega\varepsilon(r)}\right)\nabla\times H(r)$$

Tight mathematical similarity with Quantum Mechanics

PHOTONIC CRYSTAL: SYNTHETIC MEDIUM FOR TUNING LIGHT PROPAGATION



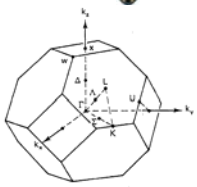
photonic BAND GAP

photonic STOP BAND (PSEUDO GAP)
gap for selected directions/polarizations only

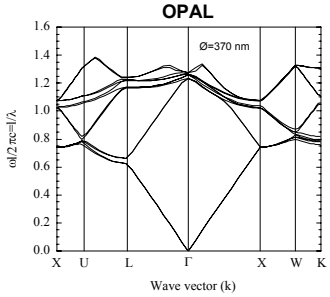
Light propagation in an uniform (effective) medium

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

EFFECT OF THE STRUCTURE AND THE DIELECTRIC CONTRAST ON THE PHOTONIC BAND GAP

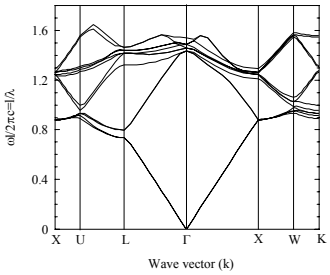


OPAL



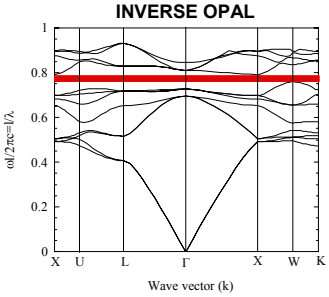
ε_a=2.12 (silica)
ε_b=1 (air)

INVERSE OPAL



ε_a= 1 (air)
ε_b= 2.12 (silica)

INVERSE OPAL



ε_a= 1 (air)
ε_b= 12 (silicon)

No full photonic band gap
(pseudo-gap only)

Photonic band gap !

PHOTONIC CRYSTALS: SCALING PROPERTIES

$$\mathbf{r}' = \mathbf{r}s$$

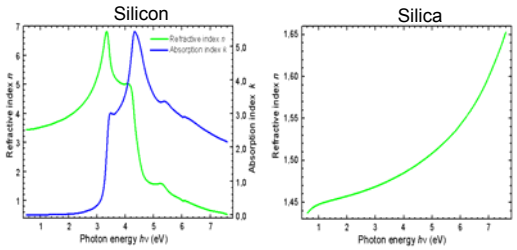
$$\nabla' = \frac{\nabla}{s} \quad \varepsilon'(\mathbf{r}) = \varepsilon(\mathbf{r}/s)$$

$$s\nabla' \times \left(\frac{1}{\varepsilon(\mathbf{r}'/s)} s\nabla' \times \mathbf{H}(\mathbf{r}'/s) \right) = \left(\frac{\omega}{c} \right)^2 \mathbf{H}(\mathbf{r}'/s)$$

$$\varepsilon'(\mathbf{r}) = \varepsilon(\mathbf{r}'/s)$$

$$\nabla' \times \left(\frac{1}{\varepsilon'(\mathbf{r}')} \nabla' \times \mathbf{H}(\mathbf{r}'/s) \right) = \left(\frac{\omega}{cs} \right)^2 \mathbf{H}(\mathbf{r}'/s)$$

$$\omega'(\mathbf{k}) = \frac{\omega(\mathbf{k})}{s}$$

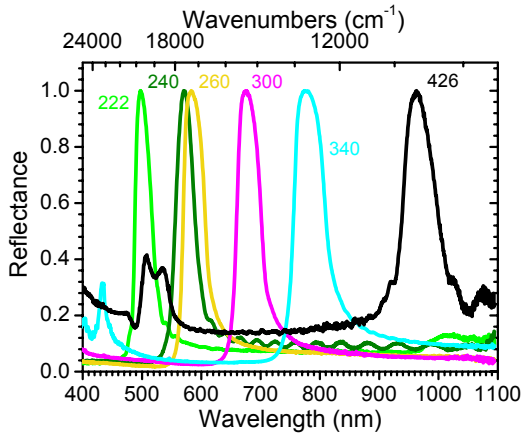


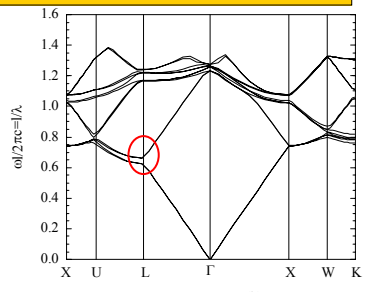
$$\varepsilon'(\mathbf{r}) = \frac{\varepsilon(\mathbf{r})}{p^2}, \quad \forall \mathbf{r}$$

$$\nabla \times \left(\frac{1}{\varepsilon(\mathbf{r})} \nabla \times \mathbf{H}(\mathbf{r}) \right) = \left(\frac{\omega p}{c} \right)^2 \mathbf{H}(\mathbf{r})$$

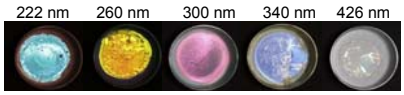
$$\omega'(\mathbf{k}) = \omega(\mathbf{k}) \cdot p$$

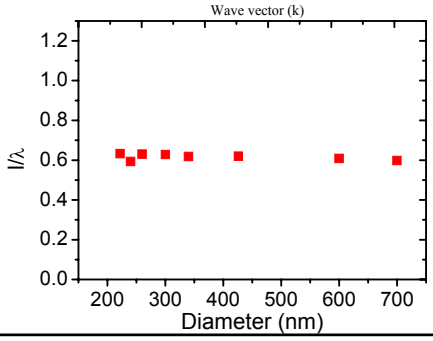
SCALING LAW





$$m\lambda = 2D_{111}\sqrt{n_{eff}^2 - \sin^2\theta} \qquad D_{111} = a\sqrt{\frac{2}{3}} = \frac{\ell}{\sqrt{3}}$$





QUANTUM MECHANICS AND PHOTONIC CRYSTALS: A COMPARISON...

QM in a crystal | **EM in a photonic crystal**

$$\hat{\mathbf{H}}\psi_E(\mathbf{r}) \equiv \left(\frac{p^2}{2m} + V(\mathbf{r})\right)\psi_E(\mathbf{r}) = E\,\psi_E(\mathbf{r}) \quad \Longleftrightarrow \quad \hat{\Theta}\mathbf{H}_\omega(\mathbf{r}) \equiv \nabla \times \frac{1}{\varepsilon(\mathbf{r})}\nabla \times \mathbf{H}_\omega(\mathbf{r}) = \frac{\omega^2}{c^2}\mathbf{H}_\omega(\mathbf{r})$$

The master equation is
a linear Hermitian operator
(Schrodinger-Maxwell)

$$V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R}) \Rightarrow \Psi_{\mathbf{K}}(\mathbf{r}) = u_{\mathbf{K}}(\mathbf{r})e^{i\mathbf{K}\cdot\mathbf{r}} \quad \Longleftrightarrow \quad \varepsilon(\mathbf{r}) = \varepsilon(\mathbf{r}+\mathbf{R}) \Rightarrow \mathbf{H}_{\mathbf{K}}(\mathbf{r}) = u_{\mathbf{K}}(\mathbf{r})e^{i\mathbf{K}\cdot\mathbf{r}}$$

Periodicity of the system
(potential-dielectric constant)

$$\psi(\mathbf{r},t) = \sum_E c_E \psi_E(\mathbf{r})e^{iEt/\hbar} \quad \Longleftrightarrow \quad \mathbf{H}(\mathbf{r},t) = \sum_\omega c_\omega \mathbf{H}_\omega(\mathbf{r})e^{i\omega/\hbar}$$

$$\int |\psi(\mathbf{r},t)|^2 d\mathbf{r} = 1 \qquad \nabla\cdot\mathbf{H} = 0$$

Main function containing all the information
(normalizable - normalizable & transverse)

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

QUANTUM MECHANICS AND PHOTONIC CRYSTALS: A COMPARISON...

QM in a crystal | **EM in a photonic crystal**

Electron-electron repulsive interaction
Large scale computation difficult

$\Longleftrightarrow$ Interaction between modes

In the linear regime, light modes can pass right through one another undisturbed and can be calculated independently

$$E_{var} = \frac{\langle\psi|\hat{\mathbf{H}}|\psi\rangle}{\langle\psi|\psi\rangle} \quad \Longleftrightarrow \quad E_{var} = \frac{\left(\mathbf{H},\hat{\Theta}\mathbf{H}\right)}{(\mathbf{H},\mathbf{H})}$$

Mode properties &
variational theorem

Eigenstates with different energies are orthogonal, they have real eigenvalues, and can be found with a variational principle

E_{var} is minimized when ψ is an eigenstate of H

Modes with different frequencies are orthogonal, they have real positive eigenvalues, and can be found with a variational principle

E_{var} is minimized when H is normal mode of Θ

The wavefunction concentrates in regions of low potential, while remaining orthogonal to lower states $\Longleftrightarrow$ The fields concentrates their electrical energy in high-ε regions, while remaining orthogonal to lower modes

QUANTUM MECHANICS AND PHOTONIC CRYSTALS: A COMPARISON...

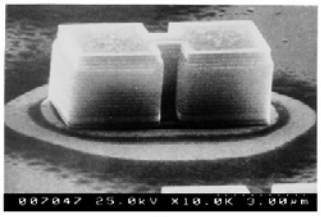
QM in a crystal		EM in a photonic crystal
The eigenvalue E of the Hamiltonian	System energy	The electromagnetic energy $E = \frac{1}{8\pi}\int dr\left(\frac{1}{\varepsilon}\lvert D\rvert^2 + \lvert H\rvert^2\right)$
The natural scale of the system is provided by the Bohr radius	Scale length of the system	There is not a natural scale: the solution are scalable to any length
The band structure $E_n(\mathbf{k})$ tells us the energies of the allowed eigenstates. The electron wave scatters coherently from the different potential regions Inside the **electronic gap** no propagating electrons are allowed to exist The band above the gap is the conduction band; the band below the gap is he valence band	Band structure and gap	The functions $\omega_n(\mathbf{k})$ tells us the frequencies of the allowed harmonic modes. The electromagnetic fields scatter coherently at the interface between different dielectric regions Inside the **photonic band gap** no modes are allowed to exist The band above the gap is the **air band**; the band below the gap is the **dielectric band**

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

QUANTUM MECHANICS AND PHOTONIC CRYSTALS: A COMPARISON...

