Liquid Crystal Infiltration of Template Patterned 3D Photonic Crystals

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Outline

- 3D Photonic Crystals
- Review of Liquid Crystals in 3D Photonic Crystals
- Tunability Schemes
- **Tunability Computations (FDTD)**
  - Opal
  - Inverse shell opal
  - Non-close-packed inverse opals
- **Experimental Studies**
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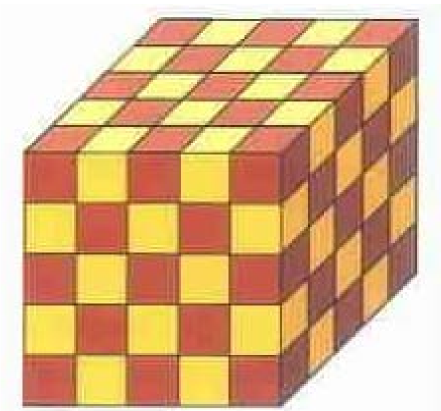
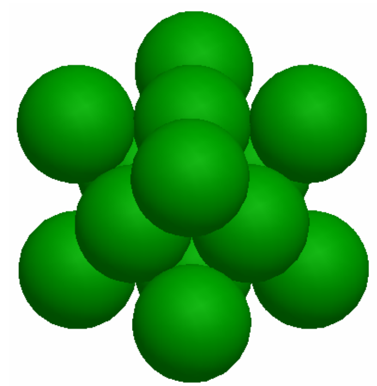
  - Pre-Sinter plus Atomic layer deposition (ALD)
  - Liquid crystal infiltration – 5CB
  - Reflectance Spectra
  - Electric field tuning
  - Hydrophobic / Hydrophilic
- Summary

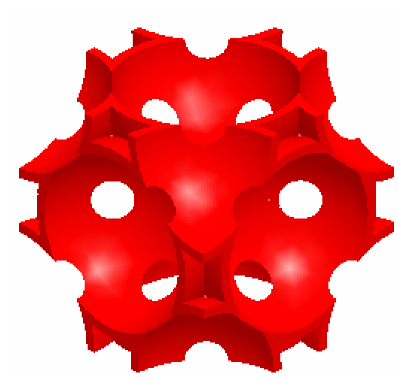
3D Photonic Crystals



Structures with a 3-dimensional dielectric periodicity.

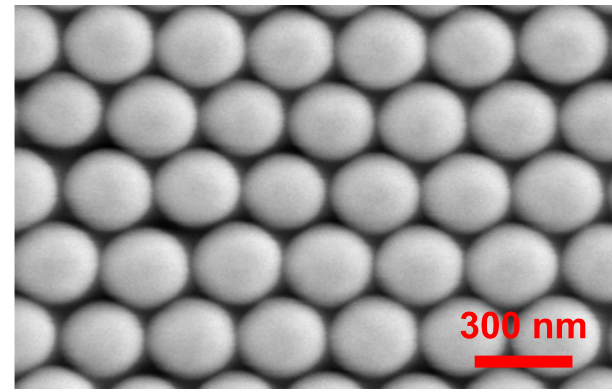


26% air

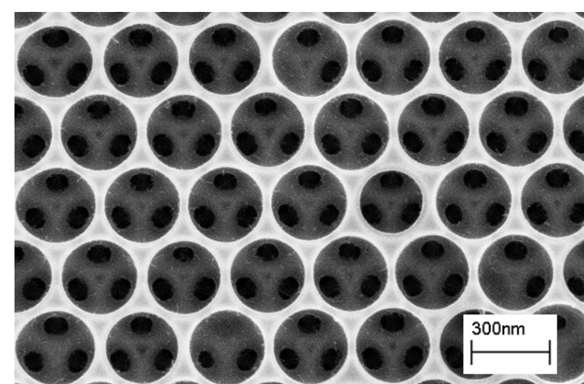


77.4% air

Opals

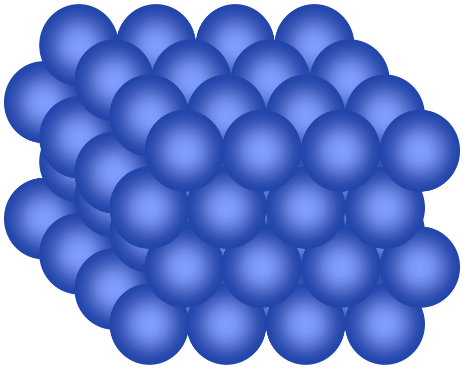


Inverse opals



3D Photonic Crystals

Opals:



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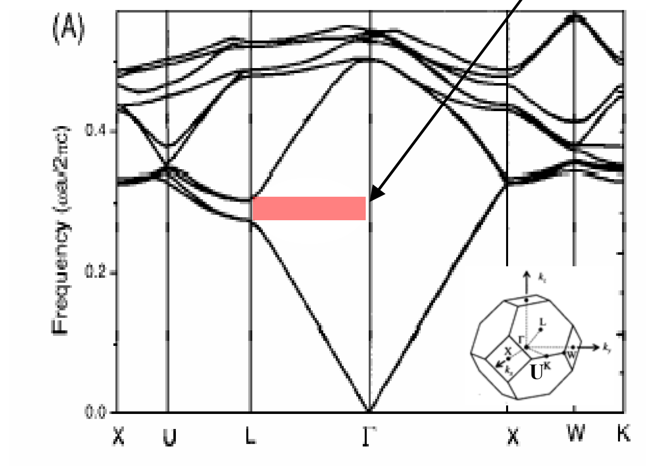
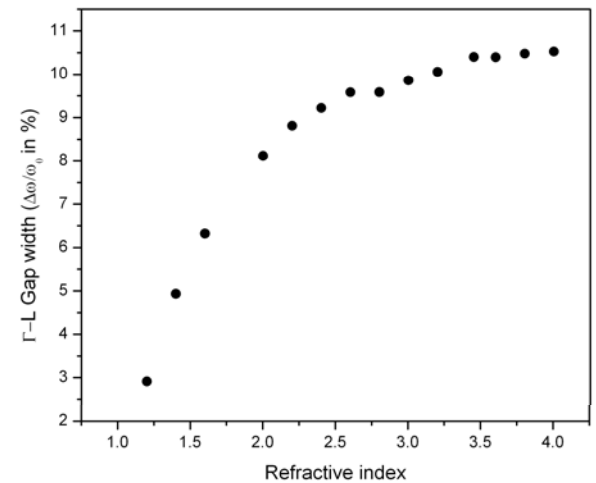
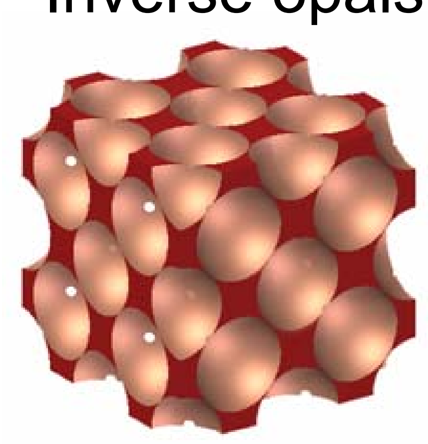
Pseudo gap

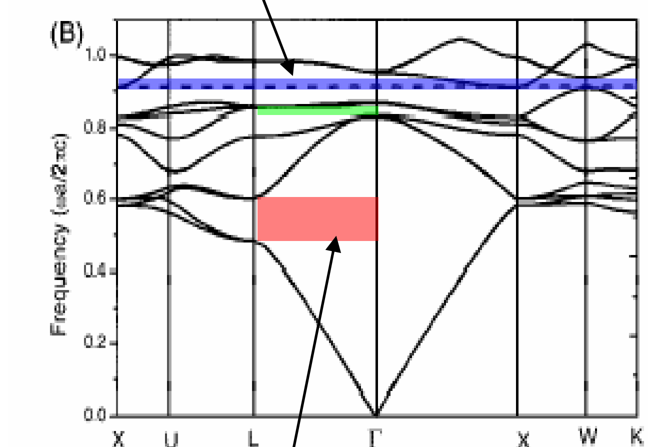




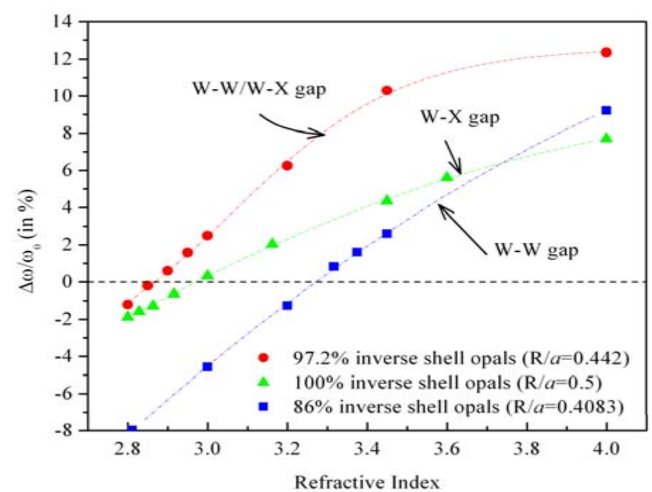
Inverse opals:



