Crystalline Colloidal Array
Optical Devices

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Hierarchically Assembled Intelligent Materials for Chemical Sensing and Electro-optics

Responsive Materials For
- Optical Limiters and Switches
- Chemical Sensors
- Optical Memory
- Magneto – Optical Transducers

Optical Materials
- Optical Limiters for eye and sensor Protection
- Photonic Materials for Optical Switching and Memory
- Display Device Applications

Chemical Sensing Applications
- In vivo Clinical Sensors
- Point of Care Sensors
- Environmental Sensors
- Biological and Chemical Agents
- Remote Atmospheric Sensing

Molecules
- Nanoscopic
  - CdS
  - Ag
  - Au
  - Fe₃O₄
- Photonic and Magnetic Quantum Dots
- Mesoscopic
- Colloidal Particles
- Macromolecules
- Hydrogel Networks

Molecular Recognition
- Photochromics
CRYSTALLINE COLLOIDAL SELF-ASSEMBLY: 

MOTIF 

FOR 

CREATING SUBMICRON PERIODIC SMART MATERIALS
Outline

- CCA and PCCA Photonic Crystal Fabrication
- Nanosecond Photonic Crystal Switches
- Hydrogel Volume Phase Transition Refractive Index Switching
  - Thermally activated
  - Chemically activated
  - Photochemically activated
Crystalline Colloidal Arrays Self-Assembly

- fabricated from monodisperse, highly charged colloidal particles

Dialysis / Ion Exchange Resin

Self-assembly

FCC

~ $10^{13}$ spheres/cm$^3$

- spacing dependent only upon particle number density and crystalline structure

Preparing ~ 100 nm Polystyrene Colloids

160 ml Water
60 ml Styrene (monomer)
2.00 g MA-80-1 (surfactant)
2.90 g COPS -1 (ionic co-monomer)
2.00 g Divinyl Benzene (crosslinker)
0.20 g Sodium Bicarbonate (buffer)
0.70 g Ammonium Persulfate (initiator)

Polymerize at 70°C for 3 hrs.

Reese, Asher et al J. Colloid Interface Sci. 2000, 232, 76
What Drives CCA Self-Assembly?

\[ U(r) = \frac{Z^2 e^2}{\varepsilon} \left[ \frac{e^{\kappa a}}{1 + \kappa a} \right]^2 \frac{e^{-\kappa r}}{r} \]

Sphere Radius
Medium Dielectric Constant
Interaction Potential Energy

\[ \kappa^2 = \frac{4 \pi e^2}{\varepsilon k_B T} \left( n_p Z + n_i \right) \]

Ionic Impurities
Particle concentration
Debye layer thickness

\[ \frac{1}{\kappa} \text{ (in pure water)} \sim 700 \text{ nm} \]
For $10^{13}$ spheres/cc $\iff$ Crystalline Colloidal Array

Spacings only depend upon the Particle Number Density and Crystal Structure.

Bragg Diffraction occurs with Phenomenal Efficiency
Transmittance $< 10^{-8}$ for 0.5 mm Thickness

- Dynamical Diffraction Limit
Bragg Diffraction

\[ m\lambda_0 = 2nd\sin \theta \]
All Light Diffracted-Finite Widths-Top Hat Profiles
Diffraction Phenomena of Photonic Crystals

* Kinematic Diffraction
  x-rays: Atomic & Molecular Lattice
  wimpy scattering
  little attenuation
  each layer contributes similarly

* Dynamical Diffraction
  strong scattering
  must consider coupled incident and diffracted wave

* Theoretical Foundation Based on Work in 1930-1940


3-D Photonic Bandgap Crystals—for much larger modulations of refractive index

Ultra Efficient Diffraction

91 nm PS CCA
100 μm = 400 layers
FCC Crystal

Stacking of closest-packed layers:

HCP: ABABABAB...

FCC: ABCABCABC...

FCC Twin: ABCABCBCABCA...