QM in a crystal		EM in a photonic crystal
A defect (foreign atom in a crystal) breaks the translational symmetry of the atomic potential and it might create an allowed state in the **electronic band** gap, thereby allowing a localized electronic state around the defect. Donor atoms pull states from the conduction band into the gap; acceptor atoms pull states from the valence band into the gap	Defect engineering	A defect changing ε in a certain region (point, line, plane) breaks the translational symmetry of $\varepsilon(\mathbf{r})$ and it might create an allowed state in the **photonic** band gap, thereby permitting a localized mode around the defect. **Dielectric** defects pull states from the **"air"** band into the gap; **"air"** defects pull states from the **dielectric** band into the gap
We can tailor the **electronic** properties of materials to our needs		We can tailor the **optical** properties of materials to our needs

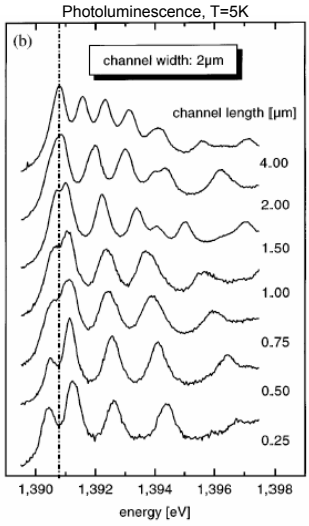
OPTICAL MODES IN PHOTONIC MOLECULES



A GaAs layer was surrounded by highly reflecting GaAsAlAs Bragg mirrors. A 7 nm wide $In_{0.14}Ga_{0.86}As$ quantum well was placed in the center of the GaAs cavity. Photonic molecules were prepared by lithographic patterning of this cavity.

Photonic Molecules

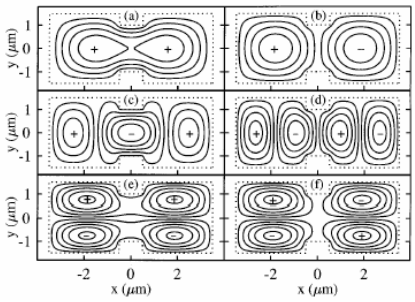
Coupled optical microcavities (similarity between the field eigenmodes and the electronic structure of real molecules)



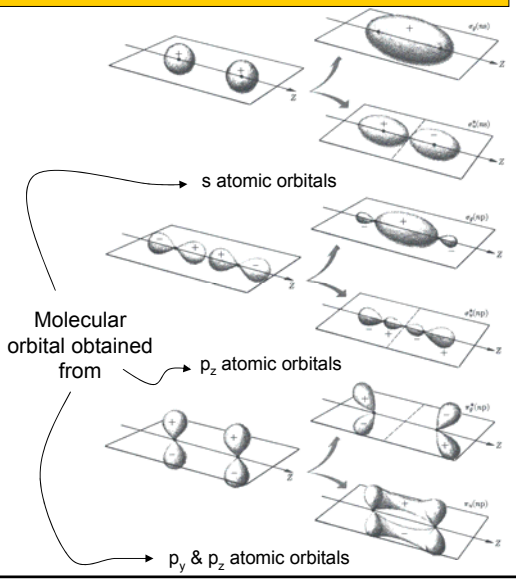
In contrast with waveguides in a PhC (line defects) where a broad range of frequencies are allowed to propagate within the bandgap, photonic molecules structure allows transmission only at cavity resonance frequencies

ANALOGIES BETWEEN MOLECULES AND PHOTONIC MOLECULES

- In molecules the bonding strength depends on Coulomb forces between nuclei and electrons
- The interaction of photon modes in photonic molecules is determined by the geometry and then can be varied by structure design (length or width of the interconnecting channel)



Calculated electric field distributions of the six lowest confined optical modes in photonic molecules.



ELECTROMAGNETIC VARIATIONAL THEOREM: AIR & DIELECTRIC BANDS

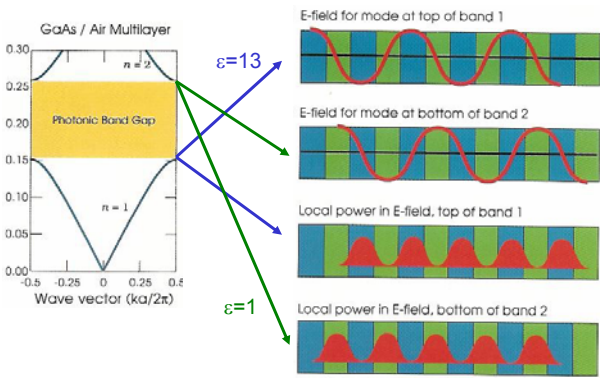
- Unlike electrons in a semiconductor which are constrained by Fermi statistics and therefore have to be excited from the valence band to the conduction band to become mobile, photons are bosons which propagate freely at frequencies both above and below the PBG.
- Thus the terms 'valence band' and 'conduction band' may not be appropriate in the context of a PhC.
- Instead, bands above and below a PBG can be distinguished by applying the electromagnetic variational theorem:

$$E_f(H)=\frac{1}{2}\frac{\left(H,\hat{\Theta}H\right)}{(H,H)}=\left(\frac{1}{2(H,H)}\right)\int dr\,\frac{1}{\varepsilon}\left|\nabla\times H\right|^2=\left(\frac{1}{2(H,H)}\right)\int dr\,\frac{1}{\varepsilon}\left|\frac{\omega}{c}D\right|^2 \qquad (F,G)\equiv\int dr\,F^*(r)\cdot G(r)$$

- According to this theorem, for modes in the lower photonic band, the power of modes lies primarily in the high-index regions, whereas for modes in the upper photonic band the power lies in the low-index regions. In PCs, the low-index regions are often air regions. For this reason it is more meaningful to refer to the band *above* a PBG as the '*air*' band, and the one below the gap as the '*dielectric*' band.

ELECTROMAGNETIC VARIATIONAL THEOREM: LIGHT LOCALIZATION

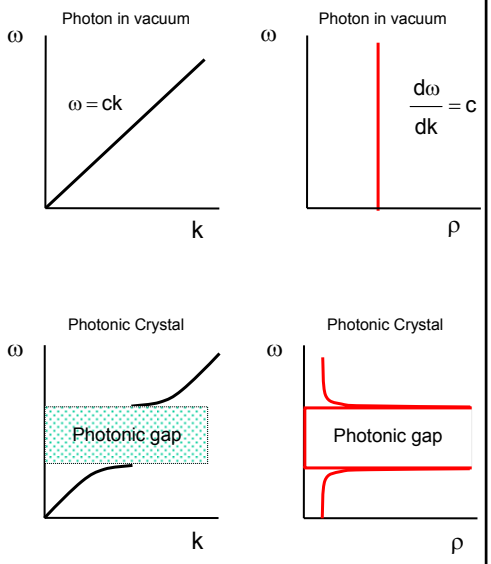
- Standing waves in the PC can be with the NODE in the high or low ε material (any other position would violate the symmetry of the unit cell about its center).
- Low frequency modes concentrate their energy in the high ε material while high frequency modes concentrate their energy in low ε material
- At the edges of the photonic band gap the field is localized in different composing material



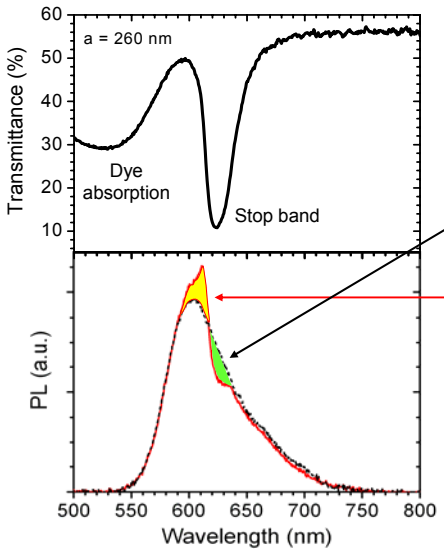
- A frequency difference exists between the two cases.
- The mode just under the gap has its power concentrated in the high ε material giving it a lower frequency.
- The mode just above the gap has most of its power in low ε regions so its frequency is raised.
- This explains in a different way the physical origin of the photonic band gap.

LIGHT LOCALIZATION

- Photons in the void possess a linear dispersion, which provides a constant density of photonic state (DOS).
- Due to their peculiar photonic band structure, PhCs modify the DOS of the void.
- At the band gap, the DOS is reduced thus preventing the light to propagate.
- At the band gap edges, bands are flat and then the DOS shows a divergence.
- Since at the band gap edges the group velocity of light is $v_g = d\omega/dk = 0$, there light-matter interaction is expected to increase.
- At the edges field localization also occurs.
- These effects have been used to enhance emission from dyes embedded inside the PhC.