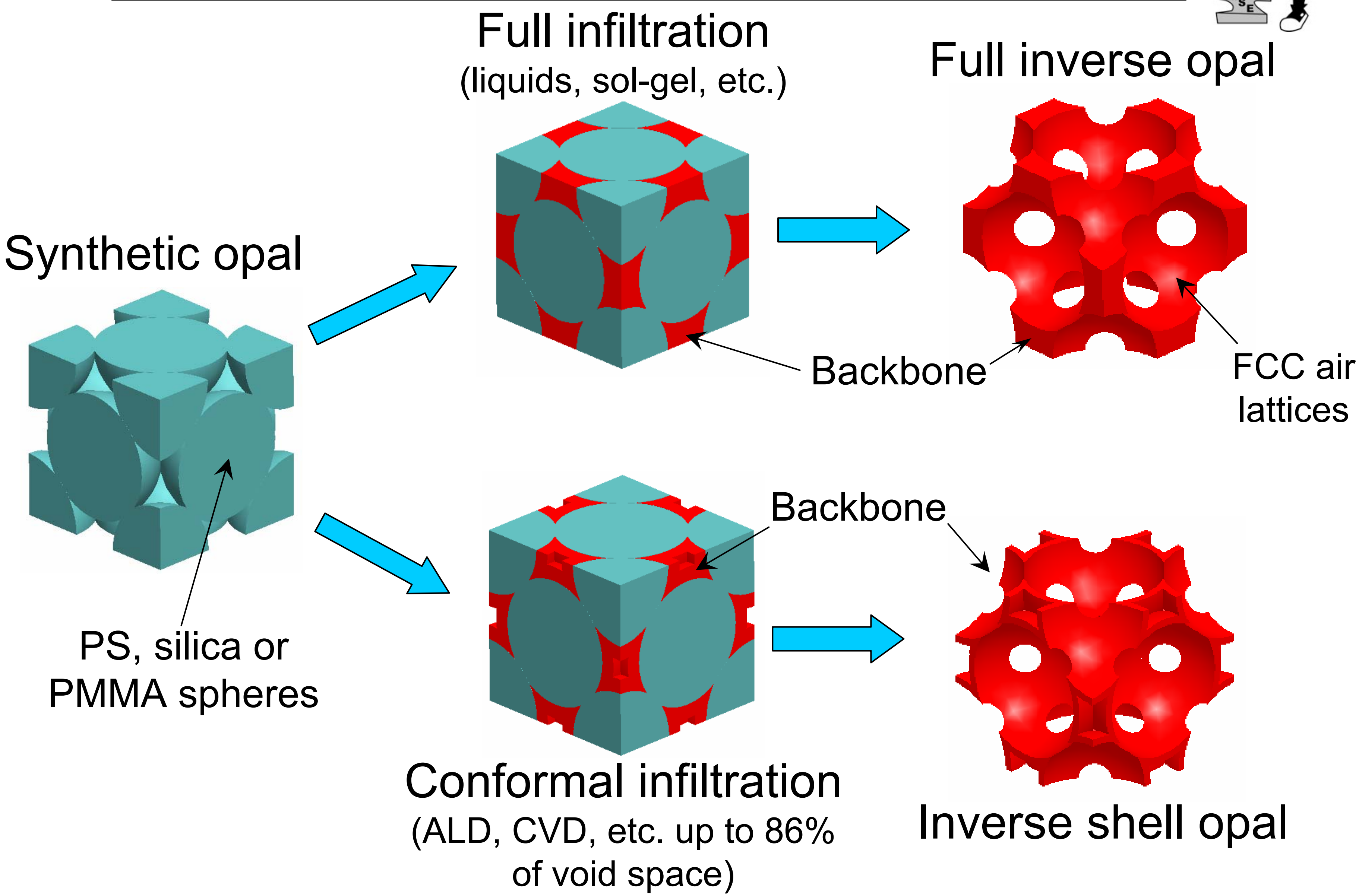
Full gap possible



Pseudo gap



Inverse Opal Structures



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Properties of Opals and Inverse Opals

- **Opals**
  - 2-3 Γ-L Pseudo PBGs observed for refractive index greater than 1.1 (PS, silica, PMMA colloidal spheres)
- **Conformally infiltrated opals (ALD/CVD techniques)**
  - Total dielectric volume < 26% (~22.4%)
  - Outer shell radius controls final geometry
  - PBG static tunability is a function of lattice constant *a*, refractive index contrast and dielectric filling fraction
- **Inverse shell opals**
  - Complete PBG predicted for *n* > 3.3 (Si, GaP, etc.)
  - FCC air lattices reported to enhance PBG properties
  - Total dielectric volume < 26% (~22.4%)
  - PBG static tunability is a function of lattice constant *a*, backbone refractive index, dielectric filling fraction and network topology

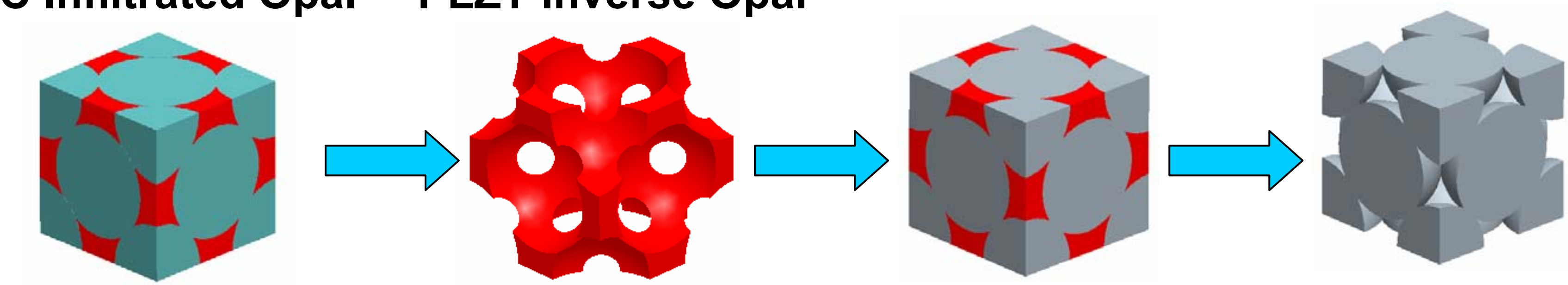
Review of Liquid Crystals in 3D PCs

- **Liquid crystal tuning in infiltrated opals:**
  - K. Yoshino *et al*. Appl. Phys. Lett. 75, 932 (1999)
  - K. Yoshino *et al*. Synth. Metals 121, 1459 (2001)
  - D. Kang *et al*. Phys. Rev. Lett. 86, 4052 (2001)
  - Q.-B. Meng *et al*. J. Appl. Phys. 89, 5794 (2001)
  - Y. Shimdo *et al*. Appl. Phys. Lett. 79, 3627 (2001)

- **Liquid crystal infiltration in inverse opals:**
  - K. Busch & S. John, PRL 83, 967 (1999)
  - P. Mach *et al*. Phys. Rev. E 65, 031720 (2002)
  - G. Mertens *et al*. Appl. Phys. Lett. 80, 1885 (2002)
  - M. Ozaki *et al*. Adv. Mater. 14, 514 (2002)
  - S. Kubo *et al*. J. Am. Chem. Soc. 124, 10950 (2002)
  - S. Gottardo *et al*. Physica B 338, 143 (2003)
  - S. Kubo *et al*. J. Am. Chem. Soc. 126, 8314 (2004)
  - S. Kubo *et al*. Chem. Mater. 17, 2298 (2005)

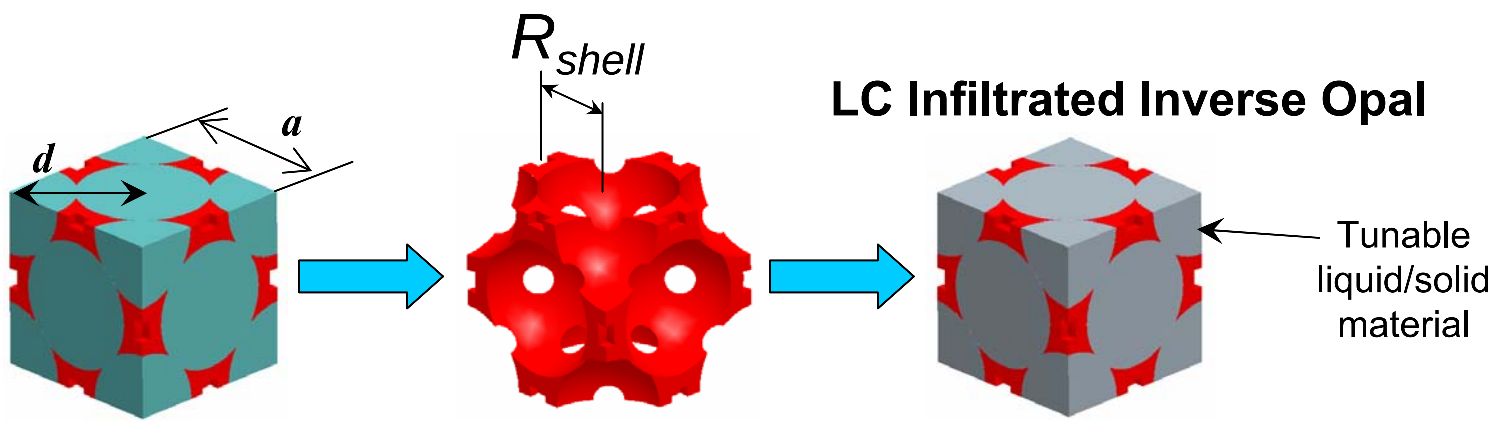
Tunability Schemes

LC Infiltrated Opal **PLZT Inverse Opal**



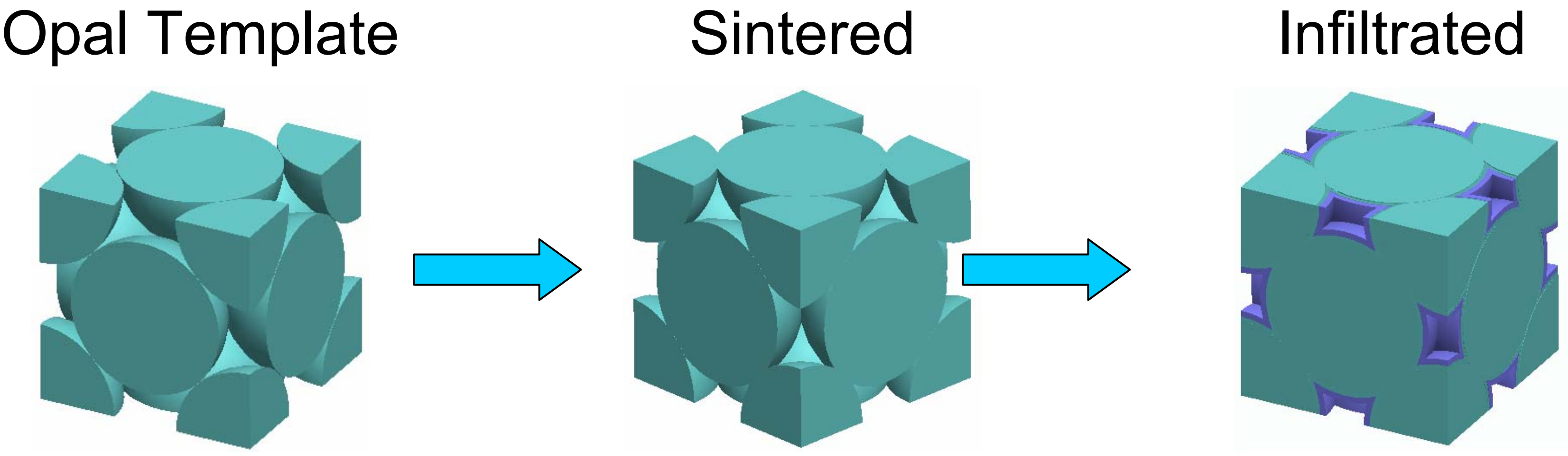
Tunable fully infiltrated opal (backbone material) | Tunable inverse opal | Tunable fully infiltrated inverse opal | Tunable opal