Twin Planes

Lamellar

FCC Twin: ABCABCBCABCAABCABC...
CCA in the middle: ABCABC layers.
Reciprocal lattice and unit cell.
Dependence of Diffraction Efficiency on Number of Stacking Faults Along 111

![Graph showing the dependence of diffraction efficiency on the number of stacking faults along 111. The x-axis represents % stacking faults, and the y-axis represents diffraction intensity ratio. Three lines are plotted for different ratios: (200)/(111), (220)/(111), and (311)/(111).]
Conclusions

• Diffraction from FCC 111 planes independent of stacking faults
• Diffraction from higher Miller index planes severely attenuated by stacking faults
• Stacking faults increase with particle spacing
• Stacking faults will be the major difficulty for fabricating 3-D photonic bandgap materials
Crystalline Colloidal Array Optical Devices

- Passive Spectral Bandpass Reject Filter

EXP: Raman Spectroscopy rejecting Rayleigh line, $\Delta \lambda = 5$ nm
First Photonic Crystal Patent

Photonic Crystals Have Revolutionary Applications in Areas Such as Optics, Optical Computing and Communications.
Cry stalline Colloidal Array Tunable Optical Devices

- Refractive index thermal nonlinearities
- Hydrogel volume phase transitions
- Photochemically accuated lattice alterations
Optical Limiter and Switch

Low Intensity

100% Transmission

High Intensity

No Transmission
Concept for Creating Nonlinear Optical Switch

Low intensity illumination:

CCA

100% transmission

★ index matched \((n_p = n_m)\)

High intensity illumination causes the sphere refractive index to mismatch that of the medium - Bragg diffraction occurs.

CCA

no transmission

★ index mismatched \((n_p \neq n_m)\)
Transmission Through CCA as a Function of the Refractive Index Between the Spheres and the Medium
Time Dependence of Submicron Periodic Thermally Non-Linear Crystalline Colloidal Array

83 nm spheres

\( n_p = 9 \times 10^{13} \) spheres/cc

\( \lambda_{\text{ex}} = 514.5 \text{ nm} \)

A

Threat Pulse

B

Transmittance limited by selective diffraction.

Nanosecond Photothermal Dynamics in Colloidal Suspension
R. Kesavamoorthy, M. S. Super, and S. A. Asher,
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Refractive Index Dependence on Temperature

Photothermal Effect: $\Delta n = (dn/dT) \cdot \Delta T$

Example: PMMA, $dn/dT = -1.1 \times 10^{-4} / 0^\circ C$

Requirements:
(1) To index match the particles to the aqueous medium ($n_{H2O} = 1.33$), we need to use a low refractive index polymer to synthesize the particles.
(2) We need to chemically bond a dye to the particles in order to prepare transparent, absorbing CCA.
Transmission Spectra of PFBMA Polymerized CCA at Different Medium Refractive Index

\[ A \sim \left( \frac{n_p}{n_m} \right)^2 - 1 \]
Covalently attached absorbing dye to the CCA in the hydrogel.
PCCA Fabrication

Experimental Set-up For Measuring Optical Switching Nonlinearity

- Pump beam
- Probe beam
- 532 nm
- 594 nm
- beam splitter
- lens
- cervical with DMSO/water
- shutter
- CCA hydrogel sample
- (reference signal)
- (diffraction signal)

Extinction vs. Medium index (n₀)
Optical Switching of Dyed PCCA

$n_m (1.390) > n_p (1.386)$, dyed PCCA

$n_m (1.382) < n_p$, dyed PCCA

$n_m (1.388) > n_p$, undyed PCCA

$T_g = 62 \, ^\circ\text{C}$

Nsec Switchable Polymerized Crystalline Colloidal Array Bragg Diffracting Materials

G. Pan, R. Kesavamoorthy, and S. A. Asher

Dependence of Nonlinear Effect on Probe Delay Time

Nsec Switchable Polymerized Crystalline Colloidal Array Bragg Diffracting Materials

G. Pan, R. Kesavamoorthy, and S. A. Asher

Conclusions

• Observed nsec photothermal switching
• Problem low efficiency (<10%) 😞!
• Stay Tuned: Inefficiency results from temperature dependence of diffraction $\lambda$
• Switching should be 99 + %
Crystalline Colloidal Array
Tunable Optical Devices