PL DIRECTIONAL ENHANCEMENT @ BAND EDGE



- Light emission is inhibited due to the reduced mode density within the Stop Band
- PL enhancement is observed at the high-energy edge of the Stop Band where localization occurs in the low ε material (solution)

J. Chem. Phys. C, in press DOI: 10.1021/jp906002q

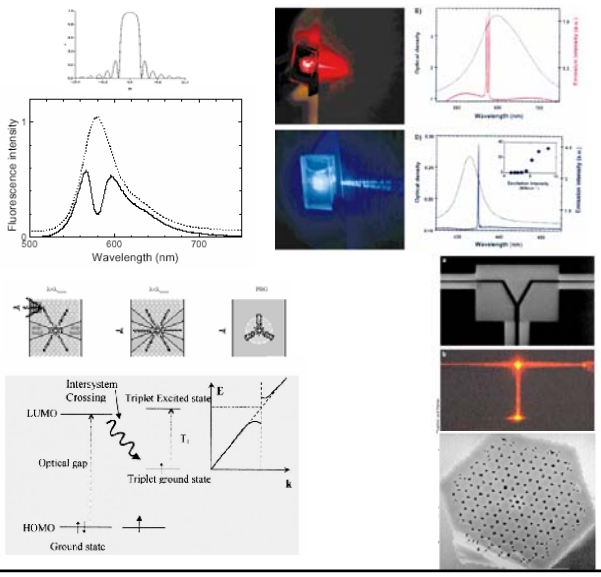
SUMMARY

INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING

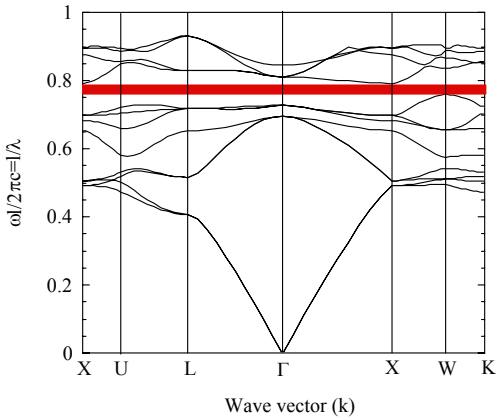
- Photonic Crystals
- Natural Photonic Crystals
- Growth & Preparation of Photonic Crystals
- Photonic Crystals Theory
- Photonic Crystals Applications
- Photonic Crystal in Photovoltaic Devices

WORKING PHOTONIC CRYSTALS

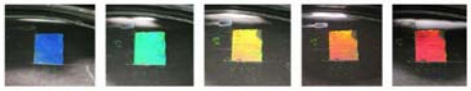
- Bragg reflectors and microcavities (dielectric mirrors)
- Inhibition of spontaneous emission inside the photonic cavity
- Thresholdless laser
- Defects acting as waveguides
- Light localization
- e-h recombination quenching in transistors and solar-cells
- Optical switching
- Sensors

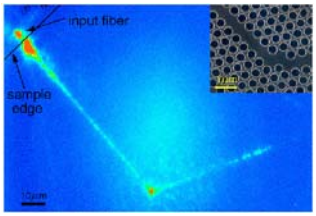


PHOTONIC CRYSTAL: SYNTHETIC MEDIUM FOR TUNING LIGHT PROPAGATION



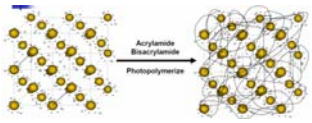
photonic band gap

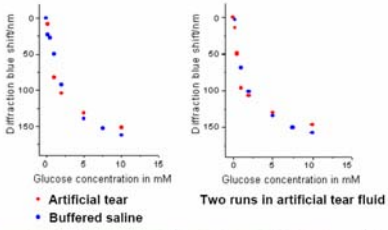


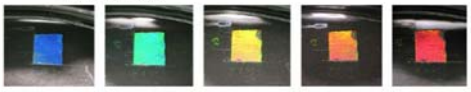


SENSING BY PHOTONIC CRYSTALS

Colloidal Crystals Arrays





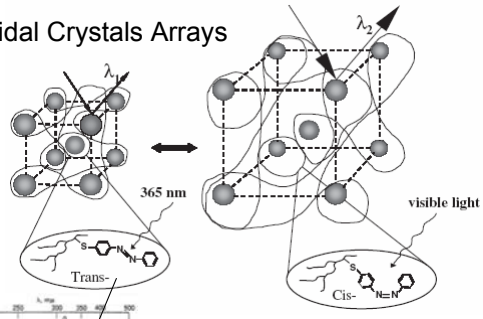


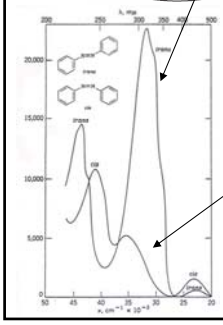
CCAs have been also used for sensing ammonia, Pb^{2+}, nerve agents, creatinine…

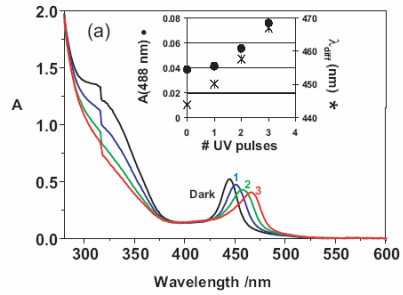
Science 274, 959 (96)
Nature 389, 829 (97)

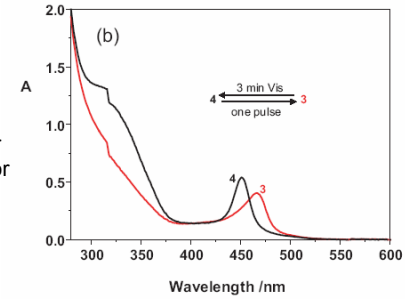
PHOTONIC CRYSTALS OPTICAL MEMORIES

Colloidal Crystals Arrays







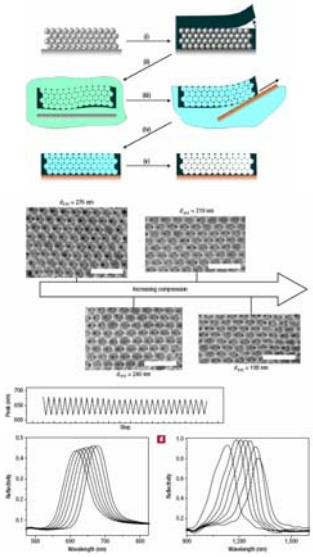


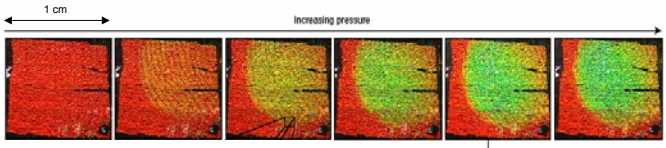
This process is suitable for optical storage (on-off) or for optical switching (fast and fully reversible).

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

COLOUR FINGERPRINTING BY ELASTIC PhC

A.C. Arsenault et al. Nat. Mater. 5, 179 (2006)



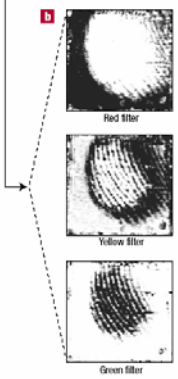


An opals is infiltrated with a suitable elastomeric polymer.

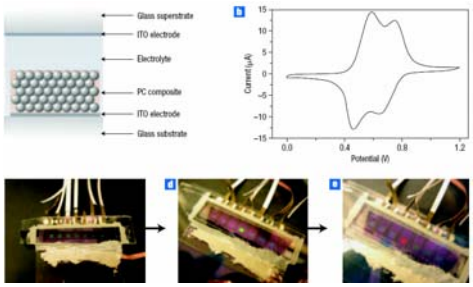
After removing the opal template, the inverse opal structure shows its peculiar optical response.

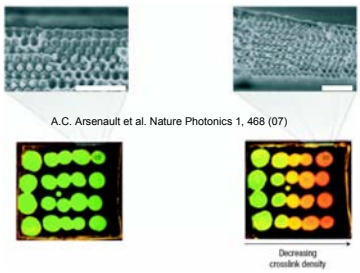
The application of a compressive stress, for instance by a finger, changes the colour of the film.

By using color filter, we can deduce the amount of pressure applied and reconstruct the fingerprint image

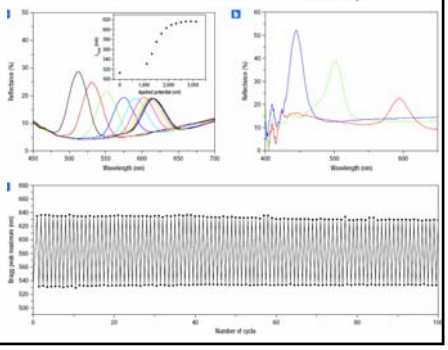


PhC FULL-COLOR PAPER-LIKE DISPLAYS





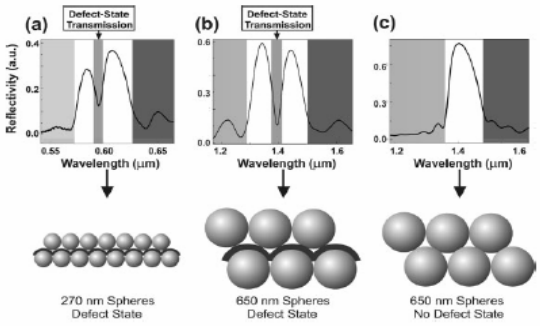
A.C. Arsenault et al. Nature Photonics 1, 468 (07)



- A silica opal is infiltrated with a crosslinked network of an iron-based metallopolymer (polyferrocenylsilane).
- Electrical actuation is achieved by an incorporated sealed thin-layer electrochemical cell.
- A change of the applied potential modify the PhC structure thus inducing a color change.
- Color tunabilility is achieved by structural changes thus reducing bleaching problems typical of molecular dyes.
- Very good reproducibility is obtained.
- This technology can be used as a photonic ink suitable for paper-like displays.

"DEFECTS" IN PHOTONIC CRYSTALS

Adv. Mater. 17, 1912 (05)

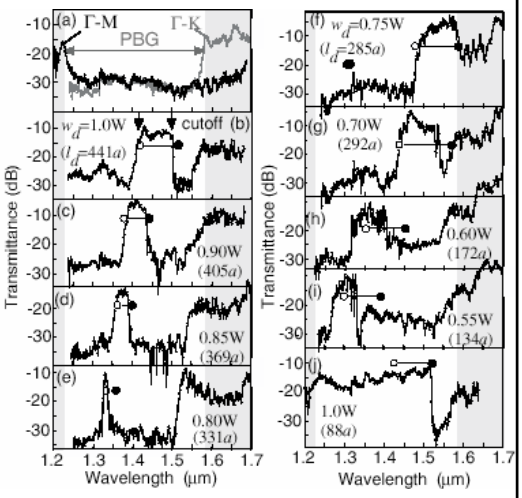


Structural/dielectric defects generate gap states (allowed modes within the photonic band gap)

Electromagnetic fields cannot propagate @ stop band, but defects relax this contraint inducing light confinement

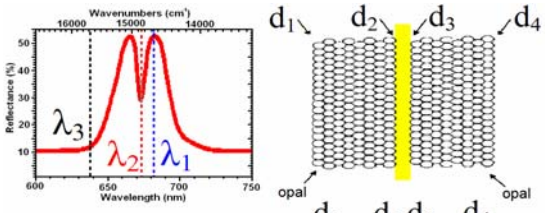
"DEFECTS" IN PHOTONIC CRYSTALS

- The frequency of a defect mode is an *increasing function of the volume of an air defect and a decreasing function of the volume of a dielectric defect.*
- For air defect, the larger the volume of material removed, the further the defect mode is pushed from the lower photonic band edge into the gap (that is, the higher the frequency of the defect mode).
- Conversely, for a dielectric defect, the larger the volume of high-index material added, the further the defect mode is pushed from the upper photonic band edge into the band gap (that is, the lower the frequency of the defect mode).
- Thus the frequency of a defect mode can be 'tuned' to any desired value within the gap by adding (or removing) the appropriate amount of dielectric material from a unit cell.