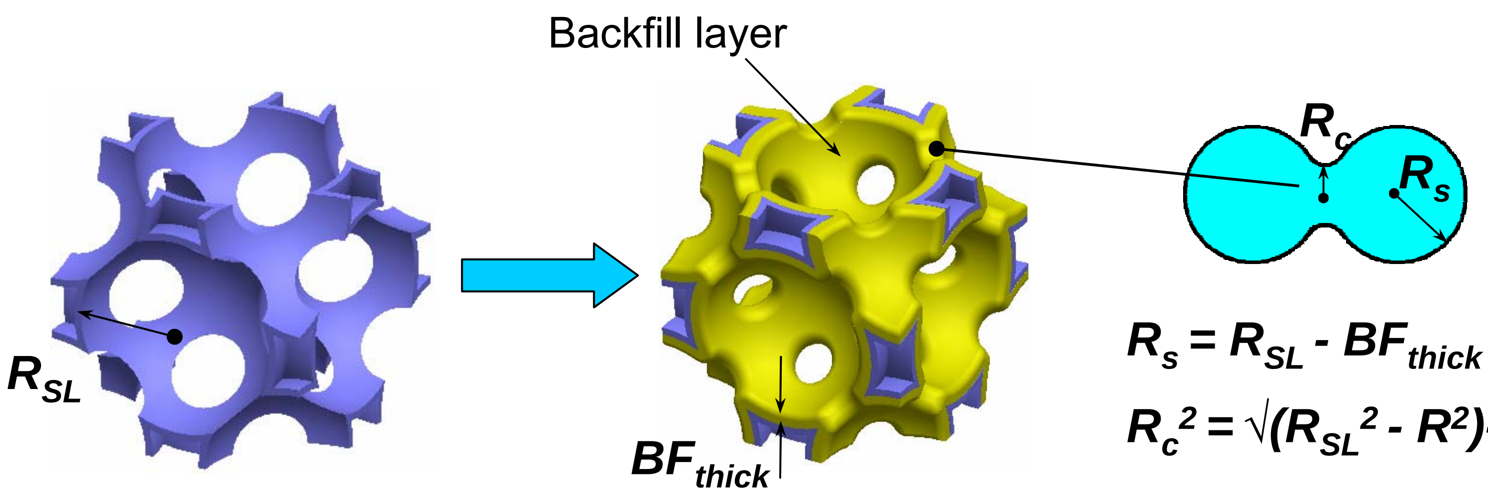
LC Infiltrated Inverse Opal



Tunable partially infiltrated opal (backbone material) | Tunable inverse shell opal | Partially infiltrated ($R_{shell}/a > 0.4083$)

Non-close-packed Inverse Shell Opals





$R_s = R_{SL} - BF_{thick}$

$R_c^2 = \sqrt{(R_{SL}^2 - R^2)} - BF_{thick}$

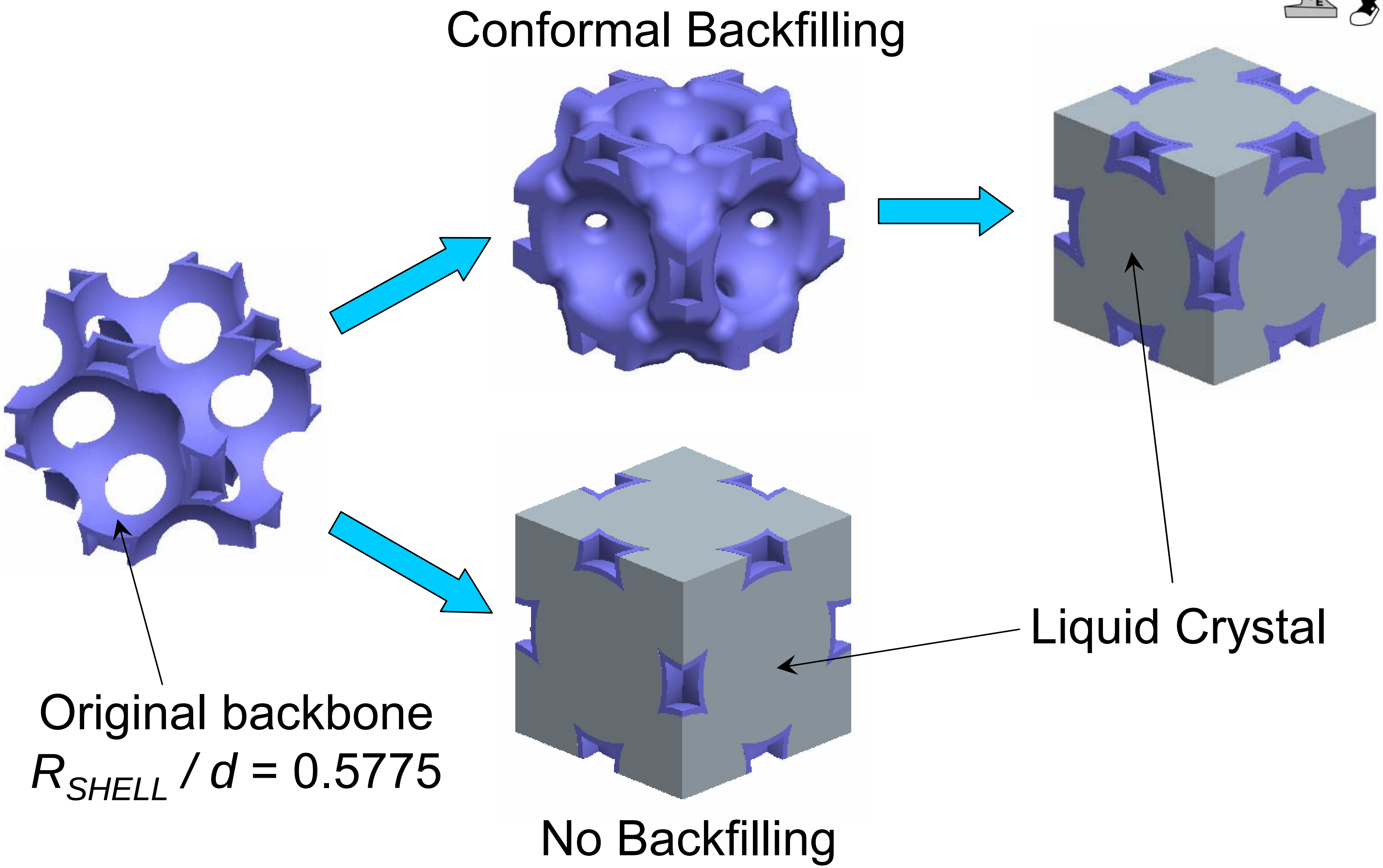
M. Doosje *et al*. J. Opt. Soc. Am. B 17, 600 (2000)
H. Miguez *et al*. Adv. Mater. 15, 597 (2003)

Properties of Non-close-packed Inverse Shell Opals

- **Non-close-packed inverse shell opals***
  - Complete PBG predicted for *n* > 2.6 in optimized structures
  - Lowest possible dielectric filling fraction (~5%)
  - Highest open volume available for infiltrated material (up to ~95%)
  - Outer shell radius and backfill thickness control final geometry and degree of connectivity
  - Wide air pores offer electro-optical material infiltration ease
  - ALD technique supports fine network topology tuning thus enabling tailoring of PBG properties
  - Structures resulting to sintered opals-like are achievable using various materials

*Gaillot *et al.* (to be submitted)

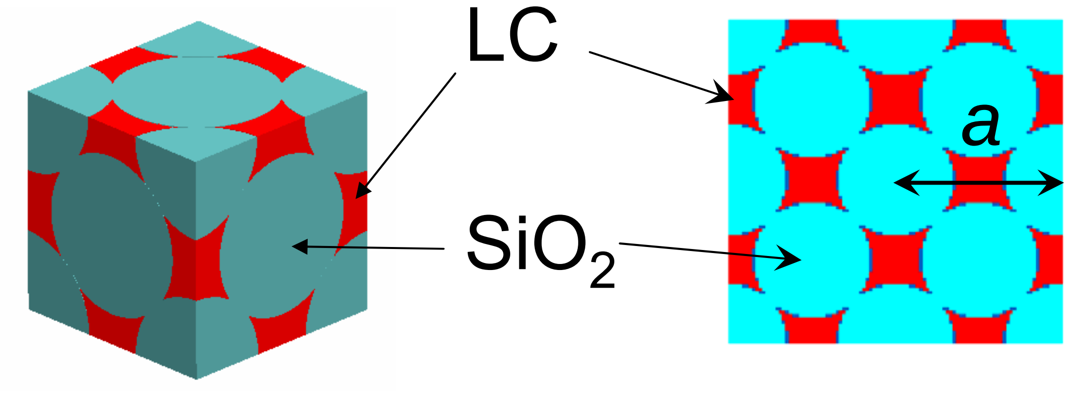
Non-close-packed Inverse Shell Opal Tunability Schemes