Refractive index thermal nonlinearities

• Hydrogel volume phase transitions
• Photochemically accuated lattice alterations
Poly(N-isopropylacrylamide) (PNIPAM) undergoes a reversible phase transition when heated above 32.1 °C. This coil-globule transition is analogous to a liquid-vapor phase transition. The recipe and synthesis conditions determine the extent of volume changes and whether they are continuous or discontinuous.
Thermally Switchable Periodicities from Novel Mesocopically Ordered Materials
J. M. Weissman, H. B. Sunkara, A. S. Tse, and S. A. Asher
Optical switching from PNIPAM CCA
Unfortunately system does not switch quickly-
CCA disorders!
NIPAM CCA Lightly Polymerized into PCCA

“Nanogel Nanosecond Photonic Crystal Optical Switching,”
C. Reese, A. Mikhonin, M. Kamenjicki, A. Tikhonov and S.A. Asher
Time Dependence of Diffraction Changes after 3 nsec T-jump
Kinetics

-Log T

605 nm

\[ \tau_1 \approx 870 \text{ ns (26\%)} \]
\[ \tau_2 \approx 19 \mu s (24\%) \]
\[ \tau_3 \approx 130 \mu s (50\%) \]

375 nm

\[ \tau_1 \approx 1.2 \mu s (28\%) \]
\[ \tau_2 \approx 21 \mu s (11\%) \]
\[ \tau_3 \approx 147 \mu s (61\%) \]
NSec Individual Sphere Volume Phase Transitions

![Graph showing wavelength vs. delay time and absorbance change](image)

- Wavelength / nm
- ΔOD
- Delay time / μs
- τ ≈ 120 ns

Legend:
- 1500 μsec
- 1000 μsec
- 200 μsec
- 20 μsec
- 2.5 μsec
- 0.4 μsec
- 0.3 μsec
- 0.2 μsec
- 0.1 μsec
- 0 μsec
Fast Kinetic Transmission Changes in PNIPAM Photonic Crystals.

- Heating pulse: 3 ns duration, 1.9 μm, ~1.3 mJ/pulse
- T-jump ~ 23°C → 30°C ± 2°C, IR spot diameter ~ 200 – 300 μm
- Transient absorption probed by temporally delayed 120 ns “white-light” pulse
Crystalline Colloidal Array
Tunable Optical Devices

• Refractive index thermal nonlinearities
• Hydrogel volume phase transitions
• Photochemically accuated lattice alterations
PHOTORESPONSIVE
POLYMERIZED CRYSTALLINE COLLOIDAL ARRAYS
AS A PHOTOSWITCHABLE DEVICE

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The graphic illustrates the transformation of PCCAs (PCCA) into PCPCCAs (PCPCCA) and PCPCCAs (PCPCCA) through a chemical reaction involving UV and Vis light. The reaction is represented as $H_2N-R \rightarrow \text{Trans} \rightarrow \text{Cis}$, where $\lambda_1$ and $\lambda_2$ represent the wavelengths for UV and Vis light, respectively.
AZOBENZENE PHOTOISOMERIZATION

- reversible photochromism in fluids and solids
- isomerization results in changes of
  1) absorption spectrum
  2) dipole moment
  3) geometrical conformation

**Trans-azobenzene**

**Cis-azobenzene**
Azobenzene (water solution) Dynamics Under UV and Vis Light

![Absorbance vs. Wavelength Graph](image)

- Dark
  - 1 min 365 nm (12 mW)
- 20 sec. 488 nm (50 mW)
- 1 cm quartz cell

![Chemical Structures](image)

- UV, Vis, Δ
Azobenzene Functionalized PCCA Dynamics Under UV and Vis Light

![Graph showing the dynamics of Azobenzene Functionalized PCCA under UV and Vis Light.](image-url)
a) Speed Limit?

b) Fig. 11
Optical Switching

- Use of Laser Heating to Drive Hydrogel Volume Phase Transition
- Use of Photochemistry to Drive Hydrogel Volume Phase Transition
- Use of Thermal Refractive Index Mismatch to Control Diffraction-Inefficiency due to dynamic diffraction wavelength shift-stay tuned
FUTURE WORK

• Optimize these sensors to combine hydrogel volume phase transition with thermal heating by nsec pulses

• Available $\Delta n > 0.15$!

• Decrease characteristic size of switching materials.
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