Transmission spectra (TE polarization) of defect-free 2D-PhC, and line defects of different widths (W)

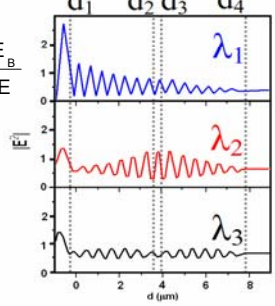
DEFECT ENGINEERING



The importance of structural defects is related to light localization effects

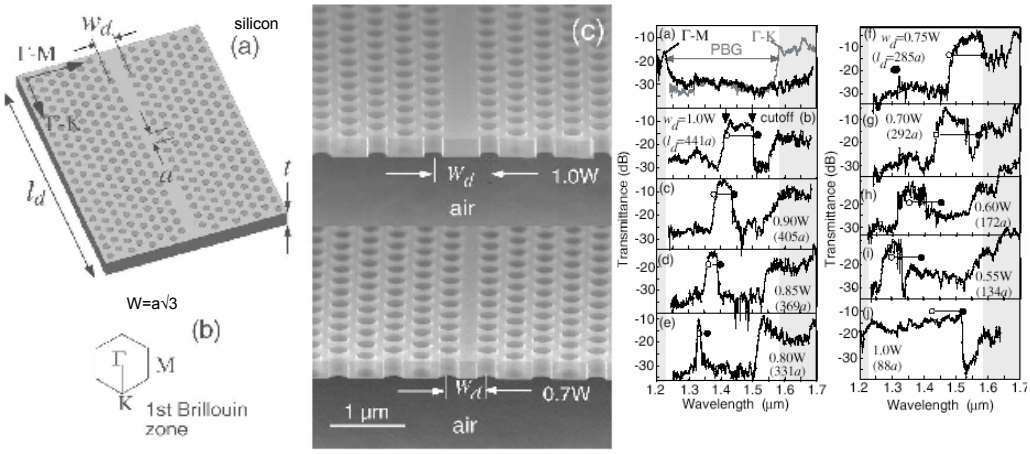
$$L_B = \frac{2DE_B}{\pi \Delta E}$$

- λ_1 (stop band), light intensity is exponentially attenuated
- λ_3 (stop band edge), light forms a stationary wave
- λ_2 (defect), light is localized within defects ▪▪▪► thereshold lowering for lasing or NLO



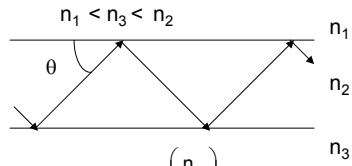
J.F. Galisteo-Lopez et al. Appl. Phys. Lett. 90,101113 (07)
PCCP 11, 11515 (09)
J. Europ. Opt. Soc.: Rapid. Publ. 11, 09033 (09)

PHOTONIC CRYSTAL WAVEGUIDES

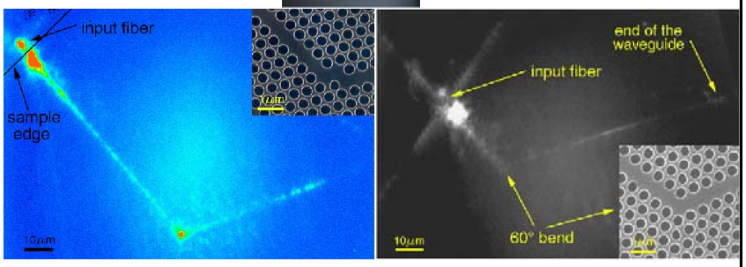


PHOTONIC CRYSTAL vs STANDARD WAVEGUIDES

- In standard waveguides, light confinement is achived through total internal reflection.
- The difficulty of guiding light **around tight bends** has limited the development of small-scale interconnections. In conventional fiber-optic waveguides, **a tight curve results in an angle of incidence that is too large for total internal reflection to occur**. **Light escapes at the corners** weakening the signals. Photonic-crystal waveguides can confine light in a narrow beam around tight corners.
- A key advantage of photonic-crystal waveguides is their size, about **100x100 μm²**, compared with conventional arrayed waveguide gratings, which are roughly **4 cm long and 1 to 2 cm wide**.

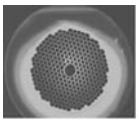


$$\vartheta < \arcsin\left(\frac{n_3}{n_2}\right) = \vartheta_{cr}$$

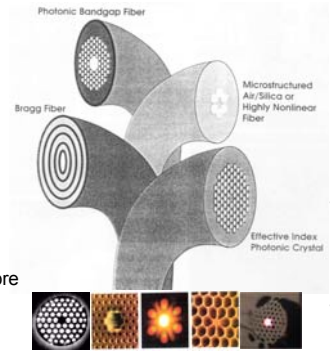


PHOTONIC CRYSTAL OPTICAL FIBERS

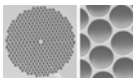
Only constructive scattering from a photonic bandgap structure can guide light down hollow-core fibers (facing left)



high-power laser signals could potentially be transmitted along the fibre without damaging



Other photonic crystal fibers use a modified form of total internal reflection to guide light along silica core (facing right)



- A drawback with conventional optical fibres is that different wavelengths of light can travel through the material at different speeds (dispersion).
- Over long distances, time delays occurs between signals that are encoded at different wavelengths.
- Then a light pulse travelling through such a fibre broadens out, thereby limiting the amount of data that can be sent.
- The "holey" fibre has a regular lattice of air cores running along its length and transmits a wide range of wavelengths without suffering from dispersion.

Whethever there is silica or air in the core, photonic crystal fibers could take the ability of optical fiber to the extreme

OmniGuide Communications claims expected loss for Bragg fibers: 0.01dB/Km and 10^4 reduction of the non linear effects (conventional silica fiber 0.2 dB/ Km).

Hollow core fibers show reduced Rayleigh scattering effects but other processes dominated over it, like leakages from the core. Measured losses are 0.3 dB/m.

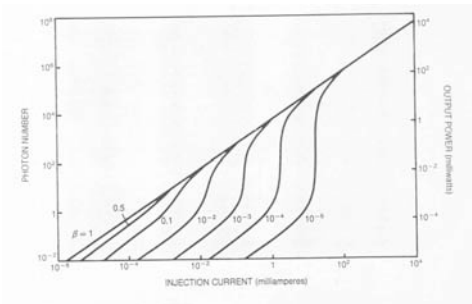
THRESHOLDLESS LASER

LASING THERESHOLD

- Active medium gain
- Cavity parameters
- Losses
- Gain volume

A. Sherer et al. Science 284,1819(99)

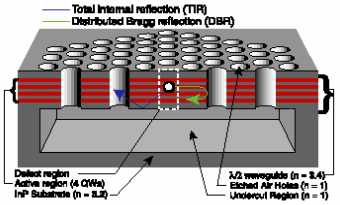
$$\beta = \frac{\text{number of photons emitted in the laser mode}}{\text{total number of emitted photons}}$$



$\beta = 10^{-5}$ in semiconducting lasers

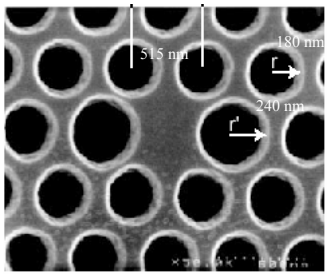
$\beta = 10^{-1}$ in microcavities

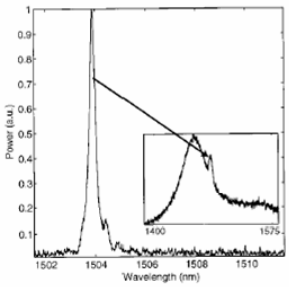
2D PBG DEFECT MODE LASER

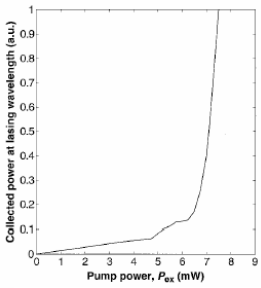


4 Strained InGaAsP Quantum Wells in InP bulk

β=0.65, Q=250





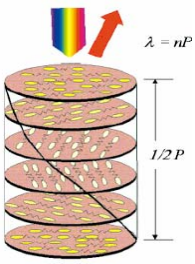


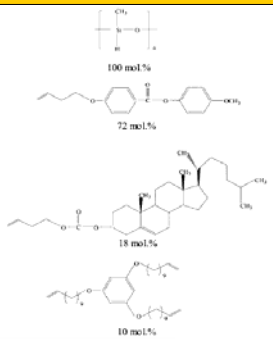
STILL LIMITING FACTORS:

- Low Q
- Poor thermal heat-sinking
- Inefficient optical pumping

A. Sherer et al. Science 284,1819 (99)

TUNABLE MIRRORLESS LASING IN CHOLESTERIC LIQUID CRYSTAL ELASTOMERS



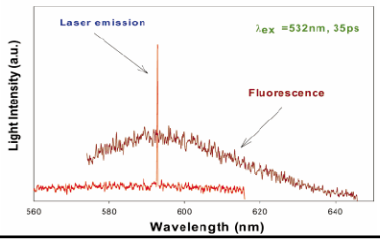


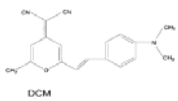
Poly[oxy(methylsilylene)]