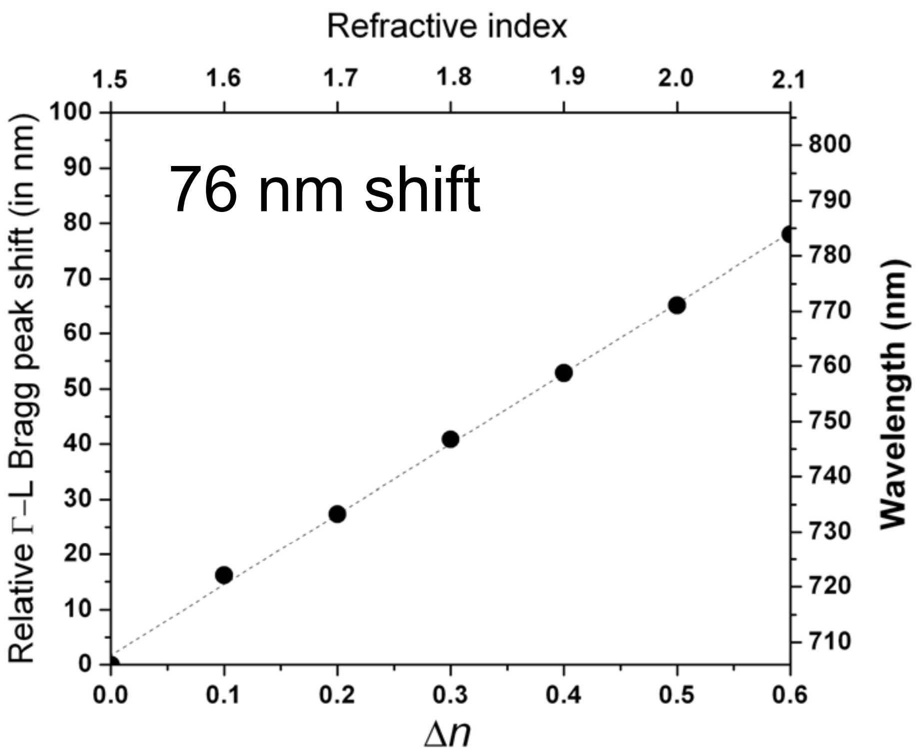
Tunability Computations

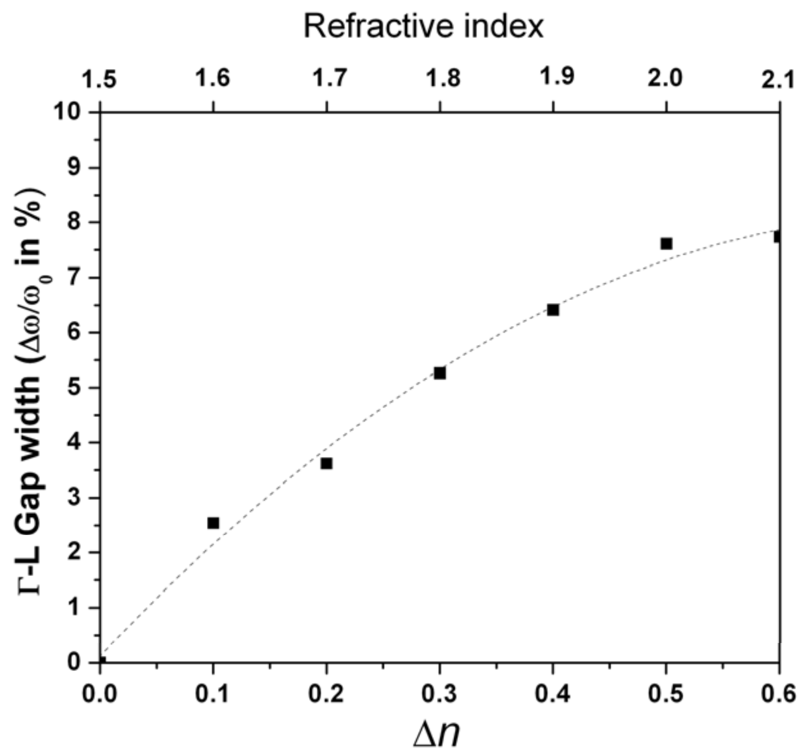
- 3D-finite difference time domain (3D-FDTD) was used as a robust and versatile technique to compute photonic properties.
- Photonic bands for the $\Gamma - L$ *k*-vector domain were computed to predict gap widths and central positions of 1st order Bragg peak.
- Structures investigated:
  - Opals
  - Inverse opals/shell opals
  - Non-close-packed inverse opals and related
- Tunable materials investigated:
  - Liquid Crystal (LC) with n = 1.5-2.1 (Δn = 0.6)

LC Infiltrated Silica Opals

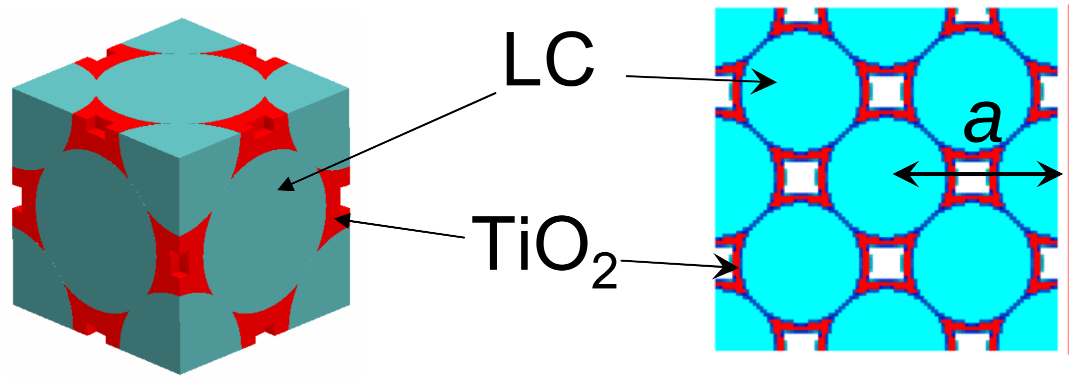


a = 400 nm



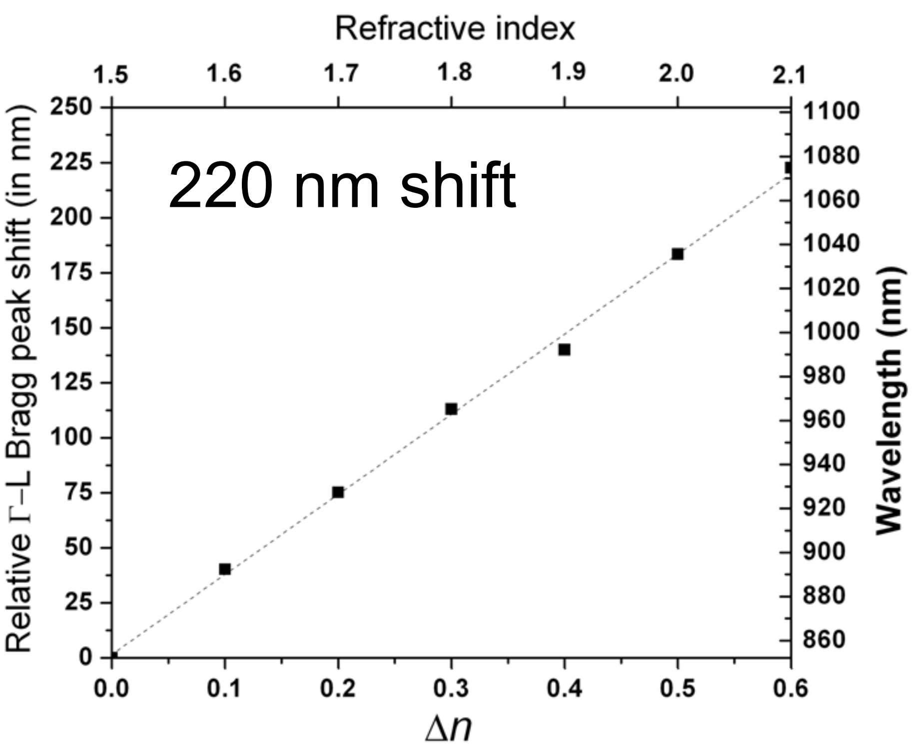


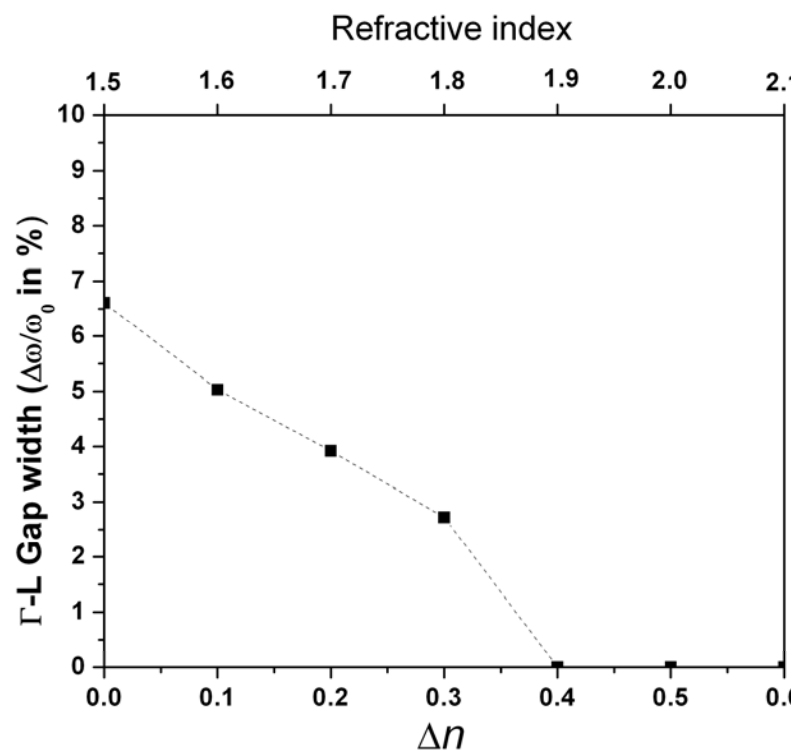
LC Infiltrated TiO_2 Inverse Shell Opals