Achiral nematogenic monomer

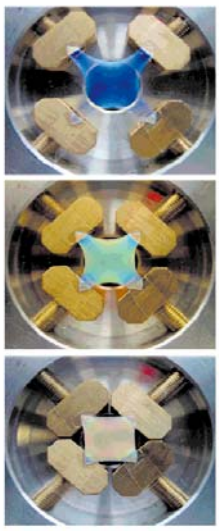
Chiral cholesterilcarbonate

Cross-linking agent





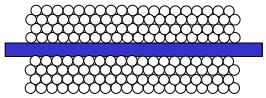
Lasing dye

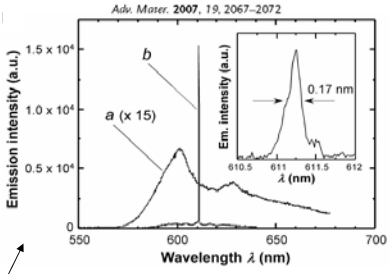


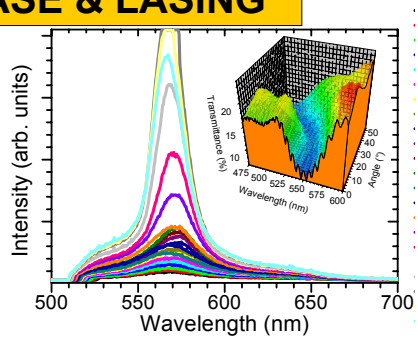
Adv. Mater. (2001) 13, 1069

DEFECT@OPAL: ASE & LASING

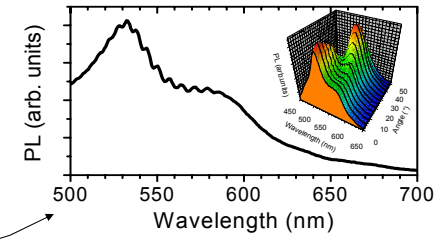
Active layer (conjugated molecule or polymer)





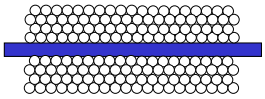


- Lasing inside the stop band
- No defect modes are reported
- In opal sandwich structures, ASE is achieved & defect modes are clearly observed

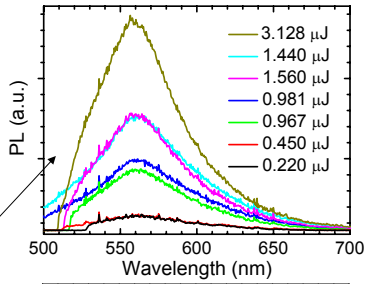


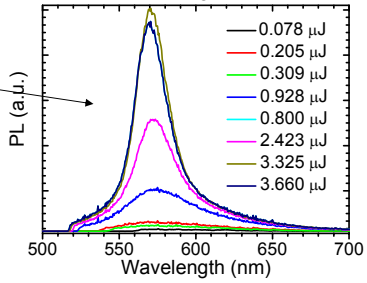
PCCP 11, 11515 (09)

DEFECT@OPAL: ASE & PHOTOBLEACHING



- For free-standing polymer film, no ASE is observed upon incresing fluence.
- For plane defect @ opal, ASE is observed upon incresing pumping fluence.
- Photobleaching prevents to achieve the lasing threshold

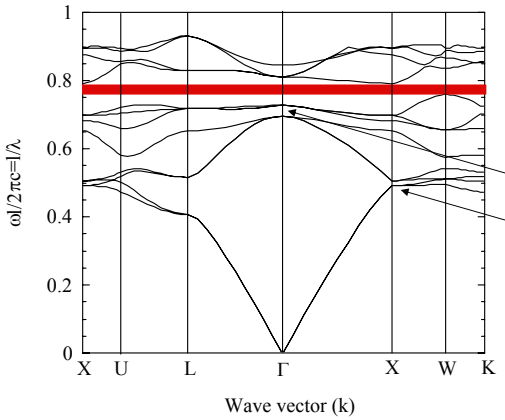




PCCP 11, 11515 (09)

PHOTONIC CRYSTAL: SYNTHETIC MEDIUM FOR TUNING LIGHT PROPAGATION

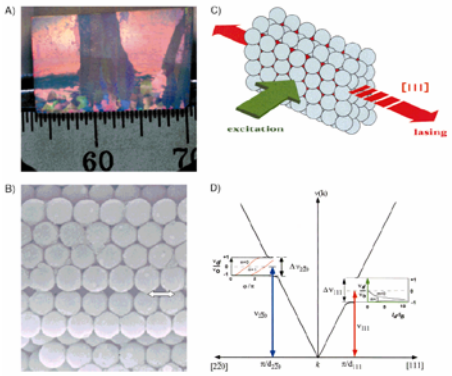
Zero group-velocity $d\omega/dk=0$: distributed feedback (DFB) lasers

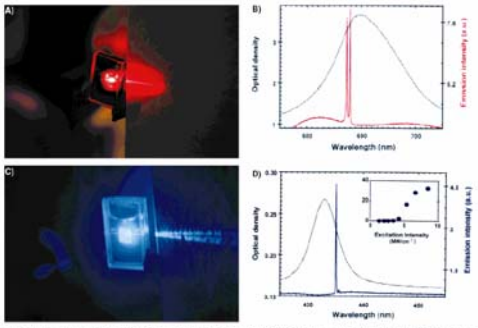


Flat bands, $d\omega/dk=v_g \rightarrow 0$
slow light, light localization, inhibition of spontaneous emission… (NLO effects, lasing)

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY, Trieste 8 – 19 February 2010

PHOTONIC CRYSTAL: LASING





- Tunable lasing emission in 3D switchable directions
- Lasing is due to gap-state (defects) with polarization 15:1
- Different types of wavelength tunability are possible [change of resonance for different crystalline plane (230 nm), change of n_{eff} (70 nm), slight change of stripe direction (6 nm)]
- Many independent laser cavities existing in a photonic crystal are observed by simultaneously lasing in various colors and directions

Adv. Funct. Mater. **2002**, *12*, No. 1, January

PHOTONIC CRYSTAL: RANDOM LASING

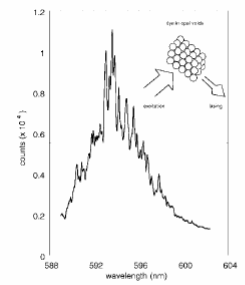


Fig. 4. Random laser emission spectrum of a DOO-PPV in toluene solution that is infiltrated into an opal photonic crystal. The inset shows the opal, which is composed of silica spheres in a closed packed lattice, and the laser excitation and collection geometries.

Adv. Mater. 13, 760 (2001)

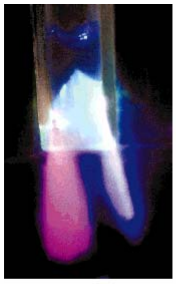
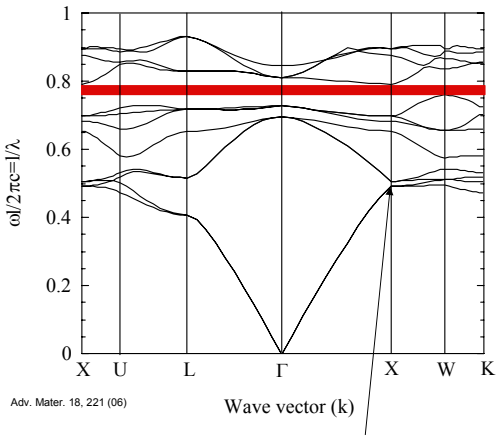


Fig. 5. The laser beams of two simultaneous random lasers in an infiltrated opal photonic crystal. The two dyes, Oxazin 670 (red) and Stilbene 140 (blue) were dissolved in methanol solution that was infiltrated into the opal. The red emission was excited at 532 nm, whereas the blue emission was excited at 355 nm using a pulsed Nd:YAG laser.

- Random lasing is a generic phenomenon that occurs in disordered media at excitation intensity regime higher than that giving rise to ASE.
- The emitted radiation is coherent and its spectrum contains many laser modes from which a typical cavity length can be obtained (polarization 1.5:1)
- Since random cavities are independent each other, laser emission in several colors is possible when mixing different dyes
- This lasing action occurs well above thershold and is unrelated to the photonic stop band, but overlapped to the dye maximum emission spectrum

PHOTONIC CRYSTAL: SUPER PRISM EFFECT

Extraordinary Angle-Sensitive Light Propagation



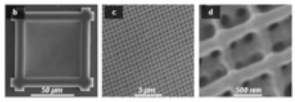
Adv. Mater. 18, 221 (06)

strong curvature (non linear dispersion): super-prisms

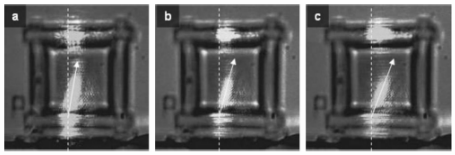
More than 10° variation of the angle by changing λ from 1000 to 1010 and then to 1020 nm

Due to band structure anisotropy, extraordinary angle-sensitive propagation of light inside a PhC can be achieved at different wavelengths.