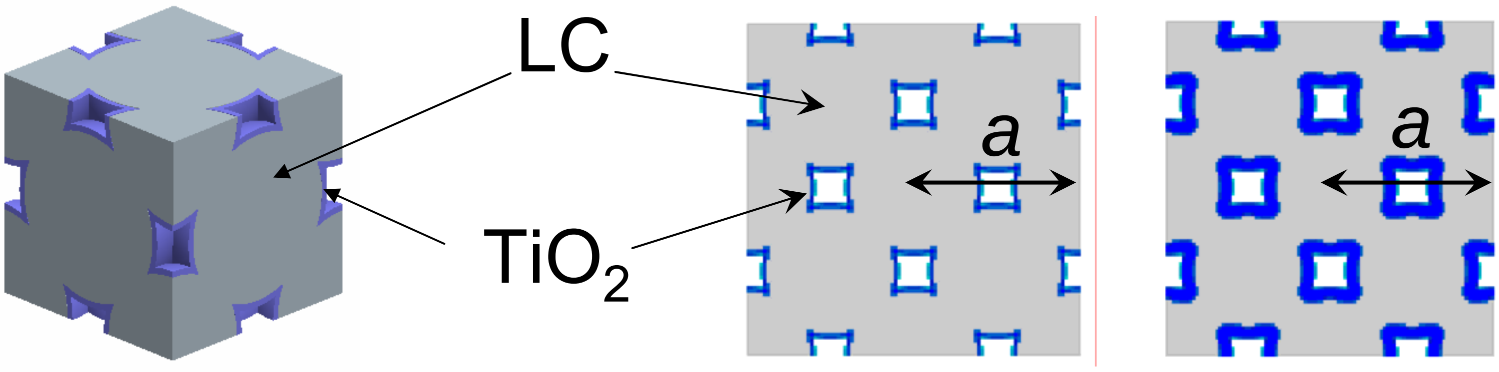
a = 400 nm

n_{TiO2} = 2.65

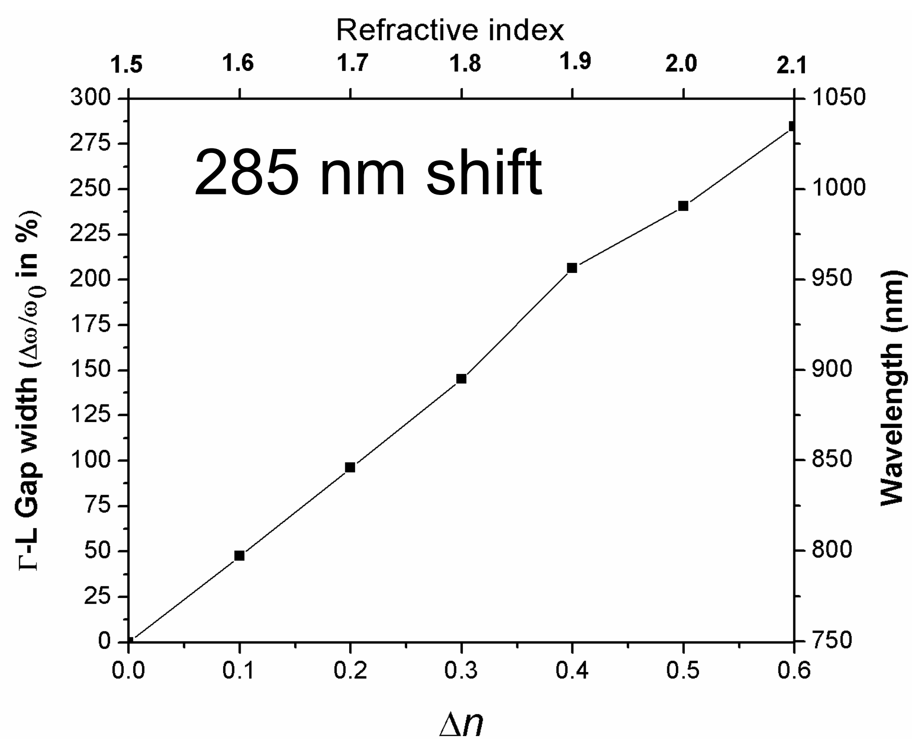


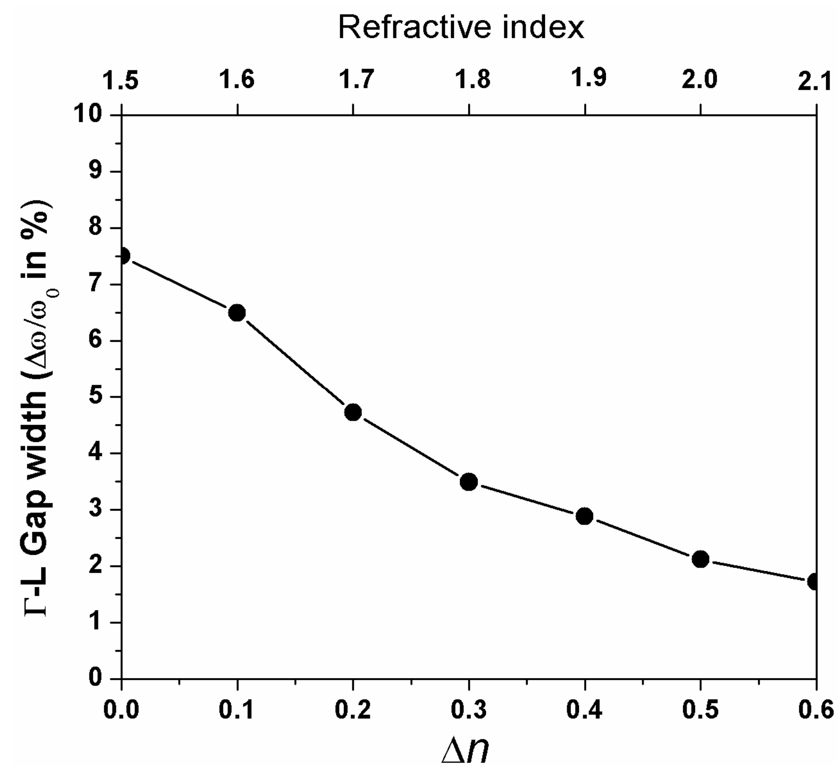


LC Infiltrated Non-close-packed Inverse Shell Opals

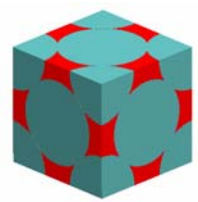
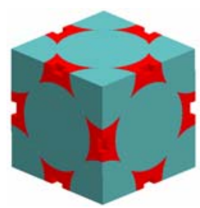
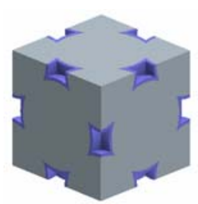


a = 400 nm

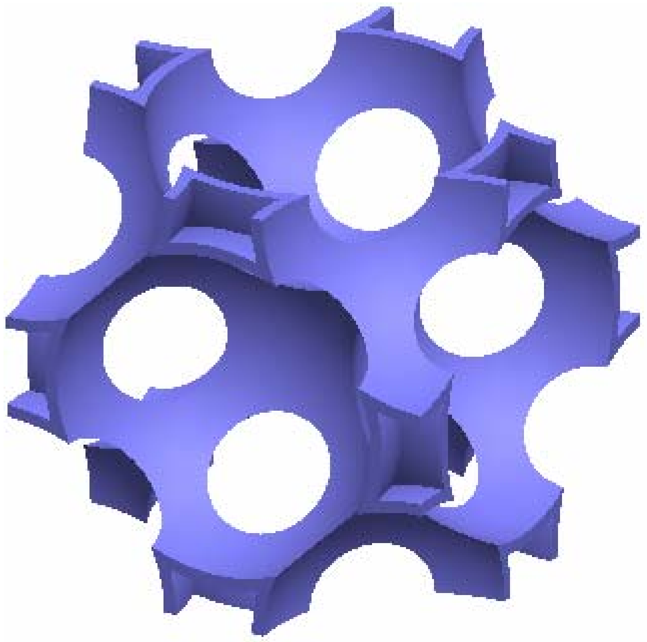




LC Tunability Results

	Structure	Max. PBG width (%)	PBG width tunability – Δn = 0.1 (%)	Γ-L Bragg peak shift – Δn = 0.1 (nm)	Maximum Volume (%)
SiO_2 Opals		8	1.5	13	26
TiO_2 Inverse shell opals		6.6	1.5	37	74
Non-close-packed inverse shell opals		2.1	1	47	90.5
Non-close-packed inverse shell backfilled opals		7.5	1.5	35	68.6

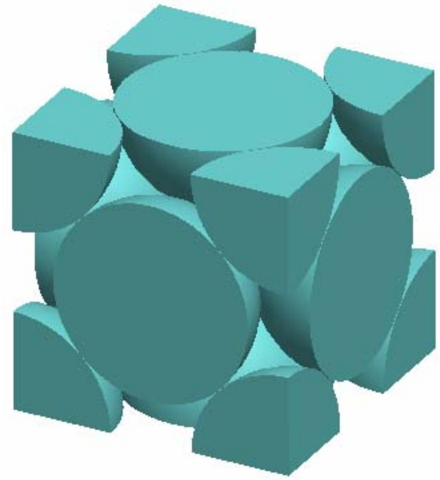
Experimental Study



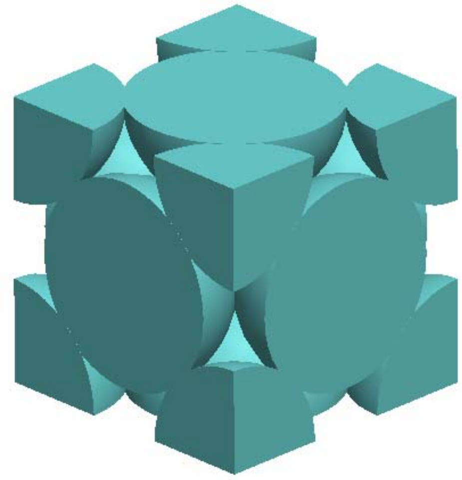
- Non-close-packed inverse shell opal structures
- Lowest dielectric filling fraction
- Large volume available for liquid crystal
- Largest shift of the Bragg peak

Fabrication of Non-close-packed Inverse Shell Opals

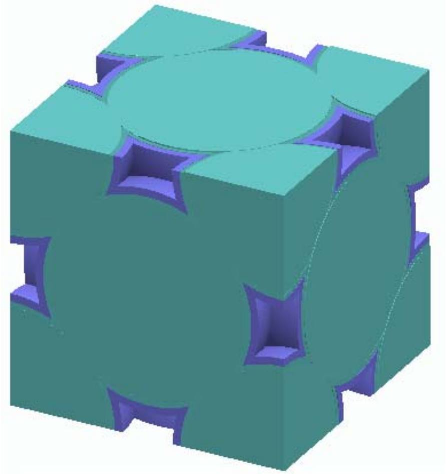
Opal Template



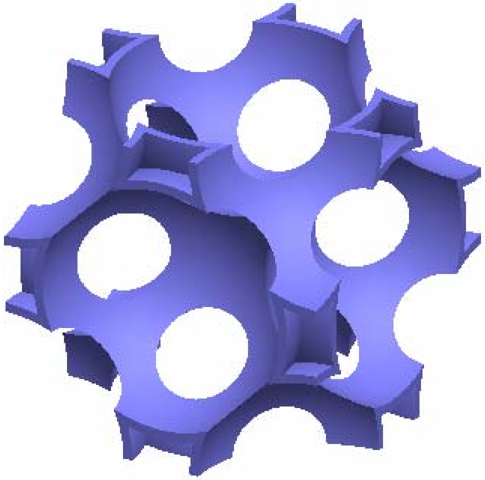
Sintered



Infiltrated

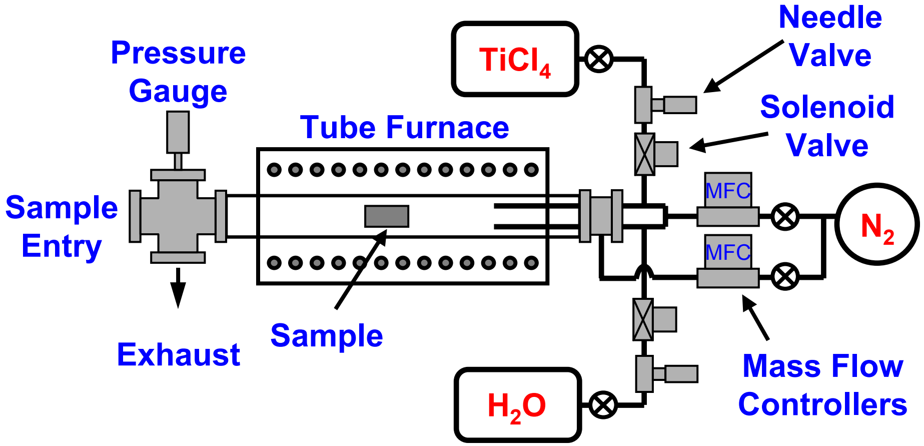


Inverted



NCP Inverse Opal Fabrication: Atomic Layer Deposition

- Atomic layer deposition in synthetic opal templates using TiO_2 and Al_2O_3.
- Surface limited growth.
- Precise digital control of film thickness.
- Low temperature growth (80°C) allows
  - Ultra-smooth conformal thin films
  - growth on PS spheres
- Selective etching