This effect, called SUPERPRISM phenomenon, is observed at high frequencies where anisotropy is strong and negative refraction and birefringence are expected



Two-photon induced polymerization

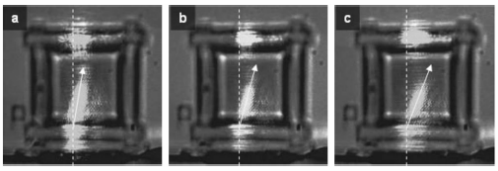


4° fixed incidence angle

PHOTONIC CRYSTAL: SUPER PRISM EFFECT

Adv. Mater. 18, 221 (06)

4° fixed incidence angle



$$n_i \sin\theta_i = n_t \sin\theta_t$$

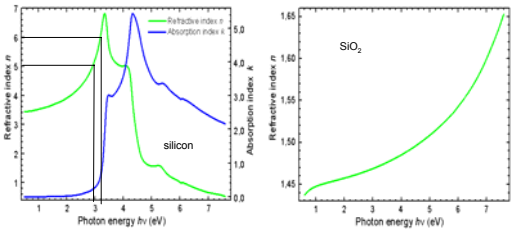
θ_i=4°, n_i=1, $\delta\theta$=10°

$n_t(1020)=n_t(1000) + \delta n$

More than 10° variation of the angle by changing λ from 1000 to 1010 and then to 1020 nm

Assuming n_t=1.3, from Snell's law θ_t=3°

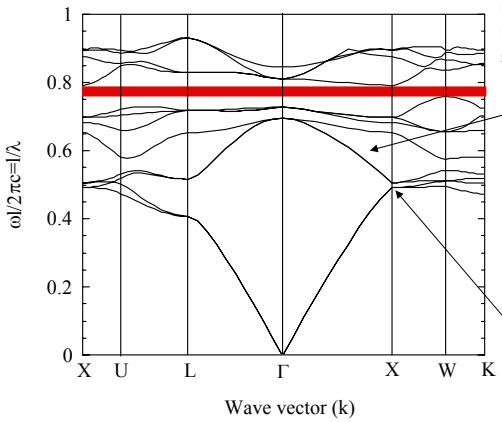
$$\delta n = n_i \sin\vartheta_i \left(\frac{1}{\sin\vartheta_t} - \frac{1}{\sin(\vartheta_t + \delta\vartheta)} \right) = 1.02$$



In a standard TRANSPARENT material, a similar variation of the refracted angle (10°) over 20 nm, would be assigned to a REFRACTIVE INDEX INCREASE OF 1!!!!

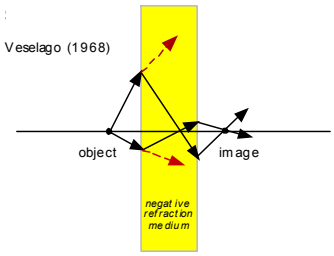
δn_{Si}(3 eV) = 1 $\rightarrow \delta\lambda$ = 83 nm

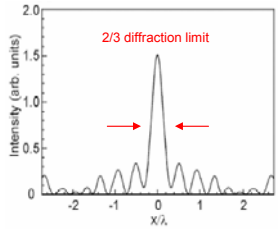
PHOTONIC CRYSTAL: SUPERPRISM & NEGATIVE REFRACTION



backwards slope: negative refraction, superlens

strong curvature: super-prisms, …





PHOTONIC CRYSTAL: SUPERPRISM & NEGATIVE REFRACTION

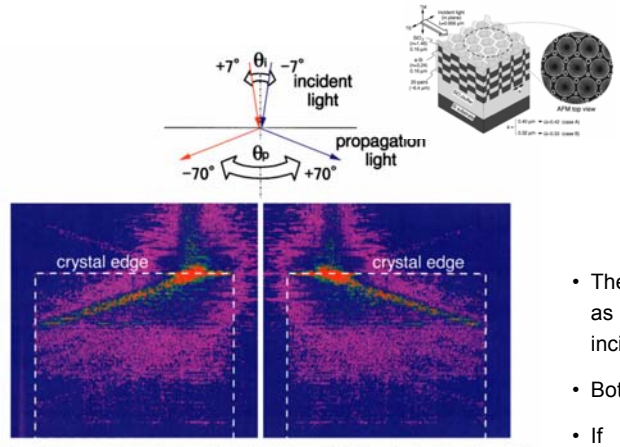
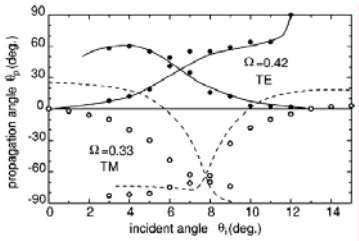


FIG. 1. (Color) Photographs showing light-beam swing inside the photonic crystal. The tilting angle of the incident light was slightly altered from +7° (left) to −7° (right). Both paths show negative bending. The incident light has a wavelength corresponding to the normalized frequency Ω=0.33 (defined later) with the TM polarization. The angles were measured from normal to the crystal edge (Γ−M crystal direction). The crystal size is 500 μm×500 μm.

Kosaka, *PRB* **58**, R10096 (1998)

Appl. Phys. Lett. 81, 2352 (2002)



- The light path swings from +70° to -70° as a results of a slight change of the incidence angle from +7° to -7°.
- Both paths show negative bending.
- If Snell's law is applied without regarding to photonic band anisotropy, this phenomenon implies a ***negative refractive index***

SUMMARY

INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING

- Photonic Crystals
- Natural Photonic Crystals
- Growth & Preparation of Photonic Crystals
- Photonic Crystals Theory
- Photonic Crystals Applications
- Photonic Crystal in Photovoltaic Devices

PHOTONIC CRYSTAL IN PHOTOVOLTAIC DEVICES

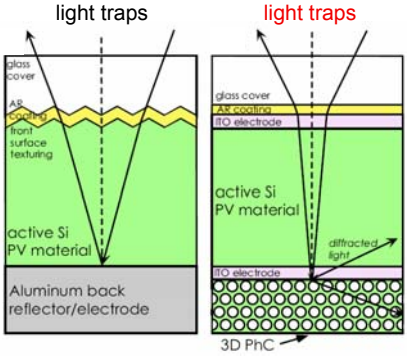
- Photonic Crystal in Photovoltaic Devices

  1) c-Silicon PV Cells
  2) Polymeric Bulk Heterojunctions
  3) Fluorescent Concentrators
  4) DSSC (3D & 1D PhC)

PhC in PHOTOVOLTAIC CELLS: c-Si

c-Si solar cell

Geometric optics light traps | Wave optics light traps



Light scattering at front textured surface + back reflection into the cell via Al mirror

DBR, gratings or PhC provide reflection, diffraction and refraction

Opt.Exp.15, 16968 (07)

Advantages of wave optics based structures:

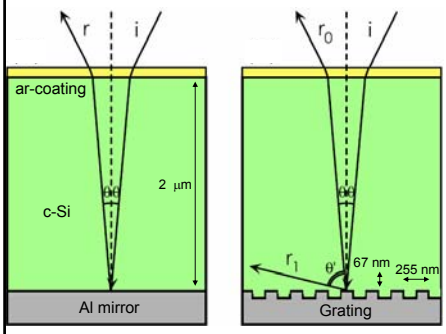
- **Reflection superior to aluminum mirrors.**
  DBR with high index contrast and PhC can reflect light over a broad range of incident angles and wavelengths since corresponding propagating modes are wholly forbidden.
  No metal required (no absorption, no charge recombination).
- **Incoming beams are diffracted into highly oblique angles, according to Bragg's law.**
  Diffraction improves light trapping by increasing the distance that light must travel to return to the front surface of the cell (optical depth).
  If the angle of the diffracted beam is greater than the critical angle, it will also be internally reflected back into the solar cell.
- **Frequencies outside the photonic band gap can be refracted into modes with a high photon DOS in order to improve absorption efficiency.**
  Coupling can take place via a superprism-type effect. All of these effects increase the time spent by photons inside the solar cell, which helps to maximize the absorption probability.

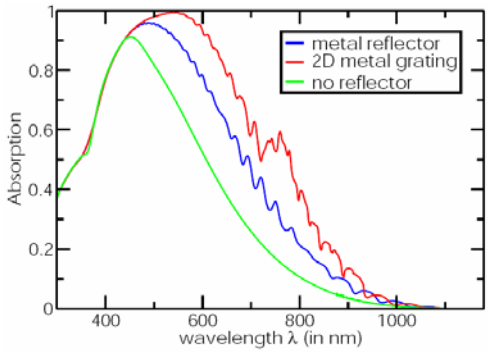
These wave optics-based approaches offer the advantage of lower materials usage (reduced thickness) as well as lower bulk recombination losses and potentially higher open-circuit voltages (increased light intensity inside the cell).

PhC in PHOTOVOLTAIC CELLS: c-Si

Geometric optics light traps

Wave optics light traps



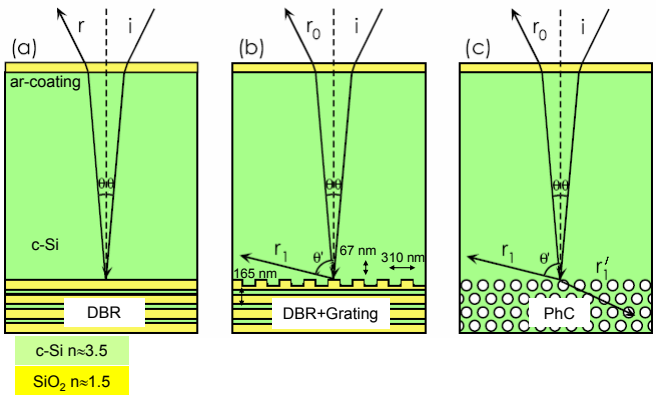


First-order diffraction (thereshold 920 nm for c-Si) Profile shape, incident angle, volume fraction, etch depth … can be optimized

The ability of the PV cell to absorb photons is enhanced when a metal grating is added.
(No recombination losses at metal surface are taken into account)

Opt.Exp.15, 16968 (07)

PhC in PHOTOVOLTAIC CELLS: c-Si



Wave optics structure	PV Cell efficiency (%)
Al reflector+,*	12.72 (13.77)
Al grating+,*	(17.88 1D-19.29 2D)
DBR (8 periods)	**12.44**
DBR+1D grating	**15.42** (+24%)
DBR+2D grating	**16.32 (+31%)**
Triangular PhC	**15.79** (+27%)
Woodpile PhC	**15.42** (+24%)
Inverse opal PhC	**15.73** (+26%)

+ Recombination losses at metal surface are NOT taken into account
* Data neglecting absorption losses are in parenthesis

- Improved PV cell efficiency is obtained for all wave optics structures.
- Careful design is needed.
- Cell production ?

Opt.Exp.15, 16968 (07)

PhC in PV CELLS: BULK HETERO JUNCTION

OPV efficiency depends three length scales: absorption penetration depth ($1/\alpha$~100 nm - 1 μm), exciton diffusion length (~10 nm), and carrier diffusion length (strongly dependent on supramolecular order).

BHJ cells have active layer thicknesses of ~100 nm which is a reasonable trade-off between optical absorption and reduced mobility.

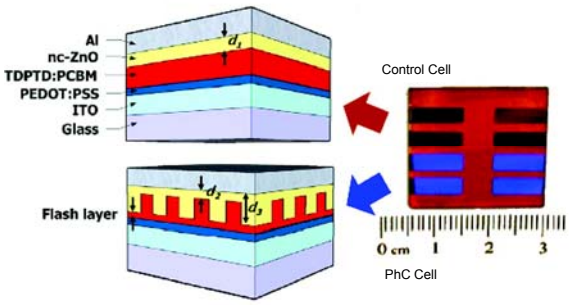
This thickness is adequate to absorb most photons in the visible range due to the strong extinction coefficient of organic materials.

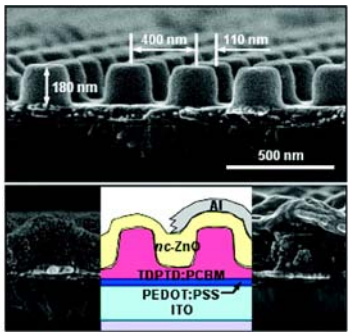
However, the sun's maximum photon flux is located around 700 nm, near the band edge of many BHJ materials where absorption is weak. In this case, reduced light absorption is expected.

Even though electronic state engineering via custom synthesis has produced low-bandgap polymers, their broad and weak absorption tails in the NIR require much larger thickness thus reducing cell performances due to carrier mobility limitations.

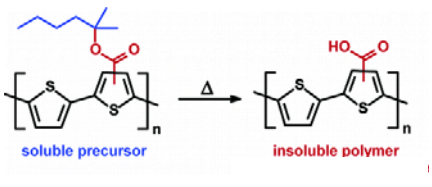
Different approaches (i.e. PhC) are investigated in order to increase light absorption.

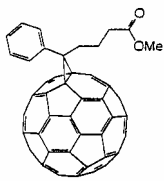
PhC in PV CELLS: BULK HETERO JUNCTION



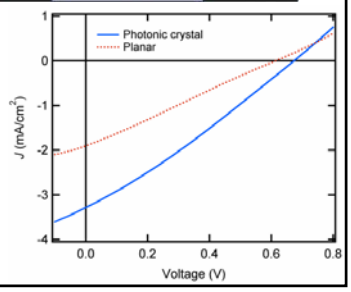


PhC obtained via Pattern Replication In Nonwetting Templates





[6,6]PC$_{61}$BM

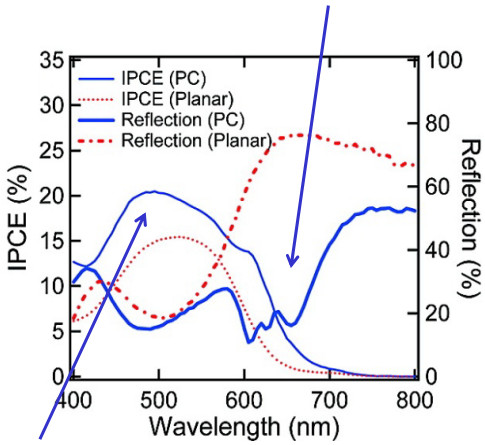


Nano Lett. 2009, 9, 2742

PhC in PV CELLS: BULK HETERO JUNCTION

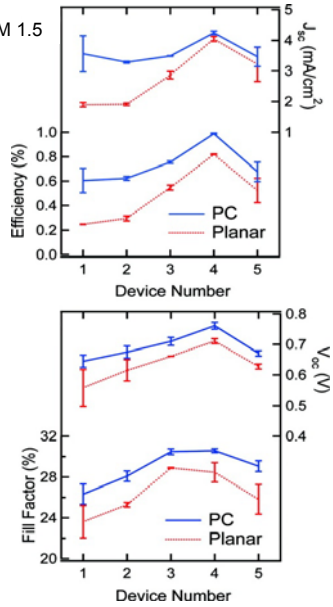
Nano Lett. 2009, 9, 2742

Reduced reflectance →stronger absorption



Increased IPCE (incident photon to current conversion efficiency)

AM 1.5



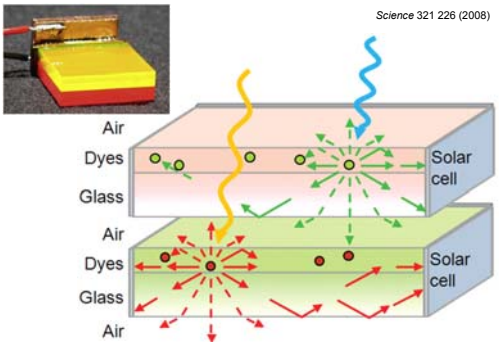
Improved performances are obtained for all relevant cell parameters indicating that both larger absorption and electrical enhancements are achieved

FLUORESCENT CONCENTRATORS

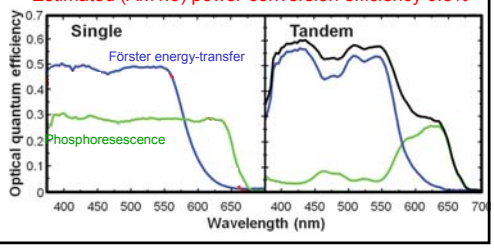
- Fluorescent concentrators (Fluko) are planar waveguides with a thin-organic film coating on the face and inorganic solar cells attached to the edges.
- Light is absorbed by the coating and re-emitted at longer wavelengths into waveguide modes for collection by side solar cells.
- Stacked flukos with spectrally matched solar cells can be obtained.
- <u>Performances of fluko is always limited by self-absorption losses that restrict maximum concentration factors.</u>
- The exploitation of different photophysical processes like Förster energy-transfer, solid-state solvation and phosphorescence enable to overcome self-absorption problem in "conventional flukos".
- In spite of that, 20-30% of emitted radiation is not guided toward solar cells.

PhCs ALLOW TO COLLECT NON-GUIDED RADIATION

Science 321 226 (2008)

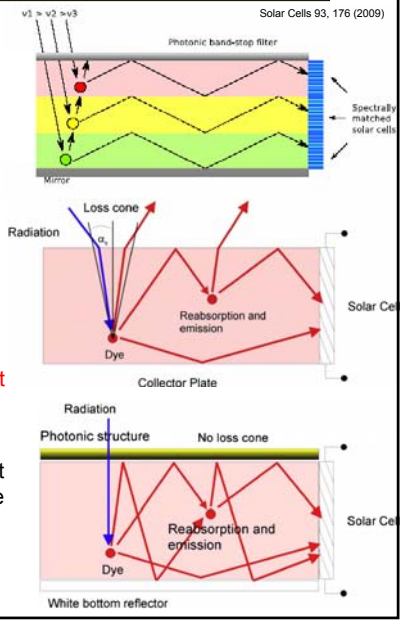


Estimated (AM1.5) power-conversion efficiency 6.8%



PhC @ FLUORESCENT CONCENTRATORS

Solar Cells 93, 176 (2009)



Fluko's key features are a stack of different fluorescent concentrators to use a broad spectral range photonic structures, which increase the fraction of light guided to the edges of the concentrator.

Solar cells are electrically independent each other thus reducing forced series connections.

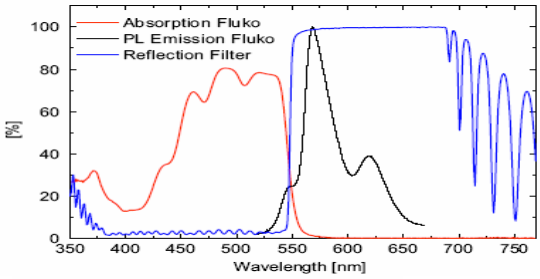
The escape cone of internal total reflection is the major loss mechanism of flukos. Light re-emitted that impinges on the internal surface with an angle greater than the critical one is totally internal reflected

$$\sqrt{1-\frac{1}{n^2}}$$

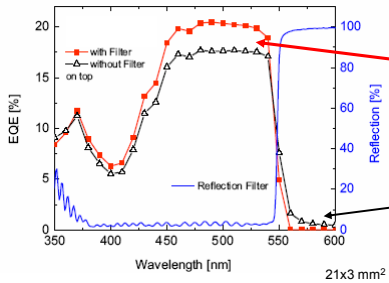
For n=1.6, 78% of light is trapped and 22% get lost

A PhC acting as a stopband reflection filter, which reflects all light in the emission range of the dye, should sugnificantly increase the collection efficiency of the concentrator.

PhC @ FLUORESCENT CONCENTRATORS



$$EQE = \frac{\text{number of harvested electrons}}{\text{number of incident photons}}$$



Strong efficiency increase is achieved in the dye absorption region

Weak efficiency reduction occurs in the high reflectivity spectral region

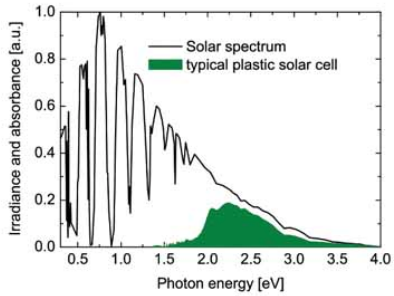
21x3 mm^2 GaInP solar cell
2x6 cm^2 fluko
$BaSO_4$ bottom reflector

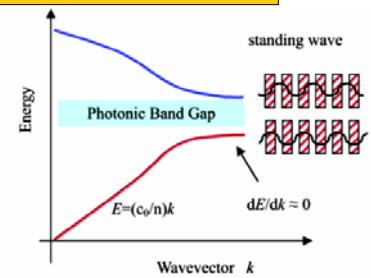
Solar Cells 93, 176 (2009)

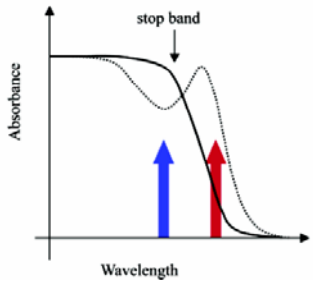
INVERSE-OPALS in DSSC

PhC induced properties useful for PV

- Inhibition of spontaneous emission.
- Light localization @ donor/acceptor interface.
- Absorption spectrum extension.
- Improved light harvesting.
- Improved carrier mobility due to ordered percolation path.
- Light insertion into the PV device.