ALD of TiO_2 at 100ºC

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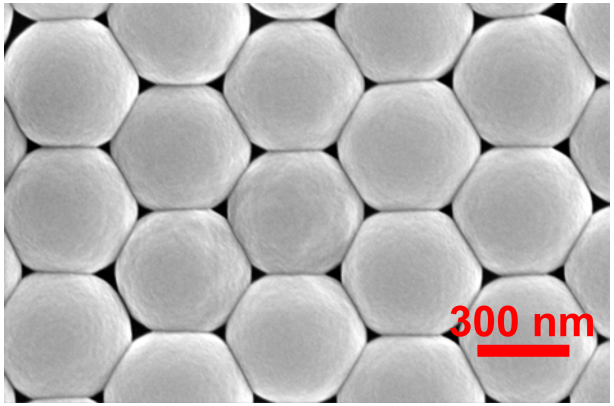
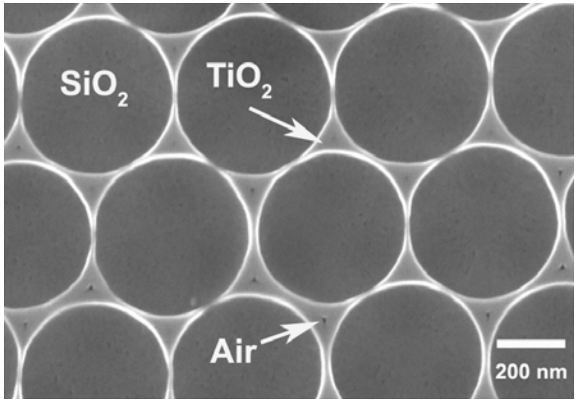
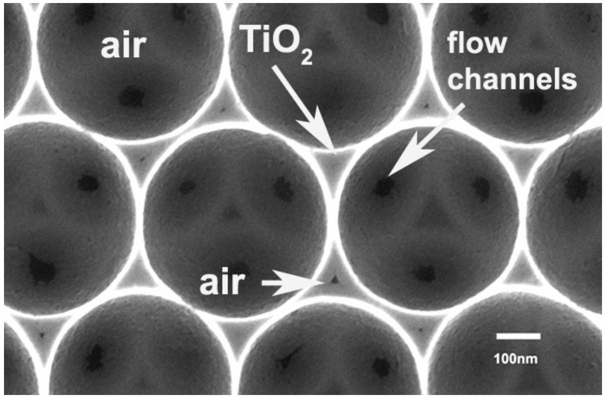
Cross-sections



433 nm opal infiltrated with 20 nm of TiO_2



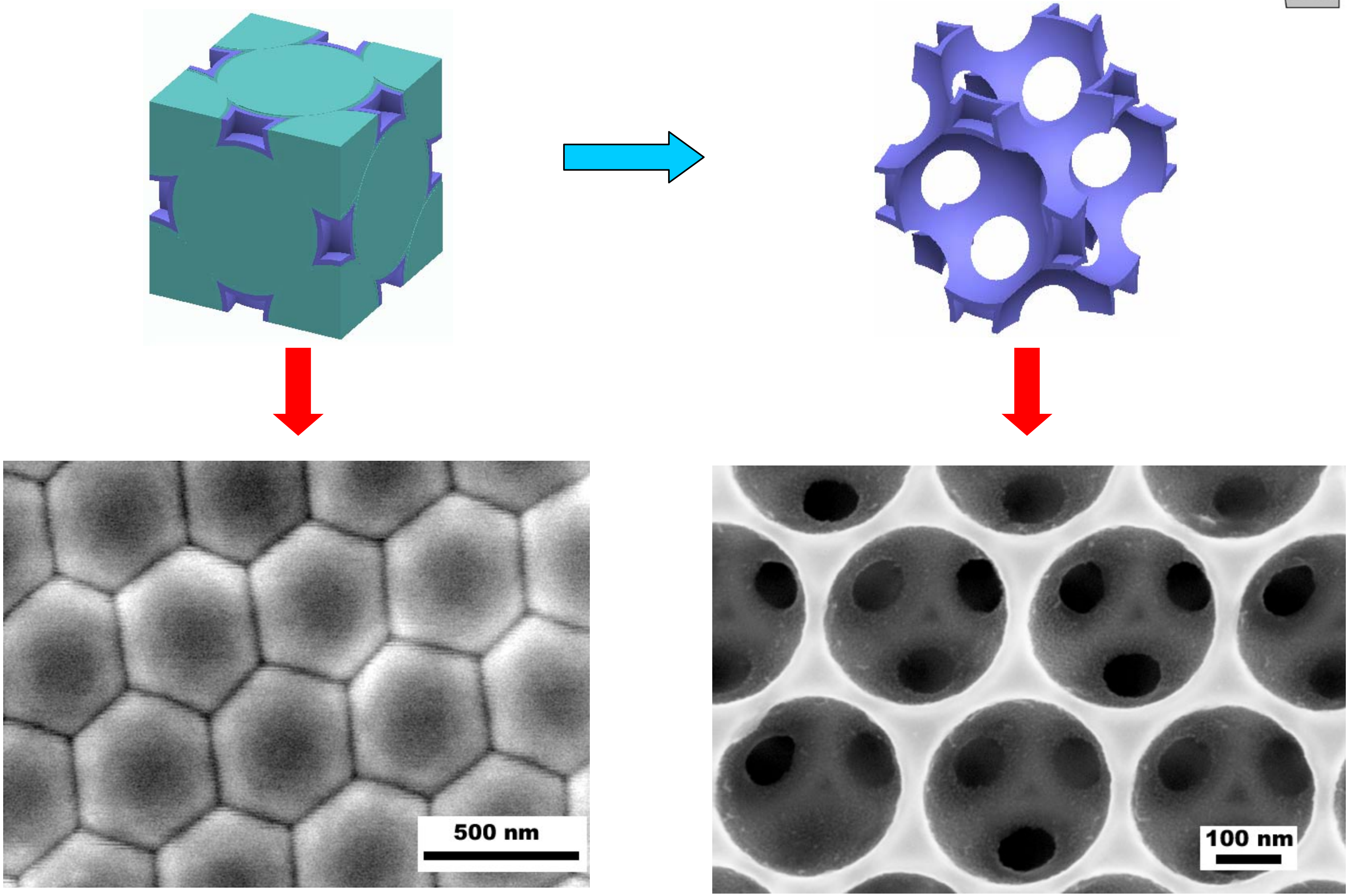
433 nm opal infiltrated with TiO_2



433 nm TiO_2 inverse opal

- TiO_2 infiltration at 100°C produces very smooth and conformal surface coatings with rms roughness ~2Å.
- Heat treatment (400°C, 2 hrs.) of infiltrated opal converts it to anatase TiO_2, increasing the refractive index from 2.35 to 2.65, with only a 2Å increase in the rms surface roughness.

Pre-sintered Non-close-packed Inverse Shell Opals

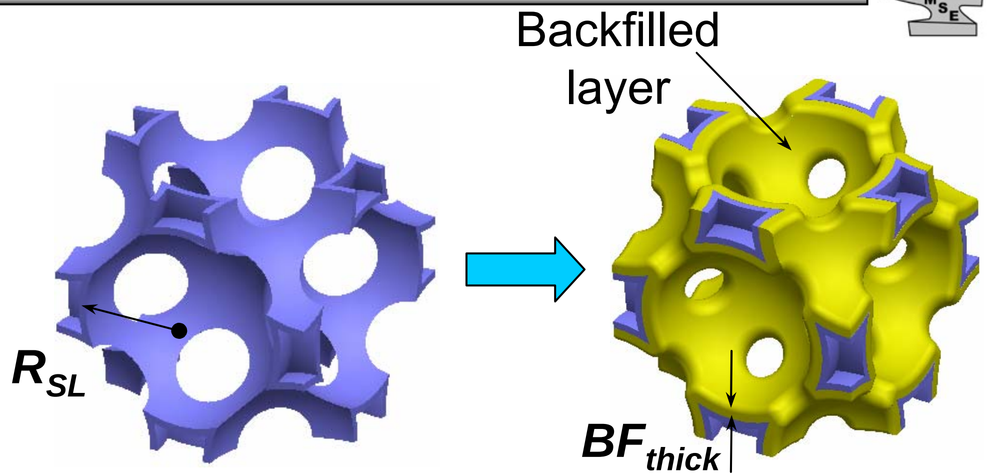


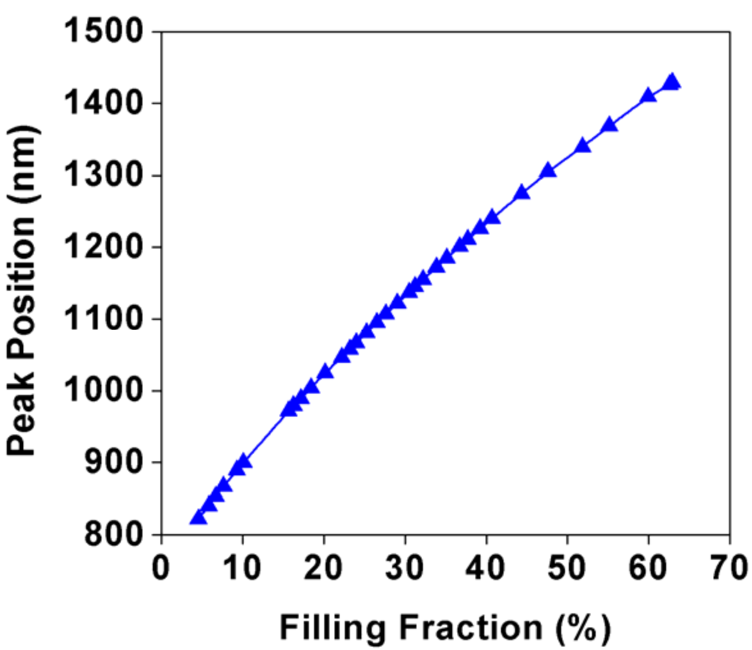
Static Tunability:

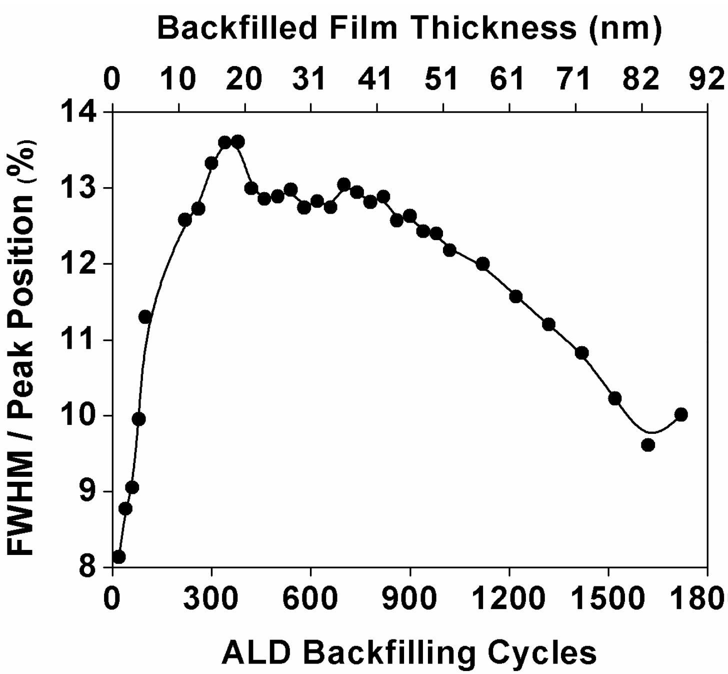
Backfilling Non-close-packed Inverse Shell Opals

Conformal Backfilling

- ALD provides precise filling fraction control
- Over 600 nm tuning
- 167% Bragg peak width enhancement

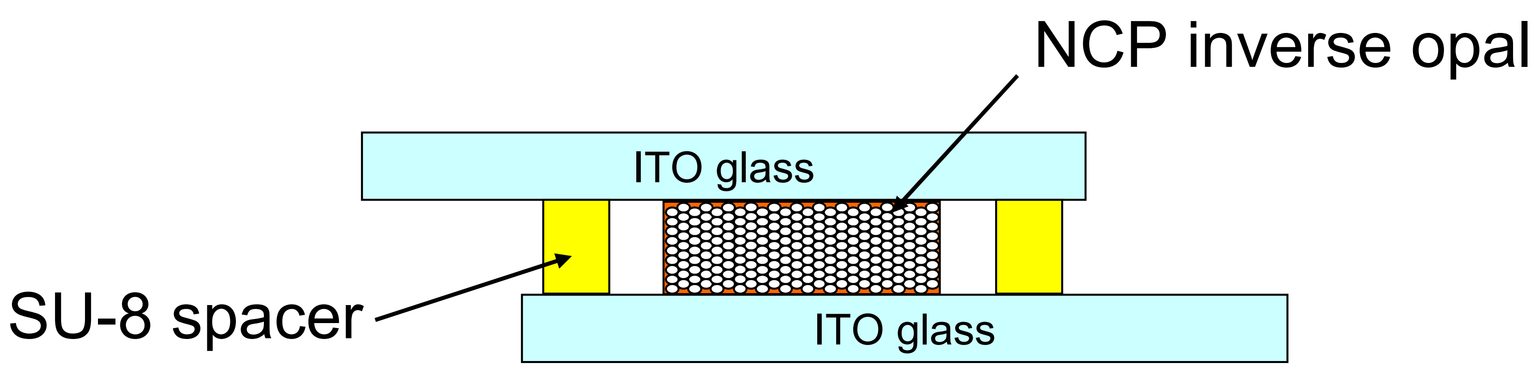






Sample Cell Fabrication

- TiO_2 non-close-packed inverse shell opals were prepared using the sinter method.
- Several samples were coated with a hydrophobic surface treatment (fluorinated chlorosilane) to minimize surface pinning.
- Individual inverse opal grains were selected and placed between cleaned ITO coated glass substrates.
- Clean 10 μm thick SU-8 spacers were used to separate the ITO surfaces.

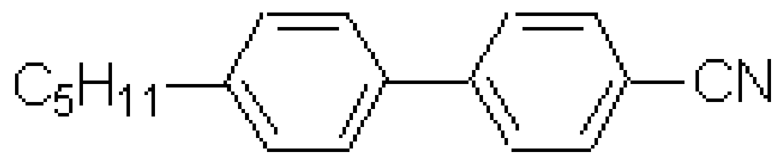


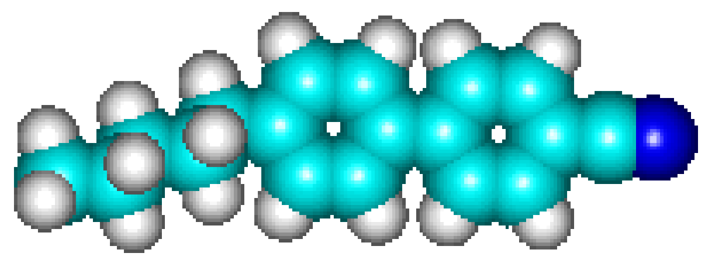
Liquid Crystal Infiltration

- Hydrophilic (untreated) samples
  - Infiltrated with pure 5CB at 50°C.
  - Drop at gap of the sample cell.
  - Immediate color change.

- Hydrophobic (treated) samples
  - Infiltrated with a mixture of 5% 5CB in ethanol at 20°C.
  - Drop at edge of partially open cell.
  - Gradual color change with repeated application
  - Post infiltration ensured ethanol removal.

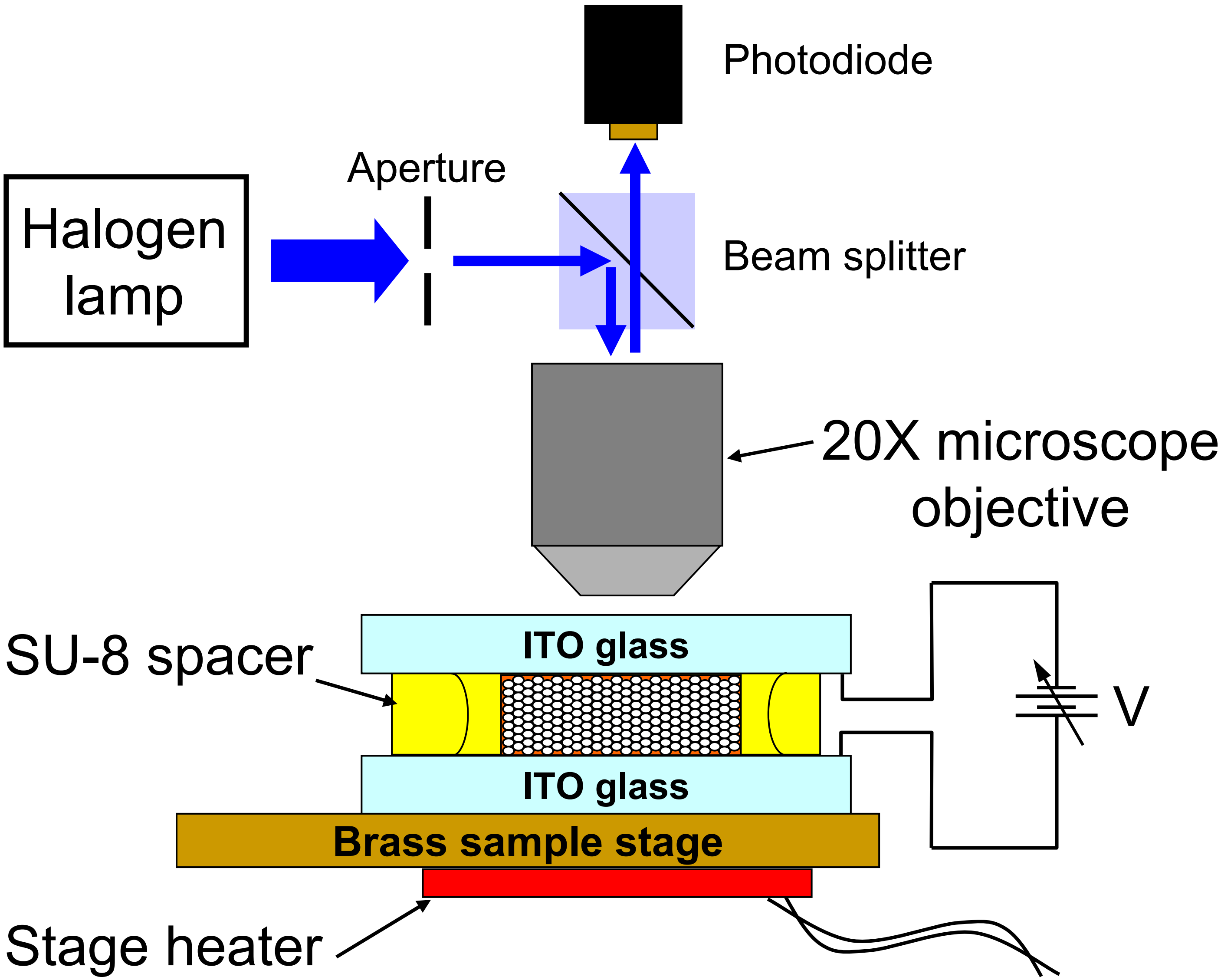
5CB





n = 1.522 to 1.706

Schematic of microscope reflectance measurement



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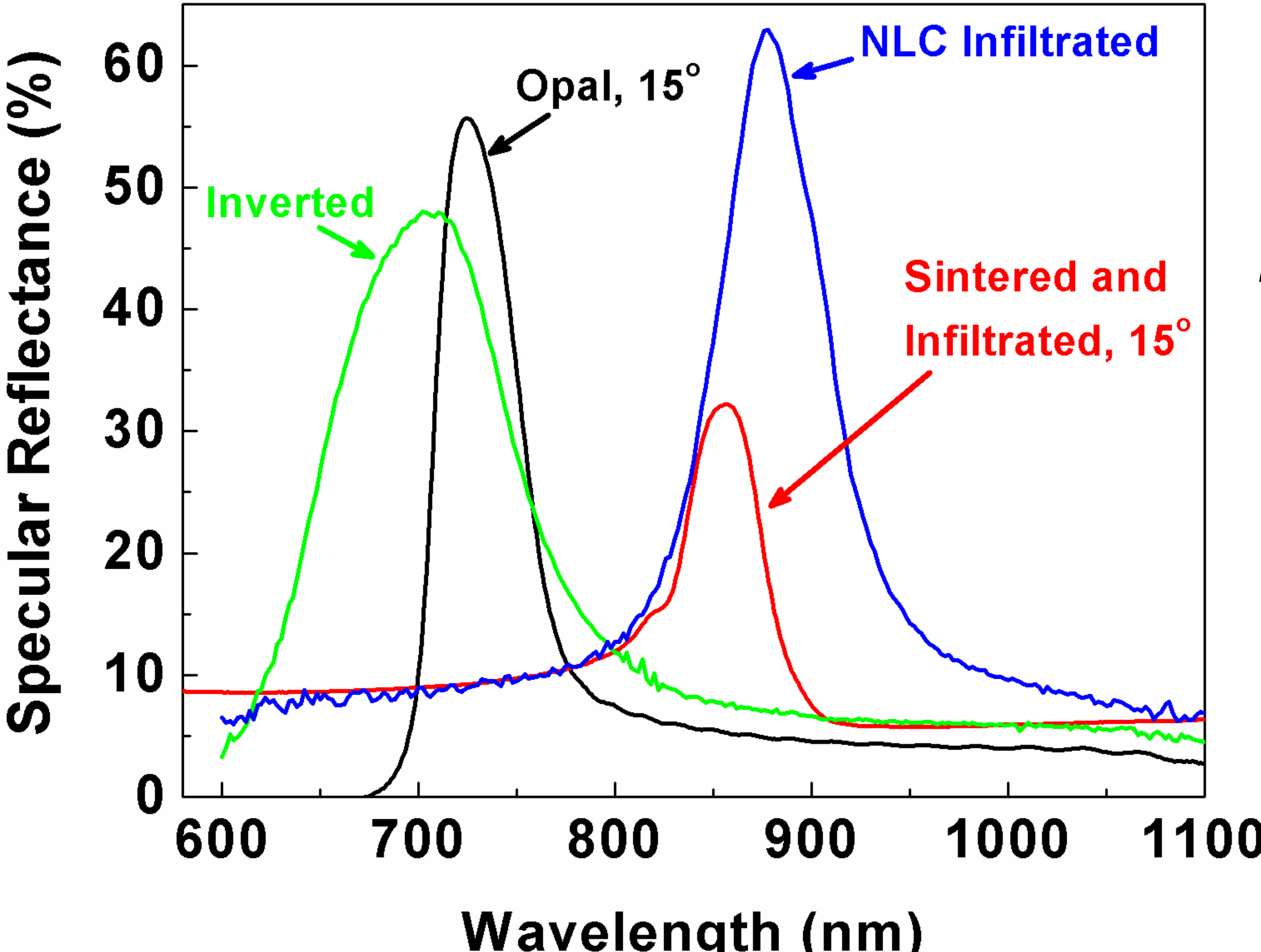
Reflectance Spectra