JACS 125, 6306 (03)
J. Phys. Chem. 109, 6334 (05)

D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

INVERSE-OPALS in DSSC

J. AM. CHEM. SOC. 2003, *125*, 6306−6310

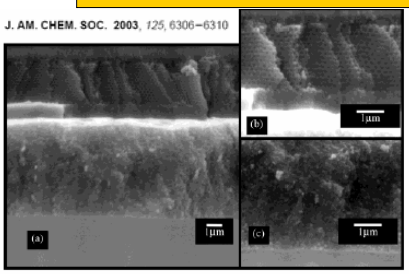
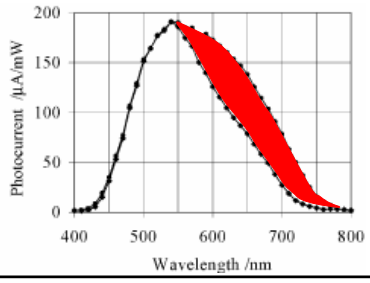
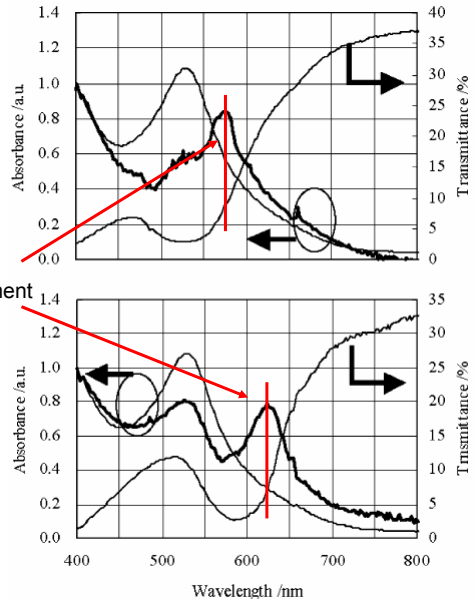


Figure 5. (a) Scanning electron micrograph of a cross section of the bilayer photonic crystal−nano-TiO_2 photoelectrode. The conductive glass is at the top of the image in (a). The photonic crystal layer and the nanocrystalline TiO_2 layer are enlarged in (b) and (c), respectively.

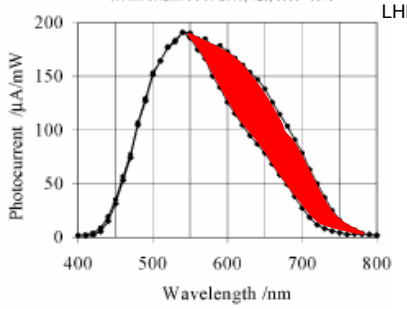


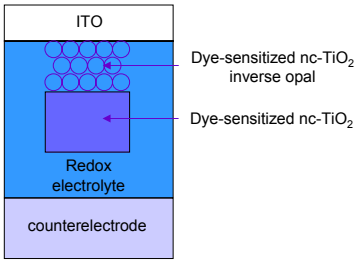
Edge enhancement



INVERSE-OPALS in DSSC

J. AM. CHEM. SOC. 2003, *125*, 6306–6310





Light harvesting efficiency
LHE(λ)= apsorptance $=I_A/I_0$

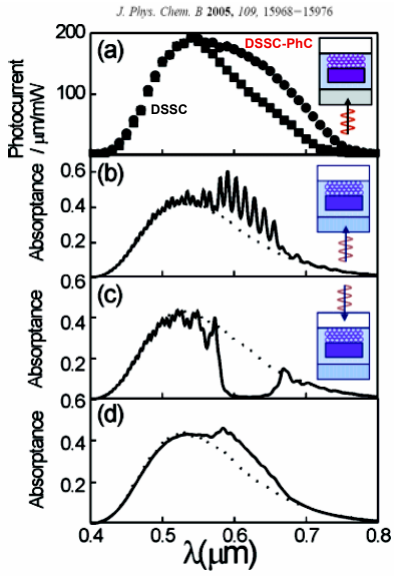
$$J_{SC} = f\left[\int LHE(\lambda)\right]$$

Front illumination: Light localized by the PhC

Back illumination: Light reflected by the PhC

Front illumination: Light localized by the PhC. Smearing out due to thickness inhomogeneity

J. Phys. Chem. B 2005, *109*, 15968–15976



D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

1D-PhC in DSSC

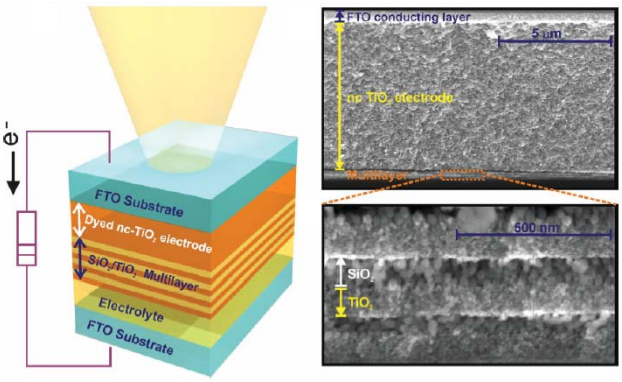
Adv. Mater. 21, 764 (09); J. Phys. Chem. C 113, 1150 (09)

- in order to improve DSSC performances, most effords are based on using different dyes or ionic conductors. They improve I_{sc}, but also cause a decrease in the V_{oc} and vice versa, due to the sensibility of the charge-transport and recombination dynamics to any alteration of the interfaces present in the cell.
- To enhance the cell efficiency without affecting charge separation and recombination, light-harvesting efficiency have to be improved.
- Reflection of unabsorbed photons back into the film improves the incident-photon-to-current conversion efficiency.
- Unfortunately, some of the most successful approaches developed to improve Si-PV based on the implementation of coherent scattering devices cannot be realized in liquid–semiconductor heterojunction cells.
- The need for an electrical contact between the electrolyte and the sensitized semiconductor slab requires the back reflector to be porous in order to allow a flow of the liquid conductor through it.
- Second, processing of these cells involves deposition of solid layers from colloidal suspensions, which complicates the implementation of quality optical components in the device.
- Inverse opals to dye-sensitized nc-TiO_2 films showed interesting results since IPCE was shown to increase with respect to that of a standard reference cell, at least as a proof of concept even tough no power conversion efficiency improvements have been measured.
- Thick inverse opals (5–10 mm thick) are very likely to have a deleterious effect on charge transport and recombination through the cell, which results in a significant reduction in both the open-circuit photovoltage and the photocurrent in real operation conditions.

1D-PhC in DSSC

Adv. Mater. 21, 764 (09); J. Phys. Chem. C 113, 1150 (09)

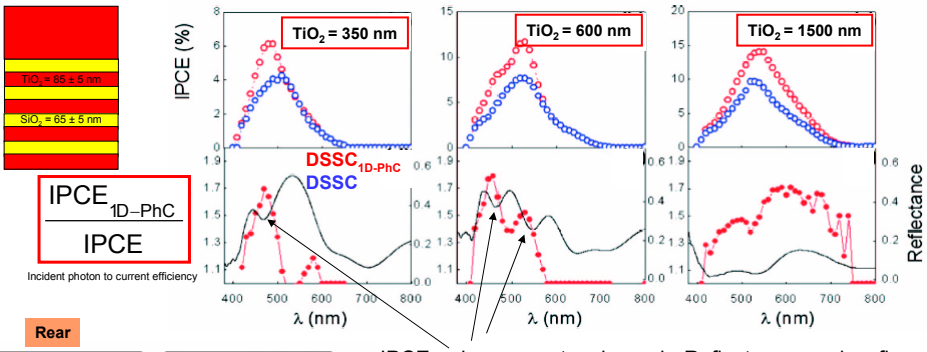
- A novel device structure based on porous 1D-PhC coupled to a dye-sensitized nc-TiO_2 electrode has been proposed.
- This coherent mirror is made by the deposition of alternate layers of SiO_2 and TiO_2 nanoparticles by spin-coating.
- With a thickness of just half a micrometer, the PhC is able to localize incident light within the nc-dyed TiO_2 electrode in a targeted wavelength range.



- Average power conversion efficiencies are improved to between 15 and 30% of the reference value attained for standard electrodes.
- The photogenerated current is greatly improved without altering V_{oc}.
- The transparency of the cell, one of its added values, remains intact, contrary to what happens when scattering layers are employed to improve light harvesting.

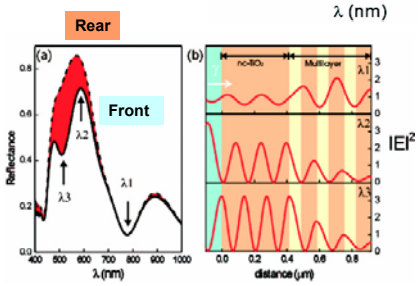
D. COMORETTO – INTRODUCTION TO PHOTONIC CRYSTALS: NANOSTRUCTURED MATERIALS TO MANIPULATE LIGHT PROPAGATION & HARVESTING
WINTER COLLEGE ON OPTICS and ENERGY , Trieste 8 – 19 February 2010

1D-PhC in DSSC



$$\frac{IPCE_{1D-PhC}}{IPCE}$$

Incident photon to current efficiency



IPCE enhancement ≡ deeps in Reflectance peak = fingerprint of light localization into the dye infiltrated TiO_2 electrode

- Localization is observed only for front light incidence and not for rear illumination.
- **Localization within TiO_2 dye-impregnated-electrode occurs at λ_2 where IPCE shows a peak.**
- Outside the stop band (λ_1) or at the reflectance peak (λ_2) reduced field localization occurs inside the photoactive layer and then lower values for IPCE are observed.

Adv. Mater. 21, 764 (09); J. Phys. Chem. C 113, 1150 (09)

CONCLUSIONS

- I hope this lecture might trigger your interest in Photonic Crystals, a new class of materials suitable for controlling light propagation.
- Once again, a multi-cultural approach mixing together fundamental knowledge in chemistry, physics and material science allows to prepare novel materials with unusual properties.