$n_{ave}^{LC} = 1.586$

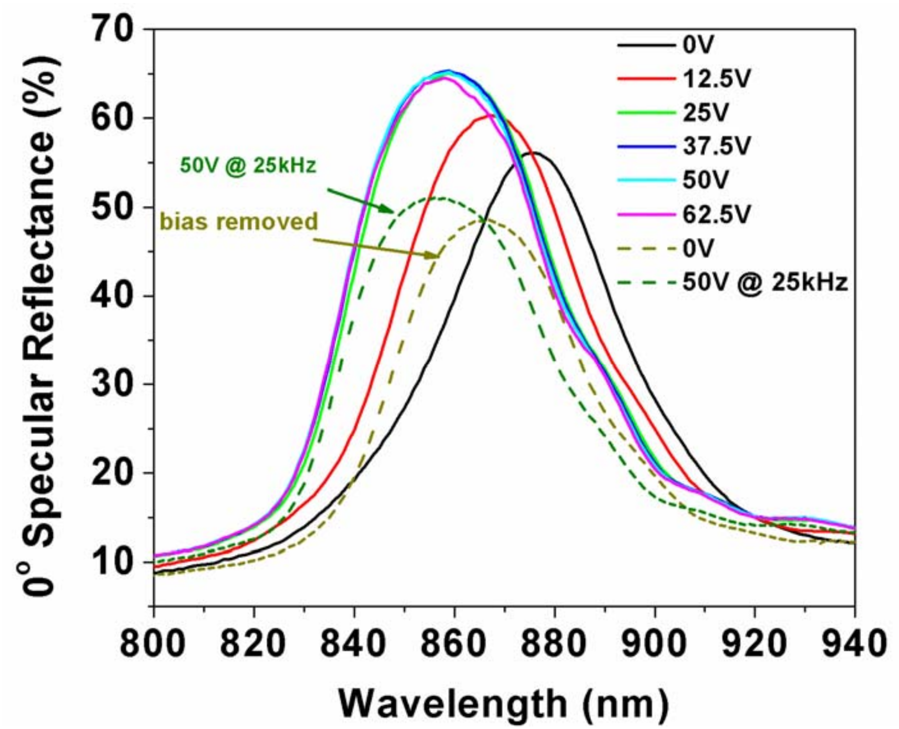
$n_{expt}^{LC} = 1.583$

Excellent agreement Indicates full infiltration and LC randomly oriented.

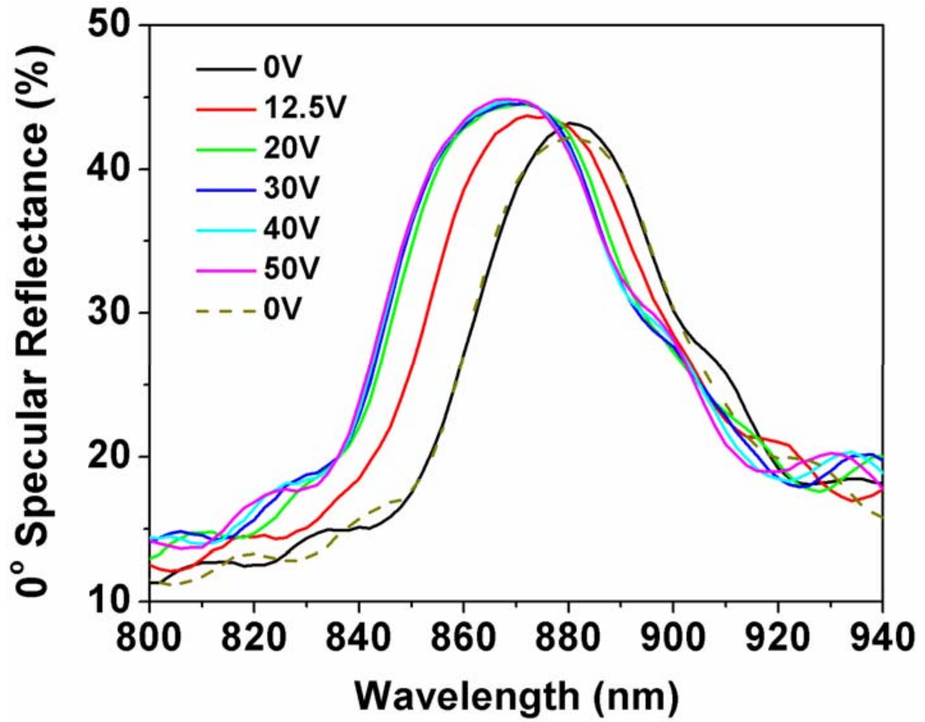
Electric Field Tuning:
TiO_2 Non-close-packed inverse shell opals

- Reflectance spectra for increasing applied electric field (bipolar square wave at 1 kHz) for NCPIO samples.

Hydrophobic treated

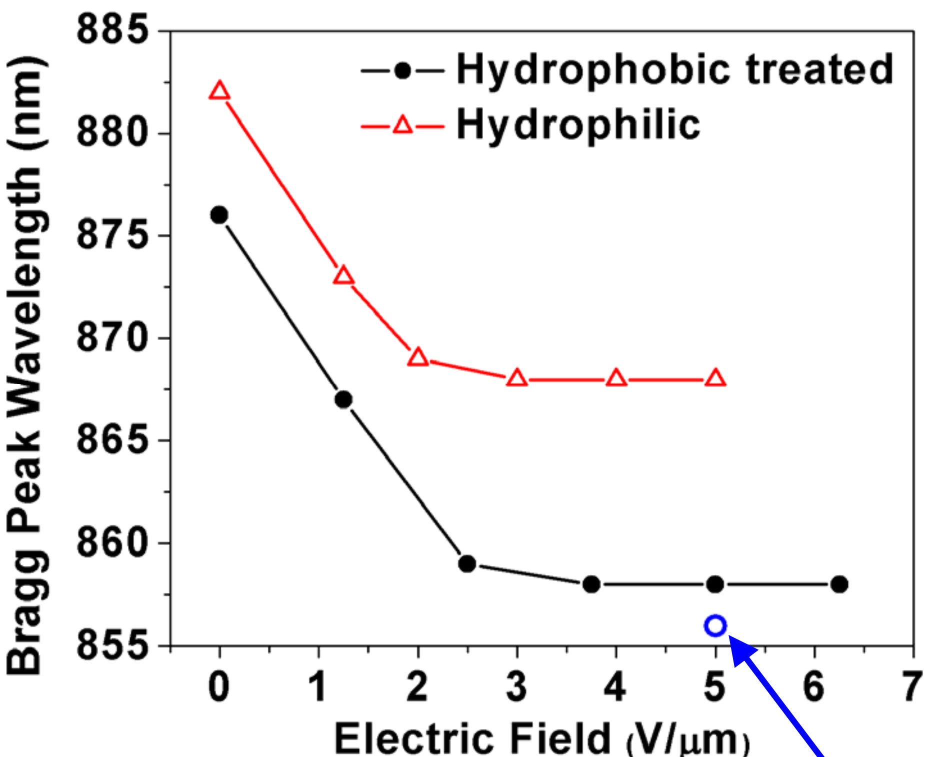


Hydrophilic



Electric Field Tuning

- Bragg peak position versus applied electric field at 1kHz
- Bragg peak width versus applied electric field at 1kHz



50V @ 25kHz → 856 nm

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Experimental Summary

- Hydrophilic (untreated) sample:
  - 14 nm shift at 1 kHz
  - 14 nm shift at 25 kHz
  - Displays no hysteresis

- Hydrophobic sample:
  - Treated with fluorinated chlorosilane
  - 18 nm shift at 1 kHz
    - Gives n_{LC} = 1.524
  - 20 nm shift for 5 V/μm at 25 kHz
    - Gives n_{LC} = 1.518
  - Displays hysteresis

Comparison with Calculation

- Experimental Results:
  - Peak Shift
    - Hydrophobic: 20 nm or Δn of 0.06
    - Hydrophilic: 14 nm
  - Peak Width Tunability
    - Hydrophobic: 0.91 %
    - Hydrophilic: 1.24 %

- Theoretical Predictions:
  - Peak Shift: 47 nm for Δn = 0.1 (28 nm for 0.06)
  - Peak Width Tunability: 1% for Δn = 0.1

Summary

- Theoretically calculated the expected performance for several opal based 3D PCs.
- Predicted optimal structures for Bragg peak tunability or Bragg peak width – **Non-close-packed inverse opal**.
- Observed a large 14 nm Bragg peak shift in high dielectric TiO_2 NCP structures.
- Observed a larger 20 nm shift for NCP structures with a hydrophobic surface treatment.
- Observed the maximum expected change of the refractive index for 5CB.
- **Pathway to a tunable full photonic band gap:**
  - Higher index backbone
  - Larger Δn opto-electronic material

Acknowledgements

- Curtis Neff
- Dr. Brent Wagner

- Mike Ciftan/Rich Hammond,

  U.S. Army Research Office
  - MURI “Intelligent Luminescence for Communication, Display and Identification”
  - Contract DAAA19-01-1-